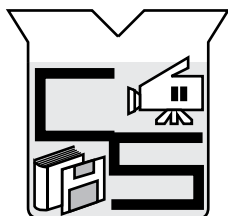
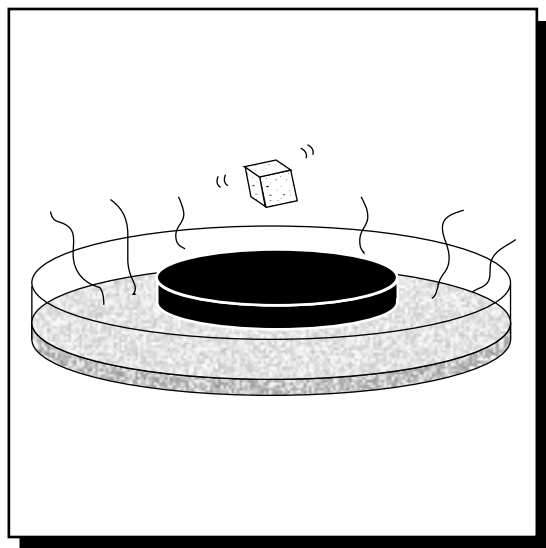


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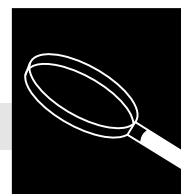


ChemSource

*Instructional Resources for Preservice and
Inservice Chemistry Teachers*

MATERIALS SCIENCE: CERAMICS & GLASSES

Topic Overview



CONTENT IN A NUTSHELL

Materials science is a most vital area of modern science and engineering. High temperature superconductors, the coating on stealth aircraft, diamond thin films, semi-conducting computer and solar photovoltaic components are all products of materials science. Metals, plastics, ceramics, glasses, and concretes that go into nearly everything in the construction environment are equally important. Concepts central to understanding materials science are bonding in the solid state and the influence of bonding on such important properties as thermal and electrical conductivity, strength, light transmission, resistance to various chemical and physical environments, and creation of and/or response to magnetic fields. Materials science exists at the interface of chemistry, physics, and engineering and can be studied at every level from descriptive chemistry to theoretical quantum mechanics.

A ceramic is an inorganic material processed or consolidated at high temperatures. Although some scientists claim ceramics are crystalline materials, most ceramists include both crystalline and amorphous materials as ceramics; therefore, glasses are usually considered as a subset of ceramics. Ceramics include a wide range of compounds including silicates, oxides, carbides, nitrides, sulfides, and borides. Although most ceramics contain metal ions, some of them, *e.g.*, silicon carbide, do not.

Ceramics are prepared differently from methods normally encountered in a study of reactions in solution or liquid mixtures. Production of ceramics involves mixing components, shaping, and heat processing. The traditional method of mixing is to grind powders together. An advantage of this method is that it is easy and cheap. The main disadvantage is poor quality control of both particle size and precise chemical composition. The powder mixture is then typically pressed into shape, and sintered to produce the final crystalline product. Sintering is a process of heating at high temperature, but below the melting points of the various components. This process causes binding between powder grains and decreases the size of the spaces between grains. Another method of preparing ceramics uses chemical mixing. This process involves precipitating the particles simultaneously, allowing precise control of both stoichiometry and particle size. This process is more expensive but allows production of more complex materials with superior quality control. Either process forms crystalline ceramics. For glasses, the mixture is typically melted and poured into molds, flattened into sheets, or drawn into fibers.

Ceramics are usually considered covalent network solids, although some of the metal-nonmetal bonds may be ionic. Their chemical reactivity depends on the particular bonds involved, especially bonds at the surface of the material. Their electrical and optical properties depend on the distribution of electrons (see Band Gap Theory in *Links and Connections within Chemistry*). Magnetic properties depend on the spatial distribution of electrons and atomic kernels. Thermal properties depend on these factors and on the masses of the nuclei. There are several ways to think about strength, including wear resistance, toughness, and resistance to shattering. These properties depend more on number and nature of dislocation and grain boundaries than on features related to bonding.

Much about ceramics is poorly understood. The properties of the new class of high temperature superconductors were not predicted from theory, for example, and many of the recent advances in that area have come from educated guesses based on periodic properties of the elements. Many of the professional opportunities for chemists into the twenty-first century will be in the field of materials science.

Materials Science includes applications of solid-state materials that can be used as an extension to topics on metals and semi-metals or amorphous and crystalline solids. This module would be appropriate to use at the end of the year.

PLACE IN THE CURRICULUM

1. Materials Science is a subtopic of solid-state matter.
2. Solids can include descriptions of physical and chemical properties such as electrical conductivity, ductility, brittleness, *etc.*
3. Materials can be classified as:
 - a. Metals, Semi-Metals, Nonmetals
 - b. Glasses and Ceramics
 - c. Crystalline and Amorphous
 - d. Conductors, Semiconductors, Insulators, Superconductors
4. The focus is on technological applications of materials science.
5. Concepts like band gap energy can be explored to explain conductivity.
6. The topic of nonstoichiometry of inorganic solids can be explored.

CENTRAL CONCEPTS

1. Electrical energy
2. Energy levels and valence
3. Magnetism
4. Physical properties of solids
5. Stoichiometry
6. Intermolecular force
7. Periodic properties
8. Covalent network, ionic, and metallic bonding in solids
9. Packing of crystals

RELATED CONCEPTS

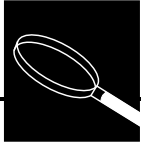
1. Stoichiometry calculations
2. Laboratory skills:
 - a. Basic manipulation of glassware and chemicals
 - b. Operation of an analytical balance
 - c. Using a high-temperature oven

RELATED SKILLS

After completing their study of materials science, students should be able to:

1. describe differences between the microscopic and macroscopic structure of materials.
2. classify everyday materials. (Consider the classroom or a room in a house and attempt to classify all the materials in it by first identifying the material as organic or inorganic, then crystalline or amorphous. Next, the materials should be classified as metals, polymers, ceramics, or glasses. Then the major chemical constituents in the material (elements, compounds or ions present) should be identified, and finally guesses should be formulated regarding how the material was fabricated into its final form.)

PERFORMANCE OBJECTIVES



3. relate properties of materials to chemical bonding and crystal structure.
4. explain how properties of materials can be altered by changing their chemical makeup or by combining them in various ways with other materials.
5. define specific terminology: sintering, crystalline, amorphous, superconductivity.
6. compare solid state reactions and solution reactions.



Concept/Skills Development

Activity 1: Preparation of Colored Glass

Introduction

Glass is an amorphous solid typically made of silica (SiO_2), soda ash (a mixture of sodium oxide, Na_2O , and sodium carbonate, Na_2CO_3), and limestone (calcium carbonate, CaCO_3), with small quantities of other materials that affect color and physical and chemical properties. Silica has a very high melting point, and soda ash and limestone are added to cause melting point lowering. These melting point lowering materials are called *fluxes*.

Scientists sometimes describe glass as a supercooled liquid because it is **amorphous** (without regular crystalline form), **isomorphi**(refracts light at the same angle in all directions), and will flow under pressure. Unlike crystalline solids, glasses do not have sharp melting points. This melting point range can be explained by considering the energy needed to break solid state bonds. Crystals are regularly repeating structures, so their bonds have the same energy and they all break at about the same energy input, or temperature. But glasses have bonds going in random directions with differing amounts of stress and strain; hence, these bonds require different energies for breaking and therefore do not all break at the same temperature.

The compounds substituted for soda ash and limestone, and added as trace compounds, determine the properties of a particular kind of glass. Glass fluxed with soda ash and limestone is **crown glass** and glass fluxed with lead carbonates and oxides is called **flint glass**. If borax, or boron oxide is added to the flux, a **borosilicate glass** is made. Such glass can withstand rapid temperature changes without shattering like flint or crown glass, and is sold under such trademarks as Pyrex™ and Kimax™. You will be making a borosilicate glass in this activity.

Transition metal (*d*-block) trace elements added to glass can cause the glass to be colored. For example, compounds of gold added to the flux produce red glass; cobalt compounds produce blue glass. (You may have used “cobalt glass” in the flame test for potassium.) In this laboratory, you will experiment with adding small quantities of *d*-block metal oxides and carbonates to glass you prepare. The purpose of the activity is to determine **empirically** (*i.e.*, by trial and error) what colors are produced by which *d*-block elements.

Purpose

To use common earth materials to make a consumer and industrial product.

Safety

1. Wear protective goggles and dust mask throughout the laboratory activity.
2. Since rapidly cooling glass sometimes shatters, you may also want to wear some jeans and a long sleeved shirt to protect your arms and legs during this activity.
3. Metal oxides are generally basic; sodium oxide is quite basic—strong enough to hydrolyze your skin and hair if it gets on you. You should likewise not breathe the dusts of these compounds, so be sure to use a dust mask.

LABORATORY ACTIVITY: STUDENT VERSION





4. Glass can *be* hot without *looking* hot. When you prepare a sample of glass, allow plenty of time for it to cool before picking it up. Even then, hold your hand close to the sample to feel any heat coming off. If it doesn't feel too hot when your hand is close to the sample, lightly and quickly touch the sample to feel how hot it is. Only if it feels cool should you pick it up.

Procedure

1. Make sure the furnace is preheated to 1050 °C.
2. A typical recipe for glass mixes one mole sodium oxide, Na_2O , one mole borax, $\text{Na}_2\text{B}_4\text{O}_7$, and two moles silicon dioxide or sand, SiO_2 . Calculate the masses for each of these components in grams and determine, by adding them together, the total mass of the glass this would make. Then calculate the mass of each component that would be required to make 10 g glass using the same recipe.
3. After you have weighed the constituents of the mixture, add them to a mortar along with a few crystals (or a little pinch of powder) of the transition metal oxide or carbonate you plan to use as a coloring agent. The more metal oxide or carbonate used, the deeper the color. Grind these materials together in a mortar with a pestle. The result should be a uniform mixture.
4. Put about 2/3 of your mixture in a clean crucible and about 1/3 in a clean dry test-tube for future reference. Make sure you record the compounds and approximate amounts you use. You will be sharing your recipe and your colored glass with your classmates at the end of this activity.
5. Using heat resistant gloves and crucible tongs, slide the crucible into the preheated furnace. If the furnace is too hot to stand in front of, you should get your laboratory partner to hold a heat shield made of sheet metal between you and the furnace door while you slide in the crucible. This should be done quickly, as the metal shield will heat up.
6. Allow your glass to melt for about 20 min. It should have the viscosity (pourability) of warm honey after this time. If it does not, turn the oven up a little and wait 10-20 min longer. (You may have to wait until the next day if the furnace is too cold.)
7. When your sample has melted to the consistency of warm honey, take it out of the furnace using the gloves and crucible tongs, and stir it with a stainless steel spatula to ensure that it is a homogeneous mixture. Once it is homogeneous, put it back in the oven to heat and melt for a few more minutes.
8. Take your homogeneous melted sample from the furnace and pour it as a puddle onto the metal plate provided for that purpose. When it has cooled just enough so that a slight tap with the spatula no longer dents it, slide it into a small metal pan and *put a piece of wire gauze over the pan*. (This is to protect you from flying glass when it shatters from the stress of contraction upon rapid cooling.)
9. When your glass has cooled, show it to classmates. If it has shattered on cooling, put the shards in a test-tube and observe the difference in appearance between the original mixture of powders and this new material called glass. From observing the colors produced by the class, fill out a chart that matches color with additive.
10. Thoroughly wash your hands before leaving the laboratory.

Implications and Applications

1. Observe the samples of oxide and/or carbonate coloring materials along with other compounds of the same transition metal ions. How do the compound colors compare with the glasses that were prepared by you and your classmates?
2. Sometimes the original trace metal ion is oxidized or reduced in reacting with the other constituents used to make the glass. If you noticed any inconsistencies in Question 1 between glass color and compound colors, try to resolve them by comparing the glass color to compounds of other oxidation states of the same transition metal ion.
3. Propose several mixtures that give colors not prepared by the class in this laboratory. Explain why you think this mixture will work, referring to the nature of colors produced by mixing and subtracting light of different colors, and to colors of compounds you propose as additives.



**LABORATORY
ACTIVITY:
TEACHER
NOTES**

Activity 1: Preparation of Colored Glass

Major Chemical Concept

The major concept of this laboratory activity is the difference between arrangements of atoms in *crystals* and arrangements of atoms in *glasses*. To support the introduction, have students build models of quartz, mica, and asbestos (regular arrangements for SiO_2), and glass in which the Si and O atoms go randomly in every direction, with strands of bonded atoms looping past and among each other in random fashion.

Level

General and honor students.

Expected Student Background

Required background includes stoichiometry, periodic properties, and electron structure of atoms. Understanding will be increased if students have also studied *d*-block elements, their compounds, and the influence of chemical surroundings on energy differences between outer shell orbitals of *d*-block ions.

Time

If students are efficient and the furnace setting is correct, students can finish in 40-45 min. Students should mix their glass powder during one period and store it in a test-tube or other container overnight. Then they will have time for mistakes and for showing each other their glass samples during a the next class period. Students who work slowly may not be able to show their glass until the third day, after it has cooled and/or been stored overnight. To do this activity properly, you should devote three full periods to it. Your faster laboratory students can make models of network solids from styrofoam balls and toothpicks or pipe cleaners while they wait for the rest to catch up. Don't rush anyone; rushing is an invitation for serious burns.

Safety

Read the *Safety Considerations* in the *Student Version*. Encourage students to take time and be careful. The furnace and glass are *hot*. Be sure you have a first aid kit with burn ointment handy. Immediate treatment with cold water is the best first aid for burns.

Materials (For 24 students working in pairs)

Nonconsumables

- 24 Dust masks
- 12 Crucible tongs
- 12 Stainless steel spatulas
- 12 Ceramic crucibles
- 12 Mortar and pestles
- Balance (precision of 0.01 g or better)
- Furnace (any furnace used for firing pottery will work well)
- Thick metal plate to be used to pour glass sample onto (stainless steel is best but iron, copper, or zinc plates are satisfactory)
- Small metal pan
- Wire gauze
- Heat resistant gloves
- Sheet metal, $1/2 \text{ m}^2$ to be used as a heat shield

Consumables

- Clean sand, SiO₂, 250 g
- Sodium oxide, Na₂O, 250 g (Alfa Research Chemicals, Telephone: 1-800-343-0660)
- Borax, Na₂B₄O₇, 300 g
- Numerous *d*-block oxides and carbonates in small quantities. (Avoid *d*-block elements such as mercury, cadmium, osmium, *etc.*, known to be toxic. Refer to the MSDS sheet for the compound's toxicity.)
- Examples of other compounds (nitrates, acetates, sulfates) formed by those same *d*-block metals.

Advance Preparation

Make sure all materials are available for the activity. Of special note is the metal plate upon which students will pour their melted glass and the small pans, screens or wire gauzes they will use for the final cooling. This is to protect students from glass shards generated by shattering when the glass is rapidly cooled. Also, you will save time if you ensure that the furnace is at the proper temperature by testing it with a batch of your own glass powder prior to student use. Once you have the proper setting, leave the furnace on.

Pre-Laboratory Discussion

How you conduct the pre-laboratory depends on the objectives selected. An approach that promotes critical thinking skills is to ask students to hypothesize the colors various additives will produce based on a comparison with the color of compounds of metal ions used as additives. Because the colors of *d*-block element compounds are not consistent, even with the same oxidation numbers, attempting to predict glass color should generate some discussion of the theoretical basis of compound color if students have had that background. Once students have discussed their predictions and reached consensus with regard to colors produced by the additives, they are prepared to test their hypotheses. If you have only a few *d*-block oxides and/or carbonates available, you might also choose to have students predict colors produced by mixtures; use appropriate questioning techniques to make sure they consider the possibility that the additives might react with each other in a redox reaction. Once students have made predictions, use whatever method you wish to assign additives to groups to ensure all available additives (and combinations of additives) are tested. Be sure to record the predictions for use during the post-laboratory discussion.

If you choose to lecture on this topic, you should review the nature of bonding in solids, comparing the organization of ionic and network covalent crystalline solids with the disorder of glasses. Follow this with a review of the relationships between compound color and electron structure as applied to the influence of trace elements on color in glass. Refer to the chart for typical colors produced by small amounts of metal compounds added to the flux.

Compound or Metal Ion	Color
Gold	Red
Selenium	Red
Copper(II)	Blue
Cobalt	Blue
Iron(II)	Green
Iron(III)	Brown
Manganese(IV) Oxide	Purple
Permanganate	Purple
Iron(II) + Manganese(IV) (or Selenium Oxide)	Grey (Colorless)



Teacher-Student Interaction

During the activity enforce safety and good laboratory procedure. As you circulate throughout the laboratory, ask each group which additive(s) they are testing and what color they believe will result.

Anticipated Student Results

Students produce glass samples of various colors (see *Pre-Laboratory Discussion*).

Answers to Implications and Applications

1. This observation depends on what compounds are available for the laboratory. Check for accuracy.
2. Again, this depends on compounds used as additives. Sometimes iron(II) oxidizes to iron(III), creating brown glass with a green additive. Sometimes pink cobalt(II) additives produce blue cobalt glass by changing the chemical environment around cobalt to make tetrahedral cobalt complexes.
3. This is an open question. Make sure students base their predictions on observed properties of additives, colors of other oxidation states, *etc.*, using chemical reasoning instead of guessing.

Post-Laboratory Discussion

Compare predictions with results and ask students to explain any discrepancies. Reasonable explanations include changes in the glass as compared with the additive compound in the chemical environment around the metal ion. This results in a change in the energy difference between electron orbitals. Changes in the oxidation states of additives also result in different species with different absorption characteristics.

Extensions

Many extensions are possible. If you have not studied glass blowing and bending earlier in the year, you can use this as an opportunity for students to practice working with glass. In addition to glass bends and pipets that students typically make, the following projects are also possible with good burners and “regular” sodium silicate (not borosilicate) hollow and solid glass tubing and test-tubes.

SAFETY NOTE: The same safety rules given in the Student Version of the activity should be used for the extensions.

1. Blow a Colored Glass Bubble

Have students use the furnace to melt the colored glass they made. As soon as the glass begins to melt (more viscous than warm honey—see Steps 6 and 7 in *Student Version*), light the burner and begin to soften the end of a clean hollow glass tube. (Students will blow on either the tube end itself, or on a piece of rubber tubing attached to the tube end, so cleanliness is the key here. If cleanliness is in doubt, use glass and rubber tubing of a size that enables you to put an individually wrapped disposable drinking straw into the end of the rubber tube to be blown on by the student.) Transfer the crucible of melted glass to a hot pad on the desk top. Place the premelted end of the glass tube (complete with rubber tube and straw if necessary for blowing) into the melted colored glass and twirl it around to pick up a glob of colored melted glass. Blow up the glass glob like a balloon. While the student blows, the glass glob should be over some heat resistant surface, such as ceramic tile. If the glass ball is blown too thin, it will be very fragile; students should also rig up

some sort of apparatus with a ring stand and clamps to hang the glass bubble until it cools. With a bit of practice, students can make nearly round hollow colored glass balls from their previously synthesized colored glass. Invite students to bring in tissue paper and small boxes to protect their colored bubbles when taken home. (Although the tube is long enough that there is no danger if a student accidentally inhales, you may wish to caution students to only exhale while glass-blowing. Alternatively, try substituting a fireplace bellows for the source of air.)

2. Make a Test-tube with a Sidearm

A trickier project is to add a glass tube sidearm to a test-tube. First, you must blow a small hole in a large test-tube, about 3-4 cm from the top. To do this, first make a “blower” from a 1-hole stopper that fits the test-tube, a short piece of glass tubing, a long piece of flexible rubber tubing, and a drinking straw to fit the rubber tubing.

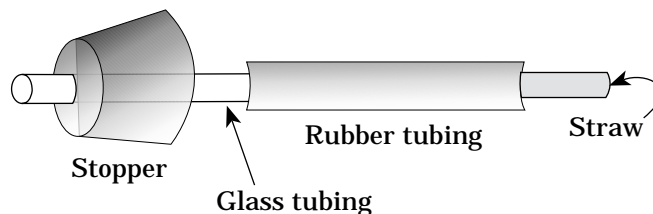


Figure 1. Glass-blowing assembly.

Place this assembly in the test-tube (about 3-4 cm from the top). Heat a very small spot on the test-tube with a burner to as high a temperature as possible until the spot gets soft. Meanwhile, a student partner can be softening the end of a hollow glass tube. When a soft spot in the test-tube has formed, blow suddenly through the straw to forcefully pop a small hole in the side of the test-tube. Keeping the test-tube in the flame, so the edges of the recently popped hole stay soft, stick the soft end of the glass tube to the soft side of the test-tube so that the glass tube goes over the previously blown hole. Take the assembly out and let it cool. The trick is to stick the test-tube and glass tube together so that the joint doesn't leak. This takes some practice. The connection should be smooth, not lumpy, or it will crack.

3. Working with a Solid Glass Rod

If you can have two different diameters of solid glass tubing for students, they can make a number of interesting art objects. For example, using a larger tube (diameter of 0.8-1 cm), you can make a swan. First, soften the glass in the middle of the tube and push it in to “fatten” the swan body. Second, behind this “fattened” part, heat the tube as hot as possible in a narrow band and quickly pull the tube apart, pulling one part of the tube at a right angle to the other, creating the “tail”. When this has cooled, soften the tube on the other side of the fattened body along several cm of tube. Pull that part more slowly, bending it into a swan's neck-shape. Make sure that the neck and the tail tip both point in the same direction. When that has cooled, intensely heat the end of the neck and pull it out into the swan's beak. Finally, intensely heat the end of a small diameter glass tubing and “paint” the wings onto the previously prepared swan. You might want to practice this until you can make a fairly decent swan and then demonstrate it to students. Having demonstrated the techniques, let them experiment, either making their own swans, or making whatever they wish with the glass.

Assessing Laboratory Learning

The content objectives are best tested with written or verbal test items. Laboratory manipulative skills are best evaluated by observing individual students' work and examining materials produced (especially in the event of the extensions described above).



Primary critical thinking skills promoted by this laboratory are hypothesizing/predicting from theory and prior observations, and explaining discrepancies in results based on theory and prior observations. This is best done *via* oral questioning in pre- and post-laboratory discussion. The key criteria for evaluation include whether or not students refer to theory and prior observations to support their predictions and explanations, and the accuracy of the observations and theoretical statements used. You might want to keep a checklist to indicate a student's level of performance and to ensure that you give all students an opportunity to respond to a question either in pre-laboratory or post-laboratory discussion. If you use the responses for grading, you should realize that students who answer later questions have likely learned from their colleagues' responses and your previous probing and follow-up questions, making their educational experience quite different in both quality and quantity from those answering earlier.

DEMONSTRATIONS **Demonstration 1: Glass Bending, Blowing, and Breaking**

Purpose

When setting up apparatus for various activities, it is often necessary to use glass tubing of various lengths and geometrical shapes. The following demonstration will show students how to make smooth right angle bends in glass, fire polish ends, and blow bubbles in the end of a glass tube. Also, a comparison of glass and ceramic material will be made.

Materials

Glass tubing, two pieces approximately 20 cm long
Burner
Flame spreader
Wire gauze
Ring stand

Safety

Wear protective goggles. Glass can be hot without looking hot. Use appropriate safety precautions.

Procedure

1. Cut off a piece of glass tubing 15-20 cm long by scoring the glass tube once with a triangular file. Moisten your finger with water and rub on the score. Cover with a piece of cloth and place your thumbs opposite the scratch. Apply pressure to break the glass. Fire polish by rotating the ends in a burner until the edges are rounded. Place a flame spreader on the burner and roll the tube back and forth until the glass becomes soft. Remove from the flame and hold for a few seconds. Then bend quickly into a right angle with a smooth curve. Place the glass on a wire gauze to cool. Mention that wire gauze distributes the heat. If you want your bend to be strong, cool it slowly by annealing. Glass is annealed by holding it in a "cold" yellow, smoky flame until the glass is coated with soot.
2. Obtain another piece of tubing at least 20 cm long and fire polished on the end used for blowing. Heat the unpolished end of the tube until molten and closed, remove from the flame, and blow gently into the tube, rotating the tube as you blow. This procedure may be repeated until there is a bubble that is at least twice the diameter of the tubing. Hold the tube with the bubble at the bottom until the glass hardens. Place it across a beaker to finish cooling with the bubble well away from the beaker glass.

3. Demonstrate the breakage of glass by placing a piece of hot tubing on the base of a ringstand. Remind students that this is what will happen to a hot beaker that is placed on the cool surface of a laboratory table. Discuss the fact that this broken glass can be recycled by melting and then used to make new products.
4. Examine a piece of ceramic tile that is made from clays and is strong, brittle, and heat and chemical resistant. (Examine a space shuttle tile if one is available). Demonstrate the breakage of ceramics by dropping a ceramic tile on the floor. Discuss the fact that once ceramics are broken, they may not be remelted and reformed, because ceramics are hardened by firing at high temperatures. Once hardened, they are resistant to extremely high temperatures.

Demonstration 2: Resistance through a Conductor

Purpose

In ordinary conducting materials, such as metal wire, the flowing electrons that represent current always encounter some resistance, similar to friction. The source of this resistance is the scattering of electrons from atoms that make up the conducting material. Scattering occurs if atoms are vibrating and/or if lattice defects are present. This resistance causes a loss in power between points in a circuit. Up to 20% of the total energy in an electrical circuit is wasted in transmission by resistance heating of wires. This demonstration illustrates the buildup of heat caused by resistance in an electrical circuit using an ordinary conductor.

Materials

Balloon
Battery or power supply
Nichrome wire, approximately 30 cm
Alligator clips

Safety

Use normal safety precautions when using any power source.

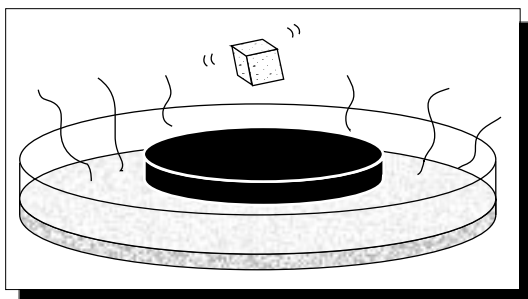
Procedure

Inflate a balloon and tape a nichrome wire or other noninsulated wire to the balloon. Attach the ends of the wire to a battery or power supply. Turn on the power source. After several minutes, the heat generated by the flow of electrons will pop the balloon.

Demonstration 3: Meissner Effect Using a Superconductor

Purpose

Moving a magnet near a superconductor induces a supercurrent (*i.e.*, a current that does not decay) within the superconductor. This supercurrent generates its own magnetic field such that the total magnetic field inside the superconductor disappears. Two opposing fields, one from the magnet and one induced by the superconductor, cause the magnet to be repelled by the superconductor, just as two like magnetic poles repel each other. If the repulsive force at the surface of the superconductor is greater than the force of gravity on the magnet, the magnet will be levitated at a distance from the superconductor. This effect can be observed when a superconductor is cooled below its critical temperature. This phenomenon was discovered by Meissner and Ochsenfeld in 1933.



In Figure 2, a magnet is levitating over a pellet of a superconducting ceramic immersed in liquid nitrogen.

Figure 2. Meissner Effect.

Materials

Kit containing superconducting ceramic pellet, magnet, and forceps.

- Kits can be obtained from science supply companies including Colorado Superconductor, P.O. Box 8223, Ft. Collins, CO 80526; Knusoft Knowledge Systems, 219 Los Cerritos Drive, Vallejo, CA 94589. Also Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706. Flinn Scientific, Inc., P.O. Box 219, 131 Flinn Street, Batavia, IL 60510; Edmund Scientific, Barrington, NJ

Liquid nitrogen (obtained from welding supply companies)

Gloves, heavy protective

Petri dish

Goggles

Safety

Liquid nitrogen is extremely cold, having a boiling point of $-196\text{ }^{\circ}\text{C}$. Since skin contact with liquid nitrogen can result in frostbite, protective gloves that can withstand these cold temperatures must be worn. Excess liquid nitrogen should be disposed of promptly; upon standing in an open container, it can condense oxygen from the atmosphere, slowly enriching the liquid with liquid oxygen. This mixture of liquid nitrogen and liquid oxygen is a powerful oxidizer and may react violently with easily oxidized substances. The levitation activity should not be performed near flames, sparks or flammable material since powder particles from the rare-earth magnet can burn in air and create sparks. Always wear safety goggles when performing demonstrations.

Procedure

Place a pellet of the superconducting material, yttrium barium copper oxide, into a Petri dish. Using protecting gloves and goggles, pour liquid nitrogen into the Petri dish until it covers the pellet. Replenish the liquid nitrogen as it evaporates. After about a minute, the pellet should be cooled below its superconducting temperature. Pick up the magnet with plastic tweezers, and place it about 2 mm above the center of the pellet. Release the magnet and it should levitate above the pellet. Run a small piece of paper between the pellet and the magnet to demonstrate the levitation. The magnet will remain suspended until the pellet warms to above its critical temperature.

NOTE: A laboratory activity, Preparation of a Superconductor, is presented in Extensions at the end of this module.

Key Questions

1. How can you categorize materials according to their physical properties? *[Physical properties such as boiling point, melting point, physical state, conductivity (electrical and thermal), index of refraction, ductility and brittleness are commonly used to classify materials.]*
2. What are some technological applications of ceramics and glasses? *[Ceramics and glasses have many technological applications including use in high tech rockets, space shuttle tiles, military helicopter armor, and Freon-alternative refrigerant semiconductors.]*
3. How is glass treated to make so many useful products? *[In the manufacture of glass materials (fluxes) in small amounts are added to lower the melting point of the silica and give the glass desired properties.]*

GROUP AND DISCUSSION ACTIVITIES

<i>Flux Additive</i>	<i>Properties</i>
<i>Boron oxide</i>	<i>Resistance to temperature change</i>
<i>Transition metals</i>	<i>Variable colors</i>
<i>Potassium oxide</i>	<i>Hardness suitable for grinding eyeglasses</i>
<i>Lead oxide</i>	<i>Crystal-like properties</i>
<i>Silver chloride</i>	<i>Photochromic properties for light sensitive eyeglasses</i>

4. What are some potential future applications for high-tech ceramic materials? *[In the future, high-tech ceramics may be used in superconducting magnets for “frictionless” trains, super high quality fiber optics for communication and information systems, and superconducting “wires” for electricity transmission.]*

Counterintuitive Examples

1. The second most abundant element in the earth’s crust is silicon. Ninety-five percent of the rocks that make up the earth’s crust are oxides of silicon. While silicon solar cells are useful devices for generating electricity, it takes many years of continuous electricity production for a single crystal silicon solar cell to “pay back” the energy needed to construct the device. In addition, the low level of power (voltage times current) that is generated by silicon solar cells severely restricts their applications. However, recent advances in solar cell construction have increased both their efficiency and their power rating. (Researchers are discovering how to make solar cells using polycrystalline and amorphous silicon that promise to deliver electricity at a lower cost.)
2. While ceramic material is frequently used as insulating material in the electronic industry, rare-earth composite ceramics have been discovered to be the most promising high temperature superconductors. A major problem with ceramic materials is that they are brittle and cannot be formed by machines into various shapes or drawn into wires. This is probably the biggest challenge to materials scientists who are examining ways to utilize superconducting ceramics in practical devices.



Metaphors and Analogies

Paul Grant, a scientist at the IBM Research Laboratory in Almaden, California, gives this analogy: “In a superconductor, atoms behave in such a way as to carry the electrons along with them like surfers on a wave. Because of the spin, superconductivity is really like two surfers riding on a wave, with one of them doing a head stand.” The wave represents the vibration in the lattice (see *Transparency Master* in the *Appendix*).

Douglas Finmore, a physicist at Iowa State University, compares the movement of electrons through a superconductor to a crowd moving across a football field. “If they act as individual particles, they will bump into one another and scatter. That’s equivalent to electrical resistance. But suppose someone starts counting cadence, and everyone locks arms and marches in step. Then, even if a person steps into a chuckhole, he/she won’t fall because the neighbors hold that person up.” This is how electrons move through a superconductor.

See *Transparency Masters* in the *Appendix* for other descriptions of superconductors, conductors, and insulators. See also *Pictures in the Mind*.

Pictures in the Mind

Charge transfer by electrons is easy to understand because the moving particle itself is charged. Charge transfer by a “hole” is harder for students to visualize. To help, ask them to imagine a row of 10 chairs with 9 students sitting in the first 9 chairs. Student number 1 moves to chair number 10, leaving chair number 1 empty for student number 2. If student number 2 moves to chair number 1, that leaves chair number 2 free for student number 3, and so forth. As students move up the line, one after the other, the empty seat “moves” in the other direction. In like fashion, “holes” in the valence band move, carrying their relatively positive charge with them.

Structure of crystalline and amorphous materials. See the crystalline and amorphous structures pictured in the *Transparency Master* in the *Appendix*.

TIPS FOR THE TEACHER

Language of Chemistry

amorphous type of disordered solid lacking a crystalline structure.

annealed heated for a time just below softening temperature and then cooled.

ceramic inorganic material processed or consolidated at high temperatures.

Strong bonds enable ceramics to withstand heat and chemical attack but also make them brittle.

conductor material that allows the flow of an electric current due to mobile electrons in the conduction band.

critical temperature temperature below which certain materials will conduct an electric current without resistance. This temperature is different from the critical temperature of condensed gases.

crystalline orderly arrangement assumed by a solid.

flux material that lowers the melting point of a solid.

glass amorphous homogeneous solid typically made when silica is mixed with other compounds, heated until it melts, then rapidly cooled.

insulator material in which there is no movement of electrons, due to the large gap between the valence and conduction bands.

Meissner effect ability of a superconductor to block a magnetic field and in doing so to repel any magnet that comes near it.

nonstoichiometric compound compounds that do not have a fixed ratio between the numbers of atoms in the chemical formula.

semiconductors substance that allows the flow of a slight electric current at room temperature but increases in conductivity with increasing temperature.

sintering heating at high temperatures but below the melting point to bind a powder mixture together.

superconductomaterial that conducts an electric current without resistance when cooled to its critical temperature.

Pattern Recognition

Silicon is a member of the carbon group and behaves somewhat like carbon. It can bind with itself to form silicon chains and oxidize to form silicon dioxide. The various silicates and aluminosilicates that make up the earth's crust contain repeating units of ionic silicon oxides. These repeating units are the building blocks for commonly found clays, sands, soils, and rocks. Construction materials such as bricks, cement, concrete, ceramics, and glasses consist largely of silicon oxides.

Repeat Unit	Si:O Ratio	Structure	Example
SiO_4^{4-}	1 : 4	Tetrahedral	Olivine
$\text{Si}_2\text{O}_7^{6-}$	1 : 3.5	Pairs of tetrahedra	Thortveitite
SiO_3^{2-}	1 : 3	Closed rings	Emerald
SiO_3^{2-}	1 : 3	Infinite single chains	Pyroxenes
$\text{Si}_4\text{O}_{11}^{6-}$	1 : 2.75	Infinite double chains	Amphiboles
$\text{Si}_2\text{O}_5^{2-}$	1 : 2.5	Infinite sheets	Talc, mica
SiO_2	1 : 2	Infinite network	Quartz, feldspars

Figure 3. Silicate structures making up the earth's crust.

Common Student Misconceptions

1. **“Glass is a crystalline solid.”**

When molten silicon dioxide (sand) is cooled, it does not crystallize. Rather it gradually becomes more and more viscous and gives rise to a stiff amorphous solid whose intermolecular interactions resemble those of a liquid. Therefore, many people prefer to describe glasses as supercooled liquids and not solids. Colored glasses can be considered metal oxide solutions in which silicon dioxide is the solvent.

2. **“Thicker bottoms on old window panes mean the glass has flowed.”**

Very old window panes are observed to be thinner at the top than at the bottom. There are two schools of thought to explain this. (1) The glass has flowed downward over the years; and (2) the glass was originally made that way. These explanations are not mutually exclusive. Students should be encouraged to research that topic. (Sources: Kolb and Kolb reference and Dr. William Dumbugh, Corning Glass Works, Corning, NY.)



3. “The Law of Definite Proportions applies to all compounds.”

The Law of Definite Proportions applies to most compounds but not all. In solid state materials, the possibility exists for the formation of nonstoichiometric compounds. The copper oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$, where x is approximately 7.4, is a case in point. However, nonstoichiometric compounds are never found in molecular materials.

Decision-Making

Have students analyze the benefits and costs of recycling glass. Discuss energy requirements for making and recycling glass. Compare the use of recyclable *versus* throw-away materials for various uses.

At one time, asbestos was a very common material in the construction industry. It has many desirable properties: nonflammability, flexibility, mechanical strength and inertness to chemical attack. On the other hand, airborne asbestos particles reach the lungs, do not dissolve and are not expelled. In the lungs they irritate the tissue and lead to scarring. Extensive exposure to airborne asbestos can lead to the disease *asbestosis* and to a greatly increased risk of lung cancer. Have students research the use of asbestos in the construction industry and consider the cost/benefit analysis of its use.

HISTORY: ON THE HUMAN SIDE

The oldest written records from northern Africa and the ancient Mideast all describe buildings made of bricks, which are synthetic rocks made by heating clay. The *Old Testament* of the *Bible* records that the Hebrews made bricks during the period they were held in slavery by the Egyptians. The hanging gardens of Babylon, one of the wonders of the ancient world, were built of brick. Bricks made by drying and heating in the sun were not ceramics and their lack of durability was a result. Since the technique of further heating sun-dried bricks in furnaces was known thousands of years ago, ancient fire-treating brickmakers were probably the first materials engineers.

Pottery has been known for hundreds of centuries. Archaeologists use pottery shards, dish design, glazes, *etc.*, as markers for particular ancient cultures. Showing that a dig at the site of one ancient culture contains pottery from another previously identified culture is strong evidence that the two cultures traded with each other. One of the most famous forms of pottery is porcelain, manufactured by the Chinese more than a thousand years ago from a special kind of clay known as *kaolin*, named after the mountain that furnished the clay. Various Chinese emperors subsidized the porcelain industry and gave awards to potters who developed new techniques, glazes, and so forth. After Marco Polo's visits to China, Europeans began to attempt duplication of Chinese porcelain. The Germans first duplicated the Chinese process and developed a strong pottery industry based on their discoveries. The British discovered an interesting variant of the same process by adding bone ash (mostly calcium phosphate) to their pottery mix. It produced a beautiful pottery called “bone china”, often called *Wedgwood China* after the original source of porcelain pottery.

Glass has also been known for many centuries, as evidenced by the glass beads found in archaeological digs. The Romans discovered glass blowing—probably around 50 B.C. In the Middle Ages, Italian and French artisans forced blown glass bubbles into various shapes and flattened them into sheets. From that discovery came a variety of bottles, jars, glasses, and stained glass windows. Experimentation with recipes and production processes also arose. Within decades of the beginning of the industrial revolution, glass products became established as economically important construction materials. Glass windows became commonplace, rather than a decoration found only in cathedrals.

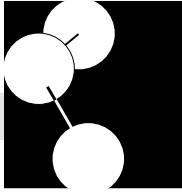


MEDIA

1. Nova Program on Superconductivity, 1988, 1 hr. PBS Video, 1320 Braddock Place, Alexandria, VA 22314, Telephone: 703-739-5000.
2. Superconductivity—A 10-min video produced by Wah Chang. Public Relations, Teledyne Wah Chang, 1600 Old Salem Road, Albany, OR 97321, Telephone: 503-926-4211.
3. InteractionsSeries—Wisconsin Public Television/AIT (20-min video on superconductivity). Contact: Customer Service, Agency for Instructional Technology, P.O. Box A, Bloomington, IN 47402, Telephone: 1-800-457-4509; FAX: 812-333-4278.
4. The Acme School of StuffSeries—TV Ontario—25-min programs that include segments on glass bottles (Show 6) and composite substances (Show 12). Films for the Humanities, 11 Perrine Road, Monmouth Junction, NJ 08852, Telephone: 1-800-257-5126; FAX: 609-452-1602.
5. TV Ontario has a videotape series that contains short videos that could be used in this module. Free previews are available. TV Ontario Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516.
6. The Pressware Story—A 12-min video from Corning, Inc. showing how Corelle dishes are made. Free rental from Corning, Inc., Corning, NY 14830.
7. *The World of Chemistry* (high school version) videotape “Number 18: Earth Materials.” WINGS for Learning/SUNBURST, 101 Castleton Street, Pleasantville, NY 10570; (800) 321-7511; (914) 747-3310; (914) 747-4109 (FAX).
8. Software published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
 - a. *Bravais*, by Philip Pavlik. Vol. III B, No. 1, for IBM PS/2 PC-compatible computers.
 - b. “Cleave,” one of the programs in *Animated Demonstrations*, by Philip Pavlik. Vol. V B, No. 2, for IBM PS/2 PC-compatible computers.
 - c. *Crystal Lattice*, by David Trapp. Vol. IV A, No. 1, for the Apple IIGS computer.
9. Videodiscs published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
 - a. “Liquid Nitrogen and Racquet Balls,” a chapter on *The World of Chemistry: Selected Demonstrations and Animations: Disc I* (double sided, 60 min.), Special Issue 3.
 - b. “Polymers,” a chapter on the videodisc *Demonstrations in Organic Chemistry* (double sided, 60 min.), Special Issue 6.
10. Materials and devices available from ICE—Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396: (608) 262-3033 (voice) or (608) 262-0381 (FAX).
 - a. Memory Metal
 - b. The Optical Transform Kit
 - c. The Solid State Model Kit

EQUIPMENT AND INSTRUMENTA- TION

Furnaces, pellet-presses, crucibles (Discussion of sources of equipment used in superconductivity is included in the superconductivity laboratory activity under *Extensions and Projects*.)



Links/Connections

1. Band Gap Theory and Conductors, Insulators, and Semiconductors **WITHIN CHEMISTRY**

Band Gap Theory explains differences in electrical conductivity among conductors, semiconductors and insulators. According to theory, atomic orbitals of atoms in a solid combine to form energy levels that extend throughout the entire solid. When many atoms interact, as in a crystal, a large number of energy levels are formed so close to each other in energy that they essentially form a continuum of levels, or **bands**, rather than the discrete quantum levels observed in atoms and simple molecules. In solids, the electrons used to hold the solid together are in the **valence band**. Electrons in energy levels that do not help hold the solid together are said to be in the **conduction band**. (The electrons not locked into bonds are free to move, and are the electrons that move when the solid conducts electricity.)

The energy distance between the valence band and the conduction band is called the band gap. Just as atoms must absorb a quantum of energy equal to the energy difference between two energy levels in order for an electron to be promoted from a lower to a higher energy level, solids must absorb a minimum quantum of energy in order to promote an electron from the highest level of the valence band to the lowest level of the conduction band. The difference between discrete molecules and solids is that, with solids, energy quanta larger than the minimum can also be absorbed. Therefore, absorption spectra of solids tend to exhibit absorption bands rather than absorption lines. In fact, this is where the name “band” originated.

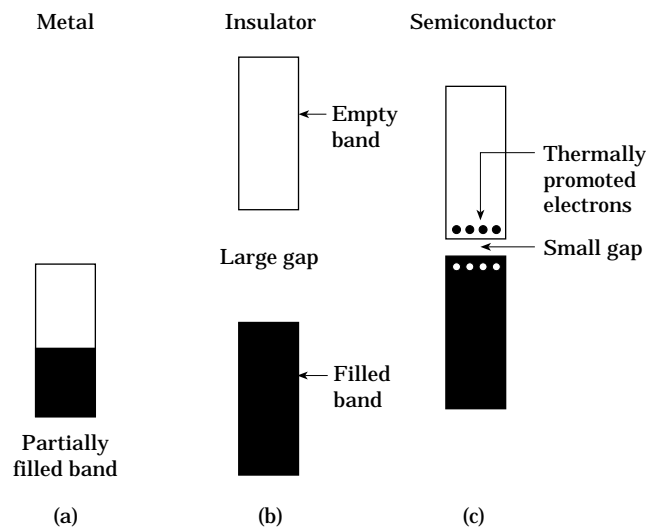
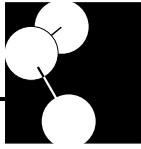


Figure 4. Band gap diagrams.



Conductivity in any solid is the result of the movement of electrons. As long as electrons are in the valence band, they are used for bonding. As soon as electrons are promoted to the conduction band, they are no longer used for bonding, and are free to move. Also, once an electron is promoted from the valence band to the conduction band, a “hole” is left in the valence band. Valence band electrons, unlike conduction band electrons, are not free to move large distances. Their movement is largely restricted to hopping over into an adjacent hole. If this movement occurs again and again, the net effect is for the hole to move (see *Pictures in the Mind*).

The magnitude of a solid’s band gap determines whether the solid is a conductor, an insulator, or a semiconductor. For example, metals and certain organic polymers are characterized by having valence and conduction bands that are very close together or overlapping. Therefore, it takes very little energy to promote an electron from the valence band to the conduction band. Once in the conduction band, the electrons are no longer used for bonding and are free to move. The hole left behind in the conduction band can also move. If such a solid is exposed to an external electric field, the electrons will flow toward the positive end of the field and the holes will flow toward the negative end. Many metals have the additional advantage of having only partially filled valence bands, allowing hole migration even if electrons are not promoted to the conduction band.

In insulators, the valence and conduction bands are separated by a large energy gap. The valence band is completely filled, and no electrons reside in the conduction band. Conductivity therefore occurs only when the applied electric fields and/or absorbed energy quanta are very large. In fact, typical insulators tend to decompose when exposed to energies that are large enough to promote electrons from the valence to the conduction band. Diamond is an example of an insulator.

In semiconductors, there is a moderate difference between valence and conduction bands. Semiconduction can occur through at least three types of mechanisms. A substance that contains a completely filled valence band and a completely empty conduction band can behave as a semiconductor. This behavior is accomplished if the energy distance or band gap is small enough that electrons from the filled valence band can be promoted to energy levels in the empty conduction band by relatively small quantities of heat or light quanta. The previously empty conduction band then contains a few electrons and the previously filled valence band contains a few holes. Both electrons and holes can move under the influence of an electric field, allowing the solid to conduct electricity. Examples include silicon and other semi-metals.

When numbers of electrons are promoted to the empty conduction band as a result of absorbing light energy, electrons in the semiconductor can be made to move through a wire in an external circuit to a region where the band is empty. This mechanism is the basic principle of the silicon photocell, which is used as a source of electrical power. Some simple silicon cells can convert over 14% of the incident light to electricity. Major research efforts are currently under way to either modify silicon solar cells or to create solar cells from other kinds of semiconductors. In 1989 and 1990, composite solar cells made of two different semiconductors were reported being 25% efficient in converting incident light to electricity.

A final way to make semiconductors is by addition of impurities that either add electrons to the conduction band or holes to the valence band or both. This process is called “doping”. One example of doping is the addition of arsenic to silicon to increase its conducting ability by adding electrons to the conduction band. The quantum properties of semiconductors can be finely tuned with appropriate types and concentrations of dopants. Materials scientists interested in semiconductor devices (*e.g.*, computer chips, lasers, photovoltaic cells) study the effects of dopants on semiconductor properties very carefully (see *Links and Connections, Between Chemistry and Other Disciplines* for additional discussion of semiconductors).

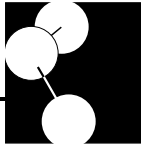
2. Cooper Pairs

The mechanism for low temperature superconductivity involves a notion that at first seems counterintuitive: electrons are attracted to each other to form what are called Cooper pairs. That two electrons, both negatively charged, would be attracted to each other seems to violate what is known about the law of electrostatics. The key to the attraction, though, is that a quantum property of electrons—the tendency to exist in pairs with opposite spins—is mediated by the crystal lattice of the superconductor. In a conductor like a metal, the positive ions, whose positions are fixed in the lattice, are surrounded by valence electrons of atoms that have been removed from their individual atoms and move about freely. As these electrons responsible for conductivity travel past the positive ions, the ions are drawn toward the path of the electron by electrostatic attraction.

The mechanism of conduction in a superconductor is different from that in an ordinary metal. In the superconductor, current is carried by electron pairs bound together indirectly through interaction with surrounding positive metal ions. The negative charge of an electron slightly distorts the lattice, creating a region of enhanced positive charge that attracts the second electron, accounting for the coupling of two electrons into Cooper pairs. The electrons in the pair have opposite spin moments.

At high temperatures, this coupling effect is overcome by random thermal motion of ions. However, at sufficiently low temperatures, motion of ions resulting from the passage of electrons is more important than random thermal motion. Because ions are much more massive than electrons and move more sluggishly, a “wake” of displaced positive charge is formed. At low temperatures, this wake persists long enough to attract a second electron, forming the Cooper pair. The pair is thus bound electrostatically by mutual attraction of each electron for positive ions in the lattice, and with quantum forces by having opposite spins. Because the Cooper pair is so bonded, combined momentum of the pair is not affected by its passage through the lattice.

Whereas the pair would become scattered by thermal motion of the ions at higher temperatures, it remains bound as a pair while moving at lower temperatures. Consequently, scattering does not provide energy transfer between electrons and lattice that produces resistance in a normal conductor. Nonrandom motion of electron pairs is not changed into random motion of the lattice, so energy is not “lost to heat” with the transmission of Cooper pairs of electrons. In the superconducting state, most conduction electrons are bound in Cooper pairs.



Sufficiently high temperatures and strong magnetic fields will result in fewer Cooper pairs being formed, and the superconductivity will be destroyed. Sufficiently large currents will likewise hinder the formation of Cooper pairs. Therefore, any superconductor has a characteristic critical temperature, T_c , critical field, H_c , and critical current, I_c . If any of these critical values is exceeded, superconduction will disappear.

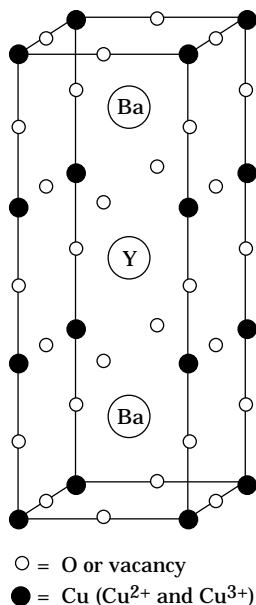
Cooper pair formation theory is very successful in explaining and predicting properties and behavior of low temperature superconductors (mostly metals). However, the theory has been relatively unsuccessful in explaining and predicting properties and behavior of high temperature ceramic superconductors. Whether the Cooper pair theory will successfully extend to the new superconducting materials remains to be seen. It is possible that these materials work by a different mechanism entirely.

3. Nonstoichiometry of Superconducting Materials

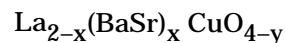
In general, if a compound's chemical formula is checked for the valence of the elements, the algebraic sum of the total positive and negative charges is zero. In a crystalline material, each unit cell in a perfect inorganic solid contains an integral number of chemical formula units. The superconductor, $YBa_2Cu_3O_7$ is a case in point. This material superconducts at 90 K. In this case:

$$\begin{aligned} Y^{3+} &= +3 \\ 2Ba^{2+} &= +4 \\ 7 O^{2-} &= -14 \\ 2Cu^{2+} + 1Cu^{3+} &= +7 \end{aligned}$$

For the three copper ions to have a total charge of +7, the copper ions must be present as +2 and +3 and implies one-third of the Cu is Cu^{3+} and the remainder is Cu^{2+} . Figure 5 shows an idealized structure of the superconductor, $YBa_2Cu_3O_7$.



Most new oxide superconductors are crystals with defects where there is a vacant lattice site, and oxygen deficiencies are very common. The term nonstoichiometric means there is a deviation from the ideal formula and there are vacant sites where atoms would normally be. Thus, the formula



represents a nonstoichiometric formula where y is an average measure of the fraction of vacant oxygen sites in the crystal. If there is an oxygen deficiency or an oxygen excess, charge neutrality demands that the average oxidation number of one of the elements in the nonstoichiometric solid must deviate from its most common value. In the above formula, if there is an oxygen excess (or a lanthanum deficiency) the oxidation state of copper will be raised. The effect is a change in the crystal symmetry and development of a defect in the structural and chemical order of the solid. In the new high temperature superconductors, crystal defects occur on a larger scale and contribute to promoting superconducting properties.

Figure 5. The unit cell structure for a perovskite superconductor made of yttrium, barium, copper, and oxygen. The formula for this material is $YBa_2Cu_3O_x$, where x is 6 or 7.

The possibility of variable oxidation states and missing oxygen or other atoms allows for the preparation of this new group of nonstoichiometric solids. Nonstoichiometric compounds do not have a fixed ratio between numbers of atoms in the chemical formula; in fact, the ratio may be continuously variable over some range. For example, iron(II) oxide has a variable composition, FeO_x with $1.05 < x < 1.13$, that does not include the stoichiometric composition $x = 1$. The possibility of forming nonstoichiometric compounds is unique to solid-state compounds and is never observed in molecular materials. It is fortunate that few nonstoichiometric compounds were known to early chemists, because ideas such as the law of definite proportions would surely not have emerged when they did, possibly delaying the progress of chemistry. Now we know that the law of definite proportions applies to most compounds, but not all; and we understand why.

4. Network Bonding of Silicon

See *Language of Chemistry in Rocks, Minerals, and Gems* module for a discussion of network bonding of silicon compounds.

5. Intramolecular Bonding and Intermolecular Forces

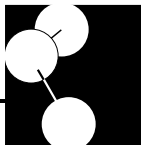
Atoms form stable units called molecules by sharing electrons. This type of sharing is called intramolecular (within the molecule) bonding. Glasses, ceramics, superconductors and semiconductors are condensed states of matter. The forces that cause the components of a substance to form liquids or solids involve covalent or ionic bonding, or may involve weaker interactions called intermolecular forces (because they occur among, rather than within, molecules). It is important to recognize when substances change from liquid to solid, the molecules remain intact. The changes in state are due to intermolecular forces rather than intramolecular forces (see *Condensed States* module).

1. Electronics

Conductivity was explained in the *Within Chemistry* section as a function of valence band and conduction band structure and band gap size. These chemical ideas can be extended to explain electronic behavior. Conductors typically decrease in conductivity as temperature increases. This behavior is explained by invoking the idea of increased random motion of ions or kernels as temperature increases. Because the band gap is small or nonexistent and numerous holes often exist in the valence band, additional thermal energy does not help conduction. Consequently, additional random motion of ions or kernels gets in the way of electrons trying to move in a nonrandom fashion.

On the other hand, the conductivity of semiconductors *increases* as the temperature increases, a behavior that is exactly opposite from the behavior of conductors and a property that is used to distinguish conductors from semiconductors. Although atoms that make up semiconductors randomly move around more as the temperature is increased, higher temperatures also provide larger energy quanta to excite electrons into the conduction band. Even though there is more blocking of current due to random atomic motion, there is much more current due to additional charge carriers. With electrons in the conduction band and holes in the valence band, the conductivity of the semiconductor increases.

BETWEEN CHEMISTRY AND OTHER DISCIPLINES



The theoretical basis for doping was also explained. For example, the small conductivity of silicon can be increased at normal temperatures if the silicon crystal is *doped* with other elements. An *n*-type semiconductor is produced when a small fraction of silicon atoms is replaced with an element such as arsenic that has more valence electrons than silicon. Arsenic is incorporated into the silicon network *via* covalent bonds to silicon, but because silicon forms only four bonds, the extra electron on arsenic is not used for bonding. When valence and conducting bands of the As-doped silicon are formed, these extra electrons end up in the conduction band and can conduct an electric current. The term “*n*-doped” comes from “negative”-doping a semiconductor so that a negative charge carrier (an electron in the conduction band) is provided.

A *p*-type semiconductor, then, can be seen to be made by providing a positive charge carrier—a hole—in the valence band. When silicon is doped with an element that has one less valence electron than silicon, a *p*-type semiconductor results. Boron is an example of such a dopant because boron has only three valence electrons. An electron vacancy or hole is produced in the structure. The mechanism by which holes serve as charge carriers is explained in *Pictures in the Mind*.

The most important applications of semiconductors involve composites connecting a *p*-type to an *n*-type semiconductor to form a *p-n* junction. Use of *p-n* junctions in printed circuits has revolutionized electronics.

2. **Art and Archaeology: Stained Glass and Chemical Additives**

Stained glass windows were used as early as the 12th century to depict Christian scenes in European cathedrals. A metal or metal oxide was added to a batch of glass; this mixture was melted and then poured into molds. Colors were produced by adding *d*-block compounds as in the colored glass activity (see *Activity 1*). The medieval glaziers did not use pure compounds, however. Their recipes included instructions to heat substances like copper and brass until it was powdered, or to add certain kinds of powdered rocks to the glass mix.

Even the noncolored components of glass can be used to identify whether windows at one cathedral were furnished from the same source as windows at another cathedral. For example, the flux to be added to sand to lower sand's melting point nearly always included ashes of various kinds. Ashes from coastal plants are typically high in soda ash (Na_2O) whereas inland plants are typically high in potash (K_2O .) Ratios of trace elements like Pb, Zn, Mn, Fe, and others can also indicate a common or similar source for the glass.

3. **Geology: Perovskites**

Many of the new high-temperature superconductors belong to a family of ceramics called perovskites. Perovskites are ceramics (solid materials combining metallic elements with nonmetals, usually oxygen) that have a particular atomic arrangement. Perovskites are the earth's most abundant minerals and are of interest to geologists seeking clues to the planet's history. They exhibit an array of electrical properties ranging from insulators to semiconductors, superionic conductors (whole ions, rather than just electrons, flow through the crystal), metal-like conductors and now high-temperature superconductors. Some of the most interesting perovskites are rocks from volcanic magma that include latrappite, loparite and leushite, which incorporate many exotic elements in their structures, including all 14 rare-earth elements. The perovskite structure is so adaptable that these minerals act like sponges, soaking up various elements that do not fit readily into other mineral structures. Perovskites currently form the basis of a \$20 billion per year electroceramics industry.

4. **Physics: Micro-Electro-Mechanical Piezoelectric Tools**

Many ceramic perovskites exhibit a property known as piezoelectricity. When an external electric field is applied to the structure, the field shifts the atoms so that the entire crystal changes shape, usually by elongation. Conversely, a mechanical deformation of some of these crystals generates an electric field. This conversion of mechanical energy into electrical energy or *vice versa* by certain perovskites can be seen in a group known collectively as PZT. For example, in the perovskite lead titanate (PbTiO_3) a slight compression of the crystal can result in the storage and release of a hundred volts of electrical potential. These materials are used in a wide assortment of devices including loudspeaker buzzers, electrical relays, pressure gauges, *etc.* In loudspeakers, for instance, barium titanate transducers vibrate against a membrane in response to electronic signals, generating sound waves. The most common single-crystal piezoelectric material is quartz (silicon dioxide), which is used mainly for frequency control in electrical oscillators, such as those found in watches.

5. **Geophysics and Medicine: SQUIDS**

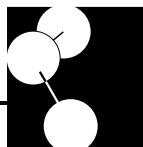
In 1962, scientists at Cambridge University determined that a supercurrent could be induced between two superconductors separated by a thin insulating layer via a quantum-physics process called “tunneling”. By directing a microwave field against the voltage, a system of measurements is created that can detect infinitesimally small magnetic fields and/or voltages. This phenomenon became the basis for an important practical application of superconductivity: superconducting quantum interference devices, or SQUIDS. These devices are used in geophysics to detect the magnetic “signatures” of minerals that indicate the presence of oil or other valuable substances underground. In brain research, SQUIDS are used to identify extremely small magnetic fields created by neurological activity.

6. **Engineering: Structural Materials**

Advanced structural ceramics are being used in a wide variety of applications ranging from scissors and tennis rackets to industrial cutting tools, engine components (engine heads, cylinders, *etc.*), heat exchangers, bearings, armored helicopters, and high-temperature rockets. They offer a combination of excellent properties including wear resistance, hardness, stiffness, and heat and corrosion resistance. They are less dense than metals and stronger at elevated temperatures. However, they also have a down side. They are brittle and sensitive to microscopic flaws like cracks, voids, and impurity inclusions. Unlike metals, they will crack and shatter under stress.

In order to remove these shortcomings, research is under way to toughen ceramics and make them more fracture-resistant. Some methods used include adding to ceramic matrices a variety of ceramic particulates, fibers, and whiskers (very strong single crystals that are at least 10 times longer than they are thick). All of these additives make the ceramic tougher by acting to deflect cracks. Whiskers and fibers can also dissipate the crack's energy through frictional forces and can actually absorb the energy of a developing crack. The addition of whiskers has yielded a composite material with five times the resistance to fracture compared to untreated ceramics.

However, progress in manufacturing ceramic parts is still plagued by inconsistent quality in the final product. Wide variations in any manufactured lot arise from the unpredictable presence of flaws in the ceramic microstructure. The flaws are due to shortcomings in the processing of ceramics and are currently an area of intense research interest.



TO THE CONTEMPORARY WORLD

Careers: Inorganic chemistry, materials science, ceramic engineering, chemical engineering, ceramics, electronics, art involving glass and pottery work, manufacturing involving ceramic and glass materials, glass conservation.

Community

1. **Field Trips** Electronics firms, telephone laboratories (fiber optics), automobile plants, universities (computer, engineering, physics and chemistry departments), stained glass art shops, pottery shops, hospitals (MRI), ceramic tile factory, bottling company and/or beverage manufacturers.
2. **Knowledgeable Individuals** Solid state electronics engineers (semiconductors); materials science engineers; mechanics (ceramics engineers); artisans who use stained glass, blow glass, or make pottery with enamels and glazes; NASA (spaceship tiles).

Societal (Science/Technology/Society; Current Events)

1. **Alternative to Freon** The solid-state alternative to using Freon for refrigeration and air conditioning is present in the Peltier effect associated with particular heavily doped semiconductors. The Peltier effect is just the reverse of a thermocouple. (When a thermocouple is heated, electricity flows from the thermocouple. When electricity is forced into the thermocouple, its temperature drops.) The solid-state opportunity exists for supplementing Freon and water-based energy conversion technologies and ultimately for replacing them.
2. **Superconductors and Trains** How soon the superconductors will go from the laboratory to the marketplace is questionable. One dream machine is a train held above a track by strong superconducting magnets. The train glides along on a cushion of air, providing a nearly frictionless ride. Maglevs are trains that operate on the principle of levitation using the old metallic superconductors and are now currently operating on an experimental basis in Europe and Japan.
3. **Ceramic Tiles and the Space Shuttle** High-tech ceramic tiles were brought to the attention of the public in April, 1981, when a dozen of the 34,000 silica tiles on the outside of the Columbia fell off, probably during lift-off. These tiles were designed to protect the space shuttle from the 1260 °C heat of re-entry into earth's atmosphere. NASA's Ames Research Center developed a new composite consisting of 78% pure silica fibers and 22% borosilicate fibers that was less dense, more rigid, and stronger than those made solely of silica. These new tiles have been installed on the Discovery and Atlantis space shuttles.
4. **Chemical Additives in Glass Making** When silica (empirical formula SiO_2) is heated above its melting point and cooled, glass results. The properties of glass can be varied substantially by changing the additives. For example, common glass results when Na_2CO_3 and CaCO_3 are added to the silica melt and then cooled. Common glass is used to make window glazing, light bulbs, drinking glasses, etc. The addition of B_2O_3 produces a glass called borosilicate glass that expands and contracts very little with very large temperature changes, making this glass useful for labware and cooking

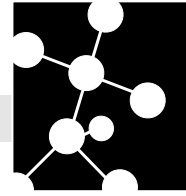
utensils. Pyrex™ is an example of this type of glass. The addition of K_2O produces an especially hard glass that can be ground to the precise shapes needed for eyeglass and contact lenses. The addition of lead oxide to glass refracts (bends) light much like a gem crystal does. Even though glass is not crystalline, leaded glass can be sculpted into beautiful works of art that sparkle like crystals. Addition of silver chloride or bromide to the glass mix will produce a transparent product that darkens in bright light, producing photochromic glass for use, *e.g.*, in lenses. Titanium (II) oxide and tin(IV) oxide are added to easily melted glass to produce enamels that are used on kitchen utensils, sinks and bathtubs. Corning Glassworks alone has recorded the properties of over 250,000 glass making formulas with different additives.

5. **Glass Ceramics** While glass is amorphous and most ceramics are crystalline, an interesting material called glass ceramics combines the features of both. The material begins as an amorphous glass; through a heat treatment process, a crystallizing agent is added, forming a polycrystalline structure. Once in this state, the glass ceramic can be machined with ordinary tools. The material can be threaded, cut into gears or similar shapes, *etc.* Space shuttle nose cones are made of glass ceramic. Pyroceram™ and Corning Ware™ are familiar brands.

6. **Emerging Technologies**

- a. **Optical Fibers.** Currently optical fibers are silicate glasses that contain only parts per billion levels of impurities. Precise control of the refractive index is necessary to insure total internal reflection as a light beam travels down the glass fiber. These fibers are important in the communications industry as they carry thousands of simultaneous telephone messages between major switching centers. They are also used to relay signals from aircraft, to direct light to inaccessible places in medicine, and for a host of other applications. Research on longer wavelength fluoride-based glass fibers is in the very early stages and is predicted to give an order of magnitude improvement in performance of optical fibers.
- b. **Diamond Thin Films.** Diamonds have long been characterized by their beauty, hardness and resistance to wear. But diamonds, both natural and synthetic, are often prohibitively expensive, particularly in industrial applications. Advances in materials science are now showing the way to put a coating of diamond on many other less exotic materials, thus imparting beneficial electronic and optical properties that only diamond has. This technology is based on using low pressure deposition of diamond from the vapor phase onto a supporting material. Applications of these thin films include depositing diamond films on cutting tools made of ceramics, high-quality loudspeakers made with diamond-coated tweeters, coatings for lenses, and electronics including semiconducting devices (see *Extensions and Projects*).

Extensions



1. **Cement and Concrete** Cement is an aluminosilicate made by heating a powdered mixture of limestone, sand, and clay to 1500°C . The resulting solid mass is powdered and mixed with a little gypsum. When cement is mixed with water, a thick viscous material is obtained that slowly hardens as interlocking crystals of hydrated aluminosilicates are formed. Cement is usually mixed with sand, gravel, or crushed rock to give a hard, strong material known as concrete. Have students work with cement. Notice the heat given off when cement hardens. The heat is the energy released when the interlocking crystals are formed. Also notice the various properties of concrete. Measure its density.
2. **Ceramics and the History of Mankind** Consider the societal connections to the ceramics industry. People have been making pottery since the earliest days of civilization. Students might find it interesting to examine developments in the technology of ceramics for various civilizations.
3. **Formation of Metal Silicates: A Chemical Garden** Fill a clear jar (1-3 L) with a saturated aqueous solution of sodium silicate (water glass) and add enough salt to cover the bottom. One at a time add crystals of various transition metal salts to the solution. The metal ions react with the sodium silicate to form a thin membrane of insoluble metal silicate. Water penetrates the membrane causing it to expand and then burst. A new membrane then forms and the process repeats, causing a column of colored metal silicate to form. Different transition metal salts give rise to different colored columns.
4. **Construction of a Device to Monitor the Meissner Effect** The following is an outline for a project in which students can closely monitor the Meissner effect, and may be a good in-depth extension of the demonstration involving a floating magnet above a cooled superconductor. Materials required are an oscillator, oscilloscope, superconductor sample (with a T_c above 77 K), two small, hollow, metal coils (that can be fashioned out of wire, if necessary), styrofoam cup, and a supply of liquid nitrogen. Coils are fastened to either side of the superconductor (accomplished by several means, tape being the easiest). One of these coils is connected to the oscillator, the other to the oscilloscope, effectively linking the oscillator to the oscilloscope, *via* the alternating magnetic field between the coils. A visual representation of the oscillator's signal will be evident on the oscilloscope's screen. At this point, liquid nitrogen can be poured onto the coil-superconductor assembly in the cup. When the superconductor cools to its critical temperature, it will block out the magnetic field linking the coils, in accordance with the Meissner effect, and the signal represented on the oscilloscope will simultaneously plummet. Devices based on this concept can be tied into a cryostatic system, which can then measure a superconductor's T_c without having to make any electrical connections to it (a sometimes tedious process when performed on ceramics).

*Further information on this project can be obtained from:
Robert Bristol, 1198 Marigold N.E., Keizer, OR 97303*

Extension Activity: Preparation of a Superconductor

Purpose

To prepare Yttrium 1-2-3 superconductor that has the formula $\text{YBa}_2\text{Cu}_3\text{O}_8$ and test for superconductivity using a small magnet.

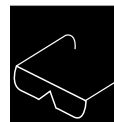
Safety

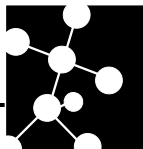
1. Wear protective goggles throughout the laboratory activity.
2. Many of the materials used for preparing superconductors are toxic. You should wear rubber or plastic gloves, work in the fume hood and wear a dust mask in addition to wearing safety goggles. Any leftover materials should be disposed of as your teacher directs.
3. Because you will be heating samples to very high temperatures (900-1000°C), you should be very careful with potentially hot materials.
4. Liquid nitrogen is also quite dangerous. If you spill liquid nitrogen on you, the part of the body that comes into contact with liquid nitrogen will become frostbitten. Don't play with liquid nitrogen. The most immediate danger from carelessness (as opposed to horseplay) is from having your feet under the table on which you are working. Liquid nitrogen flows very rapidly when spilled and will often roll off the table. Adopt a stance such that any liquid nitrogen flowing off the table will land on the floor, not on your shoes.
5. In addition, you will attempt to levitate small rare-earth magnets with your superconducting pellet. The levitation activity should not be performed near flames, sparks or flammable materials, since powder particles from the rare-earth magnet can burn in the air and create sparks.

Procedure

1. Calculate the correct masses of yttrium oxide, Y_2O_3 , barium oxide, BaO , and copper oxide, CuO , such that you get a mole ratio of 1 Y to 2 Ba to 3 Cu. Remember that one mole of yttrium oxide contains two moles of yttrium ions. Your teacher will inform you what the total mass of the mixture should be.
2. Measure the previously calculated masses on a balance that is precise to at least 0.01 g and mix the measured powders in a mortar.
3. Grind the powders together with a pestle. The better you do this job, the more likely your final pellet will be a superconductor. A key to this step is to grind until you are too tired to grind any more, and then have your laboratory partner do the same.
4. Following the directions of your teacher for the pellet press you are to use, press the powder you have just ground into a pellet. Again, the firmer the pellet, the more likely the final product will be a superconductor.
5. Place your pellet in a crucible. The crucible should either be uniquely marked, or you should put it in a location in the oven that will allow you to identify it as yours when you take it out of the oven. Put the crucible in the oven.
6. When all classmates have prepared their pellets and put them in the oven, set the oven to a maximum temperature of 950°C, turn the oven on, and let the pellets cook overnight. If your school has only one oven, your teacher may choose to have everyone put their pellets in and turn the oven on after the last class. The pellets should "cook" for at least 12 hr. If the oven you are using has an especially air-tight door (many pottery ovens in art shops can be made

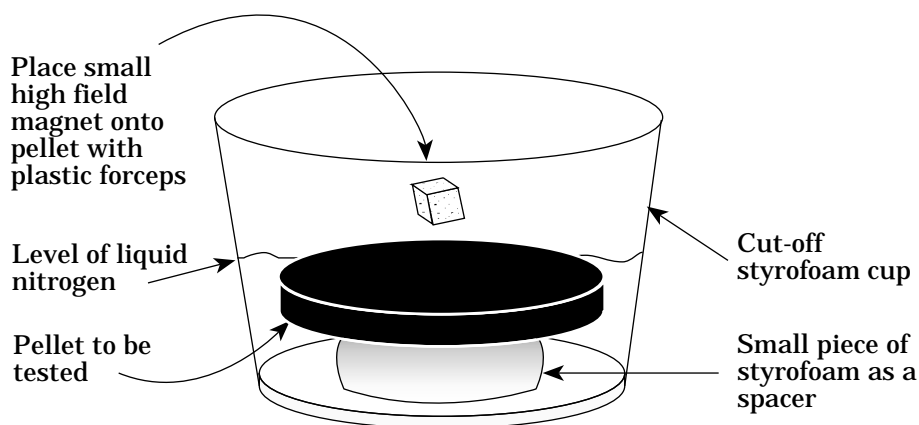
LABORATORY ACTIVITY: STUDENT VERSION





air tight so that glazes are fired in a reducing atmosphere), you or your teacher may want to crack the door occasionally to admit more oxygen as the pellets are heating. (Many scientists who prepare superconductors go to the extra trouble of having oxygen flowing into the oven during pellet heating.)

7. After the pellets have heated overnight at $950\text{ }^{\circ}\text{C}$, set the oven to $400\text{ }^{\circ}\text{C}$, and “cook” at this lower temperature overnight.
8. After the pellets have heated overnight at $400\text{ }^{\circ}\text{C}$, turn the oven off and let the oven cool overnight without opening the door.
9. To test your pellet for superconductivity, proceed as follows (see Figure A).



- a. Place the pellet in a cut-off styrofoam cup, preferably on a styrofoam spacer.
- b. Pour liquid nitrogen into the cup until it just covers the pellet to be tested. (The liquid nitrogen will bubble and vaporize until the pellet and the inside of the cup are at liquid nitrogen temperature.) Add more liquid nitrogen before the pellet cools to liquid nitrogen temperature while it is still partially immersed, as indicated in the figure.

Figure A. Testing for superconductivity.

- c. Slowly and carefully lower a small powerful magnet above the pellet. (The samarium cobalt magnets found in old “Walkman” earphones work well.) It is better to use plastic forceps to place the magnet, but you can also place it by tying a light thread to it and lowering it to the surface of the pellet. To avoid frostbite **do not** use your fingers!
 - d. If the magnet floats above the pellet, the pellet is a superconductor.
10. If time permits, use styrofoam balls of different sizes to build a model of the Yttrium 1-2-3 unit cell. Your teacher may choose to have you do this step during some of the cooling time.
 11. Thoroughly wash your hands before leaving the laboratory.

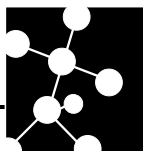
Data Analysis and Concept Development

Observe the magnet floating above your superconductor. Imagine the magnetic lines of force you would observe if you sprinkled iron filings around that magnet in three dimensions. Now imagine that the pellet is refusing to allow those lines of force to enter its surface. The magnetic lines of force, and the magnet, are being pushed away—repelled.

Look at the model you have built or a picture of a perovskite superconductor made of yttrium, barium, copper, and oxygen. Imagine the electrons moving along the plane containing Cu and O atoms such that even electrons very far from each other are spin-paired. They are dance partners—when one moves, the other makes a mirror image move.

Implications and Applications

1. Magnetically levitated trains and subways are one way of using the Meissner effect industrially to minimize friction and maximize fuel efficiency. What are some other ways the Meissner effect might be used?
2. Look at the Periodic Table. What metal oxides might be used in place of yttrium oxide, Y_2O_3 , barium oxide, BaO , and copper oxide, CuO , in making a 1-2-3 superconductor? (*HINT: Both the charge and the size of the metal ion are important. The Cu-O sheets in the unit cell structure seem to be necessary for superconductivity to occur in these compounds.*)
3. Most high T_c ceramic superconductors need to be protected from the air because they react with water vapor and carbon dioxide. Use the Periodic Table to explain why this might be true.
4. Many applications of superconductors require that they be in coils of wire. With the high T_c compounds, why might that be a problem?



**LABORATORY
ACTIVITY:
TEACHER
NOTES**

Extension Activity: Preparation of a Superconductor

Introduction

The purpose of this activity is to prepare high temperature superconductors, a very exciting class of materials first discovered in the mid-1980s. Superconductors are already used in scientific instruments such as magnetic resonance imaging (MRI) and are potentially useful in areas like energy storage and magnetic levitation. Superconductivity is a special property of some materials such that below a given temperature called the *critical temperature* or T_c , the material conducts electric current without resistance.

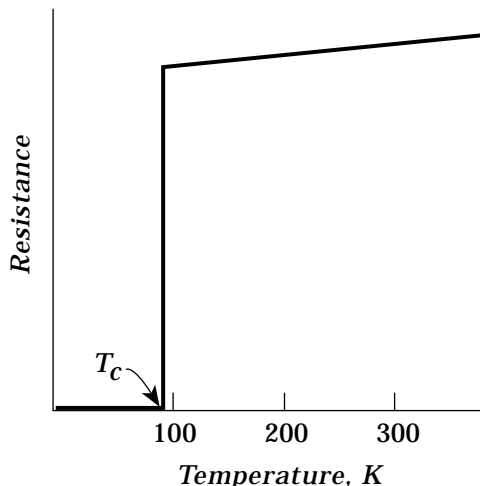


Figure B. This graph shows the resistance versus temperature of the superconductor $YBa_2Cu_3O_{6.5}$, which super-conducts below 92 K. The resistance falls to zero at the T_c

The first group of superconductors, discovered in 1918, were metals that lost all resistance when cooled to a temperature near zero Kelvin. For years, these were the only superconductors known, and had to be studied at the temperature of liquid helium. The explanation for this property was that it arose from long distance spin pairing of electrons within solids. The movement of electrons within a superconducting solid could then be compared to the movement of a crowd of people who have decided to move to a counted cadence. If everyone in a crowd leaving a ballgame decided to get through the only gate on their own, there would be a lot of random milling around, bumping into each other, and scattering. This disorganized process would resemble regular electric current with lots of resistance. If the crowd were lined up in ranks just wide enough to get through the gate and then marched out the gate to the same cadence, they'd get out much more quickly with little or no jostling, bumping and random movement. This latter arrangement resembles low temperature superconductors.

In the mid-1980s, some ceramic oxide materials were discovered to be superconducting. Not only that, they were superconducting at temperatures that were much higher than the previously known superconductors. In fact, many became superconducting at temperatures higher than the temperature of liquid nitrogen—a very cold liquid (77 K) compared with room temperature, but very hot compared with the temperature of liquid helium (4 K). The old theory of long range spin pairing of electrons was not adequate for explaining all of the behaviors of these new materials, and no completely successful theory has been developed to explain and predict the behavior of high T_c ceramic superconductors.

One of the interesting properties of superconductors is that they block magnetic fields. Because of this blocking effect, they serve as a sort of anti-magnetic mirror, reflecting any magnet that comes near them. This behavior leads to something called the **Meissner Effect**—the ability of a superconductor to make a magnet float above it, no matter what the orientation of the magnet or the superconductor.

Major Chemical Concept

The major chemical concept depends on what you wish to do with this activity. Periodic properties and a comparison of metallic, reaction stoichiometry, ionic, and covalent network bonding in solids, the possibility for solids reacting with each other, and colligative properties (melting point lowering at the grain boundaries) are a few of the chemical concepts related to this laboratory.

Level

General and honor students.

Expected Student Background

The expected student background depends on what concepts are treated. A knowledge of stoichiometry and periodic properties appear to be the minimum if students are to develop an understanding at deeper than the cookbook level. However, preparing real superconductors is fun, even if it is done as a cookbook exercise.

Time

Calculating stoichiometric masses of ingredients and preparing pellets will take a full 40-45 min period. Conducting a Meissner Effect test requires only a few minutes. (Note that two overnight heatings and one overnight cooling of the pellets is required before students can conduct the Meissner test.)

Safety

Read the *Safety Considerations* in the *Student Version*. It is quite important that students wear dust masks and wash their hands thoroughly after preparing their pellets. Liquid nitrogen safety should be rigorously enforced so make sure students follow safety procedures outlined in the *Student Version*.

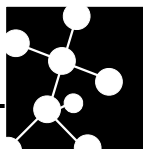
Materials (For 24 students working in pairs)

Nonconsumables

- 12-24 Ceramic crucibles
- 12 Mortars and pestles
- Balance (0.01 or 0.001 g precision)
- 12 Spatulas
- Pellet press
- 12 Crucible tongs
- Furnace
- Thread or plastic forceps
- 12 Styrofoam cups
- Scissors (to cut the styrofoam)
- Small lightweight powerful magnet (like the Samarium-Cobalt magnets sold by science supply houses or found in cheap "Walkman" headphones)
- Transparency master of Yttrium 1-2-3 unit cell

Consumables (see *Advance Preparation* for further information)

- Yttrium oxide, Y_2O_3
- Barium oxide, BaO
- Copper oxide, CuO
- Other oxides (*optional*)
- Styrofoam balls
- Stiff wire, long pipe cleaners or toothpicks



Advance Preparation

Materials must be ordered and arranged in advance. Most high schools cannot support this activity with supplies available in the storeroom.

Needed consumables depend on the laboratory. If students are to conduct this laboratory as described with no additional metal oxides tested, they need a source of yttrium oxide (Y_2O_3), barium oxide (BaO), and copper oxide (CuO). The amount of oxides needed depends on the size of pellets to be made and the number of student groups. If other oxides are to be used, students need those as well. If students are to build models of 1-2-3 compounds, they should also have styrofoam balls, stiff wire or long pipe cleaners, toothpicks, *etc.* The transparency master showing the structure of the Yttrium 1-2-3 unit cell will be needed for discussion as well as for reference during model building.

Kits

Arbor Scientific, P.O. Box 2750, Ann Arbor, MI 48106-2750 sells a kit (1990 price: \$275) for conducting this laboratory that includes everything except the balance and the furnace. The oxides sell for \$100. Even if you don't purchase the kit, you may want to get their catalog so you can show your school's industrial arts teacher a picture of their pellet press so one can be made at school. Many science education supply companies carry kits produced by Colorado Superconductor, P.O. Box 8223, Fort Collins, CO 80526. Knusoft Knowledge Systems, 219 Los Cerritos Drive, Vallejo, CA 94589, and I.C.E., Project 1-2-3, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 also supply kits.

Metal Oxide Powders

Sources of metal oxide powders, including unusual ones like gadolinium oxide, Gd_2O_3 , include: Alfa Products, Division of Morton Thiokol, 152 Andover Street, Danvers, MA 01923; Fluka Chemical Corp., 980 South 2nd Street, Ronkonkoma, NY 11779; and Cera/Pure Division, Box 1178, Milwaukee, WI 53201. (Alfa generally, but not always, has the best prices.)

Furnace

Any furnace that will serve to fire crucibles for gravimetric analysis will probably work fine. Numerous science suppliers carry small furnaces. Small Thermolyne furnaces are relatively inexpensive, easy for a nonmechanic to trouble-shoot and repair using the furnished manual, and useful for activities other than superconductor preparation (*e.g.*, the glass laboratory activity). Many science teachers have reported successfully preparing superconducting pellets in furnaces used for firing pottery. (See your art teacher about using the pottery kiln.)

Pellet Press

Pellet presses are easily made in a machine shop. The Arbor Scientific pellet press is a good model for such homemade presses. If you wish to purchase a small hand-operated press, write the Parr Instrument Company, 211 Fifty-Third Street, Moline, IL 61625.

Liquid Nitrogen

There should be numerous sources of liquid nitrogen in any fair-sized city. Liquid nitrogen is used by factories, foundries, universities and colleges, hospitals, doctors' offices, welding shops, plumbers' supply stores, *etc.* Ask around. The places that sell liquid nitrogen will also rent Dewar flasks (laboratory thermos jugs). If you do this activity a lot and want to purchase a Dewar flask, one source is Pope Scientific, P.O. Box 495, Menomonee Falls, WI 53051.

Magnets

Suitable magnets can be found by dissecting dead headphones from “Walkman” type recorders and radios. Samarium-cobalt magnets can also be ordered from Edmund Scientific, 101 E. Gloucester Pike, Barrington, NJ 08007; (609) 573-6250; (609) 573-6295 (FAX).

Since the *Introduction* mentions that superconductors find application in magnetic resonance imaging (MRI), you may wish to refer to the information about MRI presented in *Pictures in the Mind* in the *Instrumentation* module.

Pre-Laboratory Discussion

The pre-laboratory you use depends on the goals you wish to promote. This laboratory can be treated as an attempt to synthesize a compound that has some interesting and potentially useful properties, an activity many professional chemists engage in. One approach might be to use the second *Implications and Applications* question to structure the pre-laboratory discussion. After students predicted which metal oxides might be substituted for Y_2O_3 , BaO, and CuO, they would prepare regular Yttrium 1-2-3 and the substituted compound.

If you wish to lecture on the nature of high T_c superconductors, you should read some of the articles written for general readers and teachers (see the first five references under *References* at the end of this module).

If you plan to have students build models of the Yttrium 1-2-3 unit cell, discuss the transparency master and discuss model building.

Teacher-Student Interaction

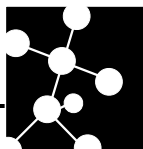
Because this is a cookbook type laboratory, your role should mostly be enforcing safety standards. Once students begin to test their pellets for superconductivity, you should ask them to explain the test, to tell other students how they made their pellet if more than one recipe is used, and so forth.

Anticipated Student Results

Many students have successfully prepared superconducting pellets using the recipes and directions given here. However, many have failed for reasons that are not well understood. There is apparently some luck involved in getting the right amount of oxygen into a furnace that does not have a continuous oxygen supply. Sometimes two different pellets pressed from the same mixture and cooked side by side in the same furnace give different results, one providing a positive Meissner test and the other testing negative.

Answers to Implications and Applications

1. Many responses are possible to this open-ended question.
2. Any $3+$ ion with almost the same ionic radius as Y is acceptable as a Y substitute. Both lanthanides and p -block scandium group and vanadium group metals are potential substitutes for Y and many researchers have tried them. Students will typically propose Ni(II) and Zn(II) as substitutes for Cu(II). Some students may also propose substituting Ag, Au, and Hg for Cu. Ca and Sr are typically proposed as substitutes for Ba.



3. The high T_c ceramics are metal oxides, that are typically basic. Carbon dioxide is an acid and reacts with the basic oxides to make carbonates. Water also acts as an acid, reacting with the metal oxides to produce hydroxides. Both carbonate and hydroxide deform the crystal structure as well as changing the chemical nature of the oxygen atoms in the ceramic compound. This question provides a good opportunity to review previously studied reactions.
4. Making materials into wires requires that they be malleable and ductile. Ceramics are brittle and will break if drawn or bent. There have been numerous attempts to overcome this problem. Ask students for suggestions—*e.g.*, cast the ceramic in the shape required, mix the ceramic with metal so that the wire is malleable and ductile and parts of it are still superconducting, *etc.* The brittleness of the high T_c superconductors shows quite clearly why industrially useful materials must have several useful properties, not just one.

Post-Laboratory Discussion

See *Teacher-Student Interaction*. Your post-laboratory discussion will be guided by the specific content objectives you have chosen to emphasize. If you have conducted this laboratory as an activity to determine what might be substituted for Y, Ba, and Cu, you should have students compare results with predictions. Slight changes in geometry or electron structure might cause large changes in superconductivity behavior.

Extensions

There are numerous extensions. In addition to trying substitute metal oxides in preparing 1-2-3 compounds, students can attempt to synthesize other combinations. High school students have successfully prepared $M_2M'_{2}M''_1Cu_2O_x$ and $M_2M'_{2}M''_2Cu_3O_x$ where M = aluminum or nitrogen group (*p*-block) metal such as Tl or Bi, M' and M'' = alkaline earth metal such as Ca, Ba, or Sr. (*Check the toxicity of these compounds before proceeding.*) Thallium compounds are especially toxic. Stoichiometric quantities of oxides or carbonates are typically ground together repeatedly, pressed into pellets, and heated at $900^{\circ}C$ for 5-10 min. Superconductivity is apparently destroyed if they get hot enough to melt at the grain boundaries between the powder grains. Safety precautions must be observed.

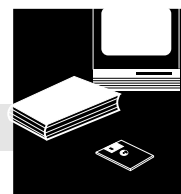
Students may wish to actually measure the T_c of a superconducting pellet. The kits cited above are best for that exercise, but students can do it without a kit if they are careful. Students should prepare a thermocouple from thermocouple wire as thin as they can get. (Omega Engineering, Box 407, Stamford, CT 06907 is the absolute best source of thermocouple materials and their catalogs contain lots of instructional materials as well, including how to use thermocouples.) Students can insert the thermocouple into a pellet either by using a tiny drill to drill a hole in the side of the pellet for thermocouple insertion, or by placing the thermocouple between two identical pellets that are then glued together with silicon sealer. (This is the technique used for some kits.) The thermocouple is connected to an appropriate millivolt meter and the thermocoupled pellet is cooled until it exhibits the Meissner effect. Students should then let the pellet gradually warm until the magnet is observed to sink down onto the pellet. The temperature at that point is approximately the critical temperature.

If your school has the appropriate apparatus, you may also measure the critical current, I_c (the maximum current a superconductor can carry without losing its superconductivity), and the critical field, H_c (the maximum magnetic field a superconductor can withstand without losing its superconductivity).

Assessing Laboratory Learning

1. Evaluate the stoichiometry calculations produced by students in order to arrive at the correct mass of each reactant.
2. The approach to producing the superconducting ceramic pellet is straightforward and “cookbook” in nature. However, there are many new laboratory experiences involving pellet presses, high-temperature ovens, *etc.* These procedures can be evaluated by observing the student’s adherence to the instructions.
3. The activity objective is to produce a superconducting ceramic pellet. Evaluate each student-made pellet by placing it in liquid nitrogen and testing it with a magnet. Does the magnet levitate, illustrating the Meissner Effect?
4. Have students describe the Meissner Effect.
5. Ask students to list problems in producing a ceramic pellet that superconducts.
6. If students have built a model of a Yttrium 1-2-3 superconductor, compare the model with the structure of the perovskite superconductor found in *Links and Connections*.

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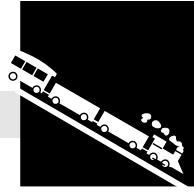
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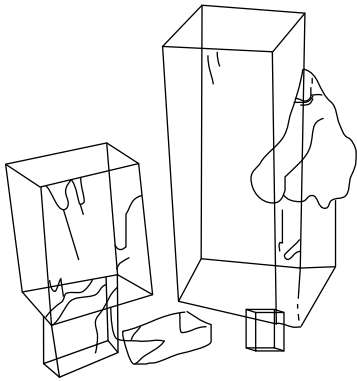
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Appendix



- **Transparency Masters**
 1. Structure of Crystalline and Amorphous Solids
 2. Current Flow and Resistance in Insulators, Conductors, and Superconductors
 3. Superconductivity Analogy
 4. Yttrium 1-2-3 Unit Cell
 5. Word Search
 6. Materials Science Crossword Puzzle

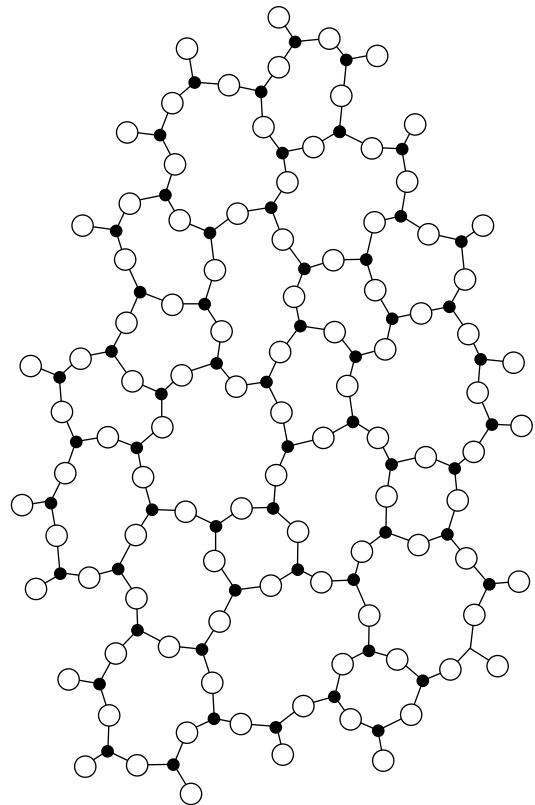
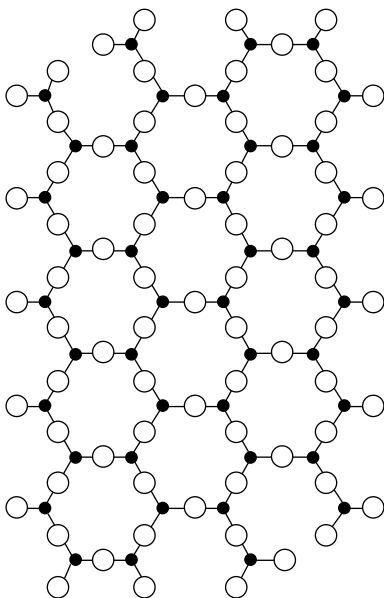
Structure of Crystalline and Amorphous Solids

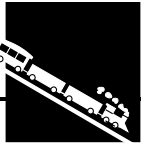


Crystalline

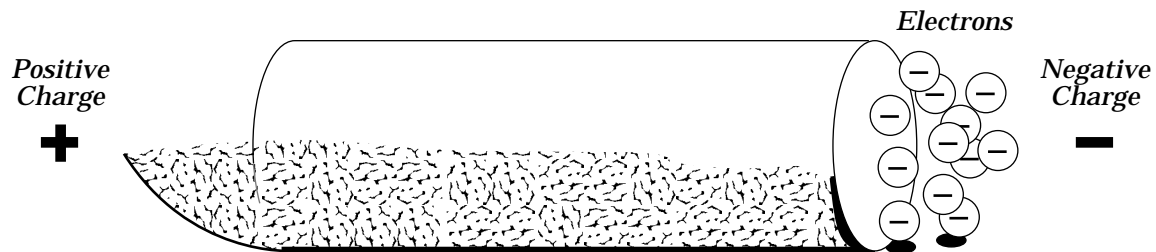


**Amorphous
(Glass)**

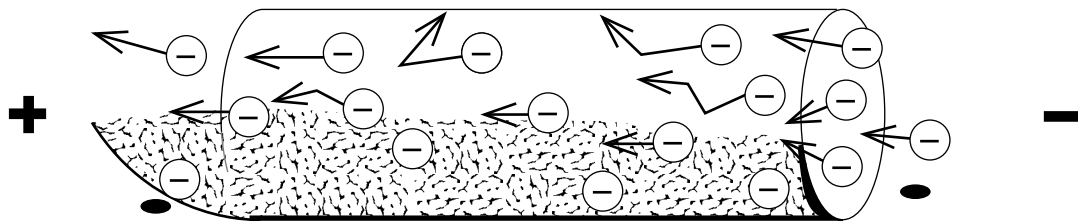




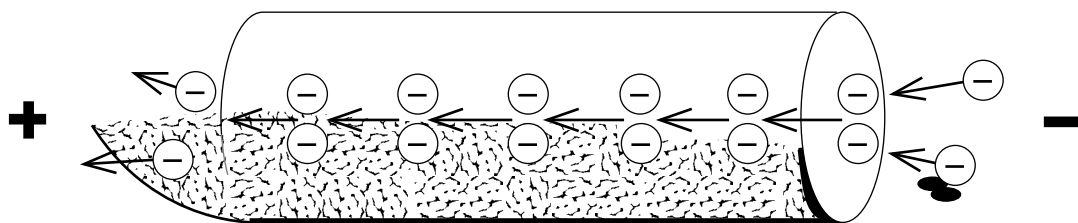
Current Flow and Resistance in Insulators, Conductors, and Superconductors



INSULATOR In materials with extremely high resistance, such as rubber or glass, electrons are tightly bound to atoms and cannot be jostled loose to sustain a flow of current.



CONDUCTOR In materials with lower resistance, some electrons are loosely bound and form a current when voltage is applied. Resistance is a measure of the energy lost in the form of heat from electron collisions.

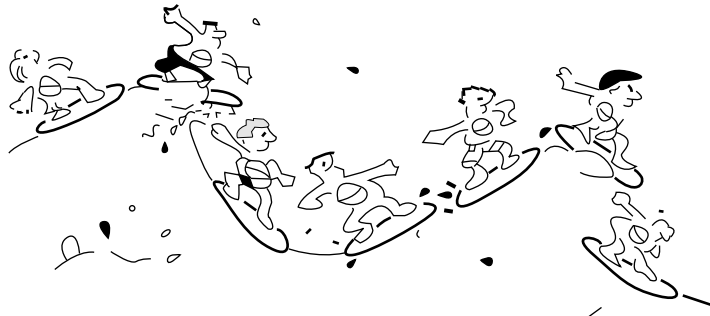


SUPERCONDUCTOR When materials become superconductive, all resistance disappears because electrons are bound into pairs, which move in step with each other, avoiding collisions. Current flows with no energy loss.

Superconductivity Analogy

Conductivity

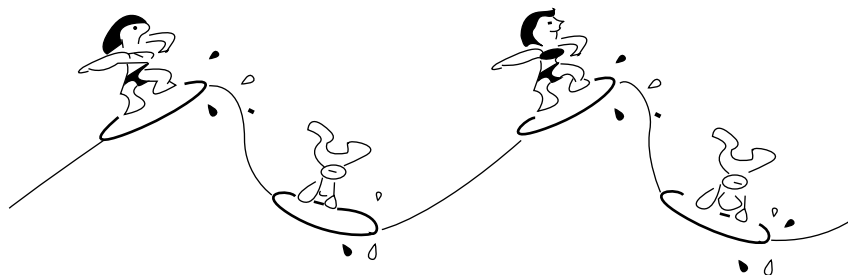
- Electricity is motion of electrons
- Electrons hit atoms = resistance



FREE ELECTRONS

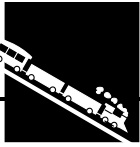
Superconductivity

- No resistance
- Electrons c-c-c-catch the *wave!!*
but—only when they are cold

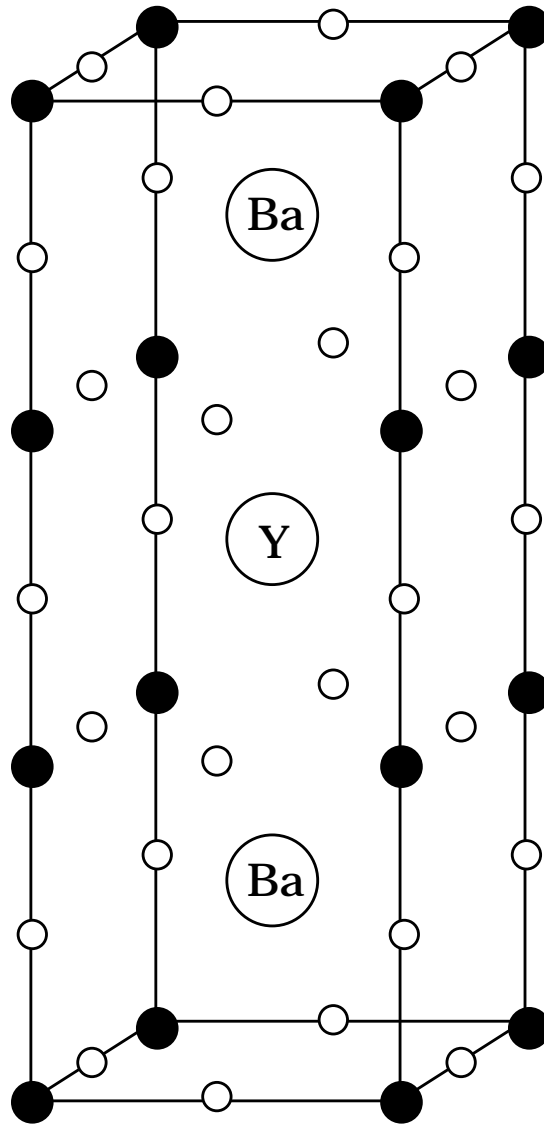


SUPERCONDUCTING PAIRS

Courtesy of Dr. A. M. Stacy, University of California-Berkeley



Yttrium 1-2-3 Unit Cell



○ = O or vacancy

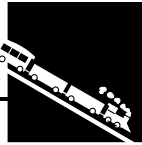
● = Cu (Cu^{2+} and Cu^{3+})

Word Search

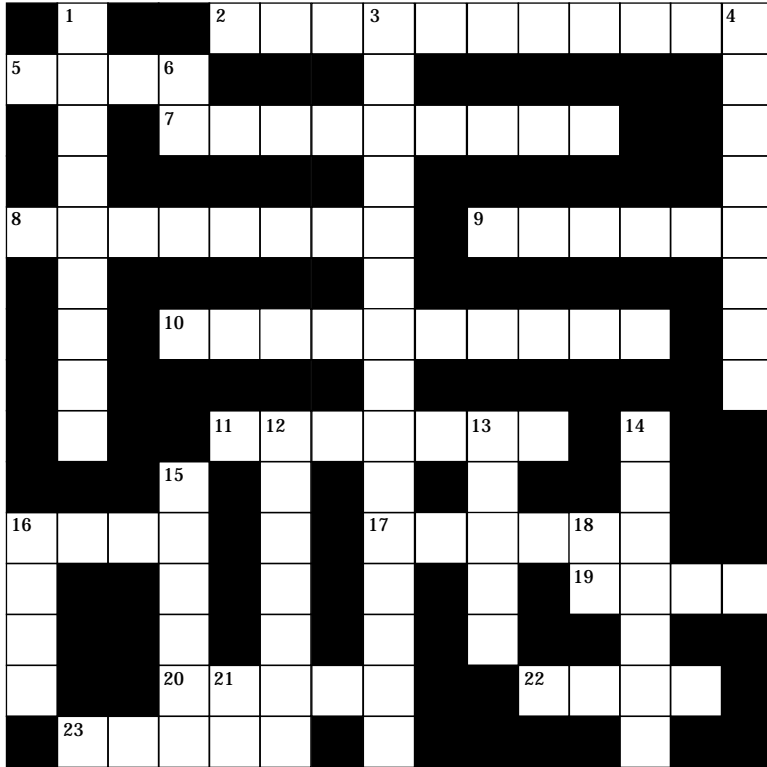
X Y S D F E G V C E R A M I C B V
A W Q T S W G E B X O H C X J E F
N G Q G P C F P M S T O R L T R C
N L J N B G T D X L A G Y E L I S
E Q I F S Q F J F G L A S S M R U
A S U P E R C O N D U C T O R Y O
L L U P L D D E V M S A A J X R H
I I Q W X N G E V B N Z L U V P P
N M F O W S B F R V I E L Q F L R
G H F O A W G A I M H F I J E V O
L A R O X C E S E N A G N A M G M
I C R V Y Q A M Y R G K E N M Q A
G A K W H I S H N N K T X M J E A

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Material that conducts electricity without resistance when cooled to its critical temperature.
2. Type of orderly arrangement assumed by a solid.
3. Material that lowers the melting point of a solid.
4. Material in which there is little movement of electrons.
5. Type of glass fluxed with soda ash and limestone.
6. Inorganic material with bonds strong enough to withstand heat and chemical attack.
7. Amorphous solid made from silica.
8. Compounds of this element when added to glass give it a purple color.
9. Describing a disordered solid lacking a crystalline structure.
10. Heating just below the softening temperature and then cooling.



Materials Science Crossword Puzzle



Across

2. Adjective describing a solid with a regular arrangement of its components.
5. Adjective describing the melting points of ceramic materials.
7. Type of solid with considerable disorder in its structure.
8. With 9-Across, ability of a superconductor to block a magnetic field.
9. See 8-Across.
10. Adjective describing the structure of certain substances like glass that allows it to transmit light equally in all directions.
11. Theory that accounts for the differences in electrical conductivity of substances due to the size of a gap in the energy levels of atomic arrays (2 words).
16. Prefix meaning "half," and used with the word conductor to denote substances whose electrical conductivity increases appreciably as the temperature increases.
17. With 22-Across, electrons with opposite spin which are responsible for most of the conducting electrons in a superconductor.
19. Word with earth or gas.
20. Physical property of many glasses and ceramic materials.
22. See 17-Across.
23. Amorphous solid obtained by fluxing silica and cooling rapidly.

Down

1. Process of heating at high temperature, but below the melting point of the various components.
3. Materials that conduct electricity without resistance when cooled to their critical temperatures.
4. Particle whose movement is facilitated when an impurity is added to a semi-conductor.
6. Symbol for element No. 105 as suggested by its discoverer, Ghiorso, but not adopted by the International Union of Pure and Applied Chemistry.
12. Heats a substance for a time just below its softening temperature and then cools it.
13. Fundamental particles that make up all materials.
14. Inorganic, nonmetallic material processed and hardened by firing at high temperatures.
15. Component of glass.
16. Property of 4-Down.
18. Element No. 68 (Symbol).
21. Element No. 76 (Symbol).

Across	Down
2. CRYSTALLINE	1. SINTERING
5. HIGH	3. SUPERCONDUCTORS
7. AMORPHOUS	4. ELECTRON
8. MEISSNER	6. Ha
9. EFFECT	12. ANNEALS
10. ISOMORPHIC	13. ATOMS
11. BAND GAP	14. CERAMIC
16. SEMI	15. SILICA
17. COOPER	16. SPIN
19. RARE	18. Er
20. COLOR	21. Os
22. PAIR	
23. GLASS	