

Fig. 2. Example of a gas-filled separator used for producing superheavy elements: the Dubna Gas-Filled Recoil Separator (DGFRS) at the Joint Institute for Nuclear Research. (JINR, Dubna, Russia)

for the heaviest nuclei. Position correlations make it possible to determine genetically related events in a decay chain occurring within the detector, and the times between such events can be measured to obtain lifetime or half-life information about the isotopes observed. Rapid identification and characterization of interesting coincidence events involving evaporation residues and alphaparticles sometimes allows the beam to be interrupted for a short time so that subsequent alpha decays or fissions occur in the detectors under lower background conditions. See PARTICLE DETECTOR.

An example of the setup for a typical superheavy experiment is shown in Fig. 2.

Because some of the more recently synthesized superheavy elements have longer half-lives, experiments to study the chemical properties of those elements can be designed. Several experiments aimed at chemically identifying the decay products of some of the heaviest elements have observed evidence for (1) dubnium (Db), a great great great granddaughter of element 115, and (2) element 112, the daughter of element 114.

Current status. Elements up to $Z = 112$ have been confirmed. Once confirmed, element names are then suggested by the scientists first synthesizing them. Scientists at GSI have been credited with discovering elements 107–112. A name for element 112 has not been proposed yet, but scientists at GSI have proposed roentgenium (chemical symbol Rg) for element 111. Elements with $Z = 113$ –116 and 118 were synthesized by a team from Dubna and Lawrence Livermore National Laboratory but have

yet to be confirmed. Another isotope of element 113 produced in the cold-fusion reaction $^{70}\text{Zn} + ^{209}\text{Bi}$ was recently reported by a Japanese group at RIKEN, but is also unconfirmed. See TRANSURANIUM ELEMENTS.

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Superionic conductivity

The electrical conductivity exhibited by a small group of solids with high ionic conductivity and negligible electronic conductivity. In general, ionic conductivity is due to the motion of ions, whereas the electronic conductivity results from the flow of electrons. For superionic conductors, also called fast ion conductors or solid electrolytes, the specific conductivity (σ) is usually within the range from about 10^{-3} to 10 siemens per centimeter. These values are very high for a crystalline ionic solid, but are still lower than many electronic conductors such as metals, which have typical values ranging from 10 to 10^5 S cm^{-1} . See CONDUCTANCE; CONDUCTION (ELECTRICITY); ELECTRICAL CONDUCTIVITY OF METALS; ELECTROLYTIC CONDUCTANCE; SOLID-STATE CHEMISTRY.

Since ionic conductivity increases with increasing temperature, many superionic conductors (such as

ZrO₂) exhibit high ionic conductivity only at temperatures substantially higher than room temperature. High temperatures provide the thermal energy needed to overcome the activation energy for ion hopping (from site to site) and increase the number of defect sites needed for ion migration. For some crystalline solids (such as Li₂SO₄ and AgI), high temperatures lead to polymorphic phase transitions, which cause an abrupt increase in the ionic conductivity. See IONIC CRYSTALS; POLYMORPHISM (CRYSTALLOGRAPHY).

While ionic conductivity is a common property of liquid electrolyte solutions or molten salts, a typical ionic solid (such as NaCl) has negligible ionic conductivity, often below 10⁻⁹ S cm⁻¹. Special structural features are required in order for a crystalline solid to have superionic conductivity. One common feature is that such solids have a rigid framework with open channels or layers along which ions can migrate. Other factors that contribute to the high ionic conductivity include small ion size, low ion charge, low coordination number for mobile ions, high concentration of mobile ions, a large number of vacant sites, and high polarizability of anionic frameworks. See CRYSTAL DEFECTS; CRYSTAL STRUCTURE; ION.

Superionic conductors. Superionic conductors can be classified according to the type of mobile ions, the dimensionality of conduction pathways, or the structure type of the nonmobile portion of the crystal structure.

Cationic conductors. Common cationic conductors usually contain ions such as Ag⁺, Na⁺, Li⁺, or H⁺. Silver iodide and its derivatives are among the earliest studied ionic conductors. At room temperature, the Ag⁺ conductivity in AgI is low because I⁻ ions adopt either hexagonal or cubic-close-packed structure. At temperatures above 146°C (295°F), AgI transforms into a polymorph in which I⁻ ions adopt an open body-centered-cubic packed structure containing disordered Ag⁺ ions and the conductivity of AgI increases sharply to about 1 S cm⁻¹. Many other similar Ag⁺ conductors have been found. One of them, RbAg₄I₅, has a specific conductivity of 0.26 S cm⁻¹, even at room temperature.

Sodium β-alumina is a well-known Na⁺ conductor whose discovery in 1960s led to an active field of research on ionic conductors. β-alumina was originally thought to be a polymorph of Al₂O₃, but it was later found to have complex compositions. Other oxides such as Na₂O are also present to stabilize its crystal structure. The general formula of sodium β-alumina is Na₂O · nAl₂O₃ (n = 5–11). Closed-packed O²⁻ layers can adopt different stacking sequences, leading to two structural variations labeled as β and β'. In both structures, 75% of the oxygen ions are missing within every fifth O²⁻ layer, creating open layers along which Na⁺ ions can migrate (Fig. 1). The conductivity of sodium β-alumina is high even at room temperature and is on the order of 10⁻² S cm⁻¹. Na⁺ ions can be readily exchanged with other cations such as Li⁺, Cu⁺, and Ag⁺, giving rise to other types of ionic conductors. In addition to sodium β-alumina, there exists another Na⁺ conductor (Na₃Zr₂PSi₂O₁₂)

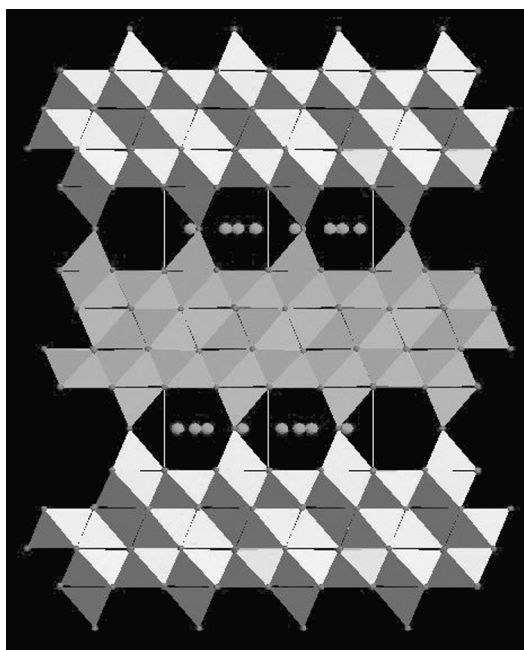


Fig. 1. Structural diagram of sodium β-alumina showing open conduction layers. Color spheres are oxygen sites and dark gray spheres represent mobile Na⁺ ions. Aluminum sites are located at the center of light gray polyhedra.

named NASICON (from sodium superionic conductor). It is a member in a family of materials with the general formula of Na_{1+x}Zr₂(P_{3-x}Si_x)O₁₂ (0 < x < 3), and its crystal structure contains channels within a three-dimensional framework built from ZrO₆ octahedra and (P/Si)O₄ tetrahedra. See ION EXCHANGE.

Li⁺ superionic conductors are highly desirable for all-solid-state lithium batteries. However, few crystalline Li⁺ compounds exhibit high ionic conductivity, particularly at room temperature. Some Li⁺ conductors are based on structures of Li₄SiO₄ and Li₄GeO₄. Substitutions of Si⁴⁺ and/or Li⁺ ions with other cations such as P⁵⁺ or Zn²⁺ could lead to substantial improvement in conductivity. One compound, Li₄ZnGe₄O₁₆, has a specific conductivity of about 10⁻¹ S cm⁻¹ at 300°C (572°F) and is named LISICON. See SOLID-STATE BATTERY.

Many proton (H⁺) conductors are based on hydrated materials and are usable close to ambient temperature. Proton conductors can be prepared through ion exchange of sodium β-alumina with H₃O⁺. Other examples include hydrogen uranyl phosphate (HUO₂PO₄ · 4H₂O) and some hydrated heteropolyacids such as H₃(PMo₁₂O₄₀) · nH₂O. High-temperature proton conductors are based on SrCeO₃ and BaCeO₃ with the perovskite-type structure. After partial substitution of Ce⁴⁺ sites with trivalent ions, such as Y³⁺, these oxides exhibit high H⁺ conductivity in a moist atmosphere. See PEROVSKITE.

Anionic conductors. Common anionic conductors are usually oxide (O²⁻) or fluoride (F⁻) conductors, such as stabilized zirconias and PbF₂, which require high temperatures for fast ion conductivity. These conductors usually have the fluorite (CaF₂) type structure in which anions (O²⁻ or F⁻) are arranged at cor-

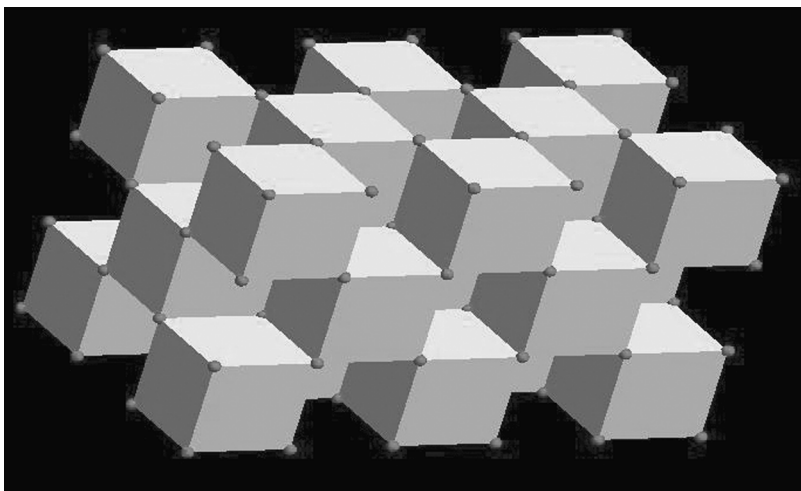


Fig. 2. Diagram of the CaF_2 type structure. Common anionic conductors, such as stabilized zirconia, adopt this structure type. Oxygen anions shown in color spheres form the cubic arrangement. Not all oxygen sites are occupied in stabilized zirconia. Cations such as Zr^{4+} occupy the center of every other cube represented by solid cubes.

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ners of a cube and cations occupy body centers of alternative cubes. Stabilized zirconias are solid solutions between zirconia (ZrO_2) and CaO or Y_2O_3 . The doping of ZrO_2 also helps to prevent phase transitions to noncubic forms, when temperatures are lowered. The replacement of some Zr^{4+} sites with lower charged cations (such as Ca^{2+} or Y^{3+}) helps create vacant oxygen sites, which contribute to the high-temperature ionic conductivity (Fig. 2). See FLUORITE.

Amorphous conductors. In addition to crystalline inorganic solids, superionic conductivity can also be found in amorphous inorganic materials. In general, glassy electrolytes based on sulfides and halides have much higher conductivity than oxides at ambient temperatures. Many Li^+ and Ag^+ conducting glasses are known. One Li^+ conducting glass with the composition $0.7\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5$ has a conductivity of 0.16 S cm^{-1} at 25°C (77°F). Even though oxide-based glasses have low conductivity, they are more stable than sulfides or halides at high temperatures. See AMORPHOUS SOLID.

Polymer-based conductors. Superionic conductivity is also known in polymer-based solids. These polymer electrolytes have two general types: polymer-salt complexes and polyelectrolytes. Polymer-salt complexes are generally made by dissolving a salt (such as LiClO_4) in a polymer [such as poly(ethylene oxide)]. Both cations and anions in polymer-salt electrolytes can be mobile. In polyelectrolytes, the polymer backbone contains covalently attached charged (positive or negative) groups and the charge-balancing counterions are able to make long-range migration. The best-known polyelectrolyte is Nafion[®] perfluorocarbon sulfonic acid polymer, which is a proton conductor under wet conditions.

Applications. Superionic conductors are an important group of materials that have large-scale technological applications in areas such as energy storage and generation (electrolyzers, batteries, and fuel cells), gas sensors, and electrochromic devices. They

are essential for the development of all-solid-state electrochemical devices, which have many advantages over those based on liquid electrolytes including ease of miniaturization and high-temperature stability. Oxygen gas sensors based on oxide conductors are being widely used to monitor automobile exhaust gases. Oxide conductors are also being studied for the construction of solid-oxide fuel cells (SOFC). Nafion and related sulfonated polymers are under investigation as proton conductors in polymer electrolyte membrane (PEM) fuel cells. See BATTERY; ELECTROCHROMIC DEVICES; ENERGY STORAGE; FUEL CELL; MICROSENSOR.

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Superluminal motion

Proper motion of an astronomical object apparently exceeding the velocity of light, c . This phenomenon is relatively common in the nuclei of quasars, many of which exhibit systematic changes in images of their radio-frequency emission over periods of months to years. In some cases, features in the image appear to separate at a speed inferred to be more than 10 times the speed of light, given the great distance of the quasars from Earth.

Superluminal motion was one of the most exciting discoveries to emerge from a technique in radio astronomy first developed in the late 1960s and called very long baseline interferometry (VLBI). This method involves the tape recording of radio signals from large antennas at up to 10-15 locations across the Earth, and the combination of these signals in a computer to form a radio image of the quasar at extremely high resolution (less than 0.001 arcsecond). A sequence of images of quasar 3C 279, one of the best-studied examples, illustrates the phenomenon of superluminal motion (Fig. 1). See QUASAR; RADIO ASTRONOMY; RADIO TELESCOPE.

Objects involved. Superluminal motion is seen mostly in quasars but also in some other active galactic nuclei. This rapid motion is confined to within a few tens of parsecs of the nucleus, whose power source is believed to be a massive black hole. Data on variability are now available on more than 60 objects of which at least 30 examples of superluminal motion are now known, and the list continues to grow. Most show apparent speeds less than $10c$, but examples of speeds above $20c$ have been found. A few quasars and galaxies with good data exhibit motion that is subluminal (that is, with speeds less than c).