



Hydrothermally grown zinc oxide crystals, which exhibit both piezoelectric and semiconductor properties, have yellow tint as a result of excess interstitial zinc

Anorganische Chemie at the Rheinisch Westfälischen Technischen Hochschule in Aachen, West Germany, synthesized single crystals of compounds such as  $\text{Li}_3\text{Na}(\text{NH}_2)_4$ ,  $\text{BaNH}$ , and  $\text{EuN}$  by using near- or supercritical ammonia (ammonothermal synthesis).

Hydrothermal crystallization has been used to prepare single crystals of oxide superconductors by Shinichi Hirano of the University of Nagoya in Japan. Hirano has grown small single crystals of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  in 4.5M potassium chloride solution at temperatures of 450 °C. The superconducting transition temperature for these crystals is 11.7 K (which is comparable to the best polycrystalline samples) and the width of the superconducting transition is only 1.8 K (which is better than in polycrystalline- or flux-grown samples). This suggests that low-temperature hydrothermal growth has a good potential for preparing superconductors such as  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and other perovskites with superconducting transition temperatures above 90 K. Recent results in my lab indicate, however, that  $\text{YBa}_2\text{Cu}_3\text{O}_7$  reacts with water, even at room temperature, with the formation of  $\text{O}_2$  and  $\text{Cu}^{2+}$ . This suggests that nonaqueous hydrothermal solvents will be required.

Hydrothermal synthesis also is of great interest for preparing other materials, although generally in the form of fine polycrystalline aggregates rather than as large single crystals. Examples are ferromagnetic oxides such as  $\delta\text{-Fe}_2\text{O}_3$  and  $\text{CrO}_2$  for magnetic recording, zeolites for catalysis ion exchange applications, ultra-fine starting materials like zirconium oxide for ceramics, and apatites for the study of teeth and bones.

Hydrothermal chemistry continues to pose research challenges. For one thing, understanding of the physical chemistry of hydrothermal solutions must be further extended so that synthesis and crystal growth can become less of an empirical art. In addition, the range of materials that can be synthesized hydrothermally needs further exploration, focusing especially on compounds from which single crystals of high quality are

difficult to grow by alternative methods because of thermodynamic or other reasons.

Quartz crystals already are grown commercially, and hydrothermal growth of crystals of aluminum phosphate, potassium titanil phosphate, and emerald is likely to be commercially viable. But hydrothermal crystal growth certainly can be further extended, especially because of the method's ability to prepare refractory materials at relatively low temperatures.

Meanwhile, our present considerable understanding of the quartz system can be further built upon, so that crystals better than the best obtainable from nature can be uniformly and reproducibly grown on a routine basis.

Hydrothermal methods can be used to synthesize some of the most-difficult-to-prepare materials known to modern technology. They will continue to provide a unique experimental milieu, as well as an intriguing intellectual milieu for testing our overall understanding of solution chemistry. □

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Laudise received a B.S. degree in chemistry at Union College, Schenectady, N.Y., in 1952 and joined Bell Laboratories after earning a Ph.D. degree in inorganic chemistry from Massachusetts Institute of Technology in 1956. Since then, he has held various positions at Bell Labs, including head of the crystal chemistry research department and director of materials research. He is past chairman of the American Chemical Society's Solid State Chemistry Subdivision and has served as president of both the American Association for Crystal Growth and the International Organization for Crystal Growth. He is a member of the National Academy of Engineering and has been honored with the Sawyer Piezoelectric Prize and the International Crystal Growth Award of the International Organization for Crystal Growth.

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