

**05.2-15** STRUCTURE AND PHYSICAL PROPERTY RELATIONS OF  $ZrO_2$ . By Doris L. Evans, Corning Glass Works, Sullivan Park, DV-19, Corning, New York, 14831.

Practical uses of  $ZrO_2$  include grinding media, refractory bricks, plasma sprayed coatings, oxygen sensors, tool applications and gem quality "fake" diamonds. The wide range of available properties originates in the three structural polymorphs of  $ZrO_2$ . Further useful development of unique properties depends upon interpreting lattice details of structural change together with macroscopic details such as heat effects and grain growth. Heat is absorbed and density increases as monoclinic  $ZrO_2$  transforms to tetragonal symmetry at  $\sim 1150^\circ C$  ( $T^+$ ). Note that the density change resembles that of ice as it changes to water at  $0^\circ C$ . During cooling there is large thermal hysteresis. Also, the heat at  $\sim 950^\circ C$  ( $T^+$ ) is emitted over a much smaller temperature range than  $\Delta T$  the higher temperature heat absorption.

Transformation by nucleation and growth (reconstructive) from low to high temperature and displacive transformation from high to low temperature are indicated.

Heat absorbing temperature intervals are regions of intrinsic reactivity where chemical reactions that are alternative to the self-reaction of phase transformation may be found.

These regions, taken together with such adjustable  $ZrO_2$  physical parameters as particle size distribution, provide means of obtaining new properties in real materials. These are generated by "designed" combinations of intrinsic properties of each of the polymorphs.

**05.2-16** COMPRESSION BEHAVIOR OF  $GeO_2$  (QUARTZ): POSSIBLE HIGH-PRESSURE POLYMORPHISM.

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Room temperature Raman spectra measurements made in the pressure range 0-10 GPa (1 GPa = 10 kbar) indicate that the compression behavior of  $GeO_2$  (quartz structure) changes character in the region of 6 GPa. The structural nature of this change interests us not only because it could represent a new polymorphic transition but because of potential implications for the high-pressure behavior of  $SiO_2$ . At present we have investigated the structural changes in the pressure range 0-5.5 GPa. Higher-pressure measurements are in progress and will be reported at the meeting.

Our X-ray diffraction measurements were made on a single-crystal  $GeO_2$  sample which was enclosed within a diamond-anvil pressure cell. The unit cell parameters at each pressure were obtained through least-squares refinement using the angular settings for 18-25 reflections. In addition, three-dimensional intensity data were collected, corrected for crystal absorption and for various systematic errors introduced by the diamond-anvil cell, and used to refine the positional and thermal parameters for this structure. The residuals for our preliminary refinements range from 0.0364 to 0.0391.

The quartz structure,  $D_3^4$ - $P3_121$ , consists of corner-linked  $MO_4$  tetrahedra, and its high compressibility (we obtained a bulk modulus of approximately 38 GPa for  $GeO_2$ ) is attributed to the relatively open nature of the structure. Previous studies (Jorgensen, J.D., *J. Appl. Phys.* 49 (1978), 5473; Levien et al., *Amer. Mineral.* 65 (1980), 920) have shown that compression of the quartz structure is accommodated through tilting and distortion of the tetrahedra. For  $GeO_2$  we found that both of these distortions smoothly increase with pressure, with the tetrahedral distortion increasing most rapidly. (In  $SiO_2$ , to the contrary, the tilt angle varies most rapidly.) The linear compressibility of the inter-tetrahedra oxygen-oxygen distances is approximately 20 times greater than that for the average intra-tetrahedra distances. Consequently, at high pressures some inter-distances become shorter than those within the tetrahedron, and the oxygen's anion coordination increases. There is, however, no evidence for a change in coordination of the metal atom.

**05.2-17** METALLIC CHARACTER AND DUCTILITY OF THE BERYLLIDES AND THEIR ZINC ANALOGS: P. J. Shlichta, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA.

Beryllium combines with small amounts of many other metals to form icosahedrally coordinated structures such as  $MBe_{22}$ ,  $MBe_{13}$ ,  $MBe_{12}$ , and  $M_2Be_{17}$ . These "beryllides" often exhibit unusually high melting points and high-temperature strengths but are presumed to be intrinsically brittle at low temperatures because of their covalent bonding.

It may be argued, however that the icosohedral bonding is really metallic and reflects a closer-than-closest packing attainable only locally or in curved space. This contention is supported by the positive thermal coefficient of resistivity shown by many beryllides.

This evidence for metallic bonding makes intrinsic ductility seem more plausible. For example, CsCl-like slip would be possible in the  $MBe_{13}$  structure if dislocation motion is associated with rotation of the beryllium-atom icosohedra. Moreover, microslip has been reported in  $NbBe_{12}$  at  $77^\circ K$  (Lewis, 1961). It therefore appears possible that sufficiently purified single-crystal beryllides will exhibit some degree of room-temperature ductility.

Zinc forms a large number of zinc-rich intermetallic phases having beryllide structures. Many of the phase diagrams are also closely similar. It is therefore likely that these "zincides" are physically as well as crystallographically analogous to the beryllides and that the observation of ductility in a zincide would be evidence for ductility in the corresponding beryllides.