

## **Synthesis and Mineral Properties of Zirconia Crystals**

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### **Introduction**

In view of the interest in yttria-stabilized zirconia as a high performance ceramic, experiments to prepare zirconia and to reinvestigate the crystal structure have been attempted extensively. The zirconium oxide is known to have 3 polymorphs under atmospheric pressure condition (VEST & TALLAN 1965, ANTHONY et al. 1966, MADEYSKI & SMELTZER 1968, KUMAR et al. 1972, SCOTT 1975, ALDEBERT & TRAVERSE 1985). It is monoclinic at room temperature and occurs in nature as mineral baddeleyite. Upon heating to about 1100°C, this undergoes a phase transformation leading to the tetragonal phase. At about 2300°C, there is another change leading to the cubic form of ZrO<sub>2</sub>. The latter two high-temperature forms are unstable at room temperature. This same sequence is performed in the reverse direction when cooled (WYCKOFF 1963).

Among the polymorphs, the cubic form has been of great interest especially in gemology because it is the most convincing diamond simulant yet produced. The cubic symmetry is stable only at high temperature and is known to be preserved at room temperature by adding some chemicals, i.e., calcium oxide, magnesium oxide, or yttrium oxide as a stabilizer. Various methods have been employed by many workers to prepare cubic symmetry zirconia. DUWEZ et al. (1951) synthesized zirconia from zirconia-yttria mix and reported that at least 7 mole % yttria is required to preserve cubic symmetry at room temperature. One year later, they prepared cubic form zirconias from zirconia-calcia and zirconia-magnesia mixes by firing them in an oxyacetylene furnace, and proposed

that 16~30 mole % calcia or 16~25 mole % magnesia were required to stabilize zirconia into the cubic form. Reviewers of their manuscript, however, mentioned at the end of their article that 10 mole% calcia or 12 mole% magnesia were sufficient. Since the phase diagram of  $ZrO_2$ - $Y_2O_3$  was investigated first by DUWEZ et al. (1951), parts of the phase diagram have been modified by many workers including SCOTT (1975) and YOSHIMURA (1988). Contrary to the fact that 7 mole % yttria were necessary to stabilize cubic zirconia as proposed by DUWEZ et al. (1951), SCOTT (1975) indicated that all specimens containing more than 13 mole %  $Y_2O_3$  were cubic and that there was an apparent continuous transition from fluorite structure at low yttria content to the type C rare earth structure (yttria structure) at high yttria content, with a consequent doubling of the lattice parameter. STEELE & FENDER (1974) synthesized three yttrium zirconia samples with compositions  $Zr_{0.82}Y_{0.18}O_{1.91}$ ,  $Zr_{0.78}Y_{0.22}O_{1.89}$ , and  $Zr_{0.74}Y_{0.26}O_{1.87}$  by heating at 1800°C under a  $10^{-3}$  bar vacuum, for 15 minutes within an induction furnace. Tsukada et al. (1999) succeeded in synthesizing yttrium-doped zirconia  $[(Zr,Y)O_2]$  crystalline powder by low-temperature hydrothermal method, by reacting  $Zr(OH)_4$  and  $Y(OH)_3$  in aqueous solution at 100°C in an open vessel under highly alkaline conditions (pH~14). The most conventional processing technique, however, currently used in ceramic industry to produce cubic form zirconia is the coprecipitation/calcination/heat treatment process (RAMANATHAN et al. 1992, TORAYA, 1989) with yttria as stabilizer.

Nevertheless, all the materials prepared by the mechanisms mentioned above were polycrystalline powders and of no use in gemological purpose. In order to use zirconia as diamond substitute, it is essential to grow a crystal large enough to be suitable for gemstone. The best technique for this purpose is known to be the skull-melting method, but only very little information about its experimental growth of the crystal with  $(ZrO_2)_{0.875}(Y_2O_3)_{0.125}$  composition is disclosed (ROULIN et al. 1969). NASSAU (1980) stated that most cubic zirconia for gemstone purpose has been made using a little less than about 65 wt.%  $Y_2O_3$ . without mentioning any details.

The aim of this paper is, therefore, to repeat on yttria-stabilized cubic zirconia produced by skull-melting method and to describe the detailed experimental results.

## Experiments and Results

Starting material  $ZrO_2$  (99.8% purity) and stabilizer  $Y_2O_3$  (99.999% purity) were purchased from MEL, England. In order to find out the optimum condition for the growth of a colorless and transparent single crystal, variable amounts of  $Y_2O_3$ , i.e., 15, 20, 25, and 30 wt.% were added to the  $ZrO_2$  powder and tested.

Weighed amounts of three chemicals were thoroughly mixed in a mechanical mixer for 5 hours and then put into a cold container of 105 mm inner diameter and 135mm height. A small piece of Zr metal was also included into the container. The skull was then placed inside a copper coil which was connected to a LEPEL radio frequency generator of 50 kW and 2~5 MHz capacity. Shortly after heating to 2900°C, the electric power was reduced slowly and the skull was lowered at various speed, i.e., 6mm/hr, 10mm/hr, 13mm/hr, and 16mm/hr, out of the heating coil. For all the cases, a skin solidified over the top of skull contents, and useful crystal growth appeared to begin at the bottom of the skull. Parallel columns of crystals, nucleated near the bottom of the skull, grew upwards until the whole melt solidified. Zirconia crystals thus obtained invariably showed yellowish color with differing diaphaneities.

To remove the yellow color from the crystal, very small amount (up to 0.1 wt.%) of  $Nd_2O_3$  (99.999% purity), also purchased from Mel, England, was added to the zirconia and yttria powders. Then, the same procedure described above was repeated. This time it showed a different phenomenon. When  $Nd_2O_3$  of less than 0.03 wt.% and more than 0.05 wt.% were added, the crystal remained slightly yellow and purple, respectively, regardless of the amounts of  $Y_2O_3$  in the mixes. Therefore 4 wt.% of  $Nd_2O_3$  were added to all the mixes to grow colorless crystals. The crystal grown now showed different quality depending on the amount of  $Y_2O_3$  added. When 15 wt.%  $Y_2O_3$  were applied, the crystal became cloudy and opaque. When 20 wt.%  $Y_2O_3$  were added, most crystals were colorless and transparent. But some portion, grown especially near to the inner wall of the crucible, remained cloudy. When 25 wt.%  $Y_2O_3$  were added, the whole crystal became colorless and transparent. With 30 wt.%  $Y_2O_3$  the crystal became yellowish. Therefore, the highest optimum amount of the stabilizer and decolorizing agent was 25 wt.% and 0.04 wt.%, respectively. Lowering rate of the skull did not affect the quality of the products. Further annealing process has not been applied to all products, although ROULIN et al. (1969) annealed their crystals at about 1400°C in air for 12 hours to

remove any residual strain.

For the whole crystal block grown from the mix containing 25 wt.%  $Y_2O_3$  and 0.04 wt.%  $Nd_2O_3$  prepared in this study, the dimensions are about 100mm in diameter and 100mm in height (Fig. 1). It consists of numerous columnar crystals of approximately 20 x 15 x 40mm in size and shows a vitreous luster with an oily appearance. It does not have cleavage but exhibits conchoidal or uneven fracture on the broken surface of the crystals. The crystal is rather brittle and with Mohs hardness value of  $8 \sim 8\frac{1}{2}$  using the hardness pencils. Under a polarizing microscope, the zirconia crystal is optically isotropic, and is entirely free from normal or abnormal double refraction. Refractive index of the material is greater than 1.81 by a standard gemological refractometer. A faint white glow is seen under both the long- and short-wave ultraviolet light.

The chemical composition of the specimen, determined by a JEOL electron probe microanalyser, is 73.8~74.2 wt.%  $ZrO_2$  and 24.6~25.9 wt.%  $Y_2O_3$ , suggesting a chemical formulae  $Zr_{0.73}Y_{0.27}O_{1.87}$ . Amount of  $Nd_2O_3$  was not analysed precisely, mainly due to extremely small amount. For X-ray powder diffraction analysis a small fragment of zirconia was ground into fine powder under acetone in an alumina mortar. A Rigaku Dmax II X-ray diffractometer with Ni-filtered  $CuK\alpha$  ( $\lambda=1.5418\text{\AA}$ ) radiation was used. Lattice indices for X-ray reflections are given in Table 1. The refined cell parameter ( $a=5.157\text{\AA}$ ) was calculated by a least-squares method.

Single crystal X-ray diffraction, using a CAD4 4-circle diffractometer with  $MoK\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) for a crystal of 0.4 x 0.2 x 0.2 mm in size confirms the cubic symmetry, space group  $Fm\bar{3}m$  ( $O_h^5$ ) with  $a=5.1552(5)\text{\AA}$ .

The cell parameters ( $a$ ),  $5.157\text{\AA}$  and  $5.1552(5)\text{\AA}$  obtained respectively by X-ray powder diffraction and by single crystal diffraction are in good agreement with that ( $a=5.1562 \pm 0.0003\text{\AA}$ ) of STEELE & FENDER (1974) measured for the compositionally similar phase ( $Zr_{0.74}Y_{0.26}O_{1.87}$ ). When considering  $a=5.0858(2)\text{\AA}$  for  $Zr_{0.87}Y_{0.13}O_{1.87}$  (HOWARD et al. 1988) and  $a=5.1487 \pm 0.0002\text{\AA}$  for  $Zr_{0.78}Y_{0.22}O_{1.89}$  (STEELE & FENDER 1974), there is a good linear relationship between the cell parameters ( $a$ ) and the amount of  $Y_2O_3$ . i.e., cell parameter increases as the concentration of  $Y_2O_3$  increases.

The density of cubic zirconia, synthesized in this study, is measured to be 5.85 by the hydrostatic weighing technique, which corresponds very well with the calculated value of 5.84.