Synthesis and Crystal Structure of Yttria-Stabilized Zirconia

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이트리아를 첨가한 저코니아의 합성과 결정구조

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요 약: 등축정계의 결정구조를 지니는 무색 투명한 저코니아($Zr_{0.73}Y_{0.27}O_{1.87}$) 결정을 Y_2O_3를 안정제로 사용하여 Bridgman-Stockbager법(또는 Skull 용융법)으로 합성하였다. 육성된 결정은 유리광택을 나타내며 동시에 약간의 지방 광택도 띤다. 저코니아 결정은 편광현미경하에서 등방성을 나타내며 이방성의 징후는 발견되지 않는다. 모스 경도는 8~8½이고 비중은 5.85이다. 자외선하에서는 약한 백색 형광을 낸다. 단결정법으로 결정한 저코니아의 결정구조는 등축정계이며, 공간군은 $Fm3m(O_h^5)$이다. 단위포 상수(a)는 5.1552(5)Å이며, V=136.99(5)Å³, Z=4, R=0.0488이다. 저코니움 원자는 각 모서리에 산소 원자가 자리잡고 있는 육면체의 중심에 위치하고 있으며, 각 산소 원자는 저코니움 원자로 되어 있는 사면체의 중심에 위치하고 있다. 결국 8:4의 배위수가 성립하는 구조를 하고 있다.

주요어: 저코니아, 합성, 결정구조, 이트리아 첨가, 산화이트리움

Abstract: Colorless and transparent cubic zirconia ($Zr_{0.73}Y_{0.27}O_{1.87}$) crystal has been synthesized by the Bridgman-Stockbager method (also called Skull melting method). Y_2O_3 is used as stabilizer. The crystal shows a vitreous luster with a slight oily appearance. Under a polarizing microscope, it shows isotropic nature with no appreciable anisotropism. Mohs hardness value is measured to be 8~8½ and specific gravity 5.85. Under ultraviolet light it shows a faint white glow. The crystal structure of yttria stabilized zirconia was determined, using single crystal X-ray diffraction techniques, to be a cubic symmetry, space group $Fm\bar{3}m(O_h^5)$ with a=5.1552(5)Å, V=136.99(5) Å³, Z=4, and R=0.0488 for 29 unique reflections. Each zirconium atom is at the center of eight oxygen atoms situated at the corners of a surrounding cube and each oxygen atom is at the center of a tetrahedron of zirconium atoms. So a coordination of 8:4 holds in the structure.

Key words: Zirconia, synthesis, crystal structure, yttria-stabilized, yttrium oxide

INTRODUCTION

Synthesis and crystal structure of zirconia have been of great interest in gemology because the most convincing diamond simulant yet produced is the cubic form of zirconium oxide (ZrO_2). The zirconia is monoclinic at room temperature. This form also occurs in nature as mineral baddeleyite. On heating to about 1100°C this undergoes a phase change leading to the tetragonal form. At about 2000°C, there is another change leading to the cubic form of ZrO_2. On cooling this same sequence is followed in the reverse direction (Wyckoff, 1963). It is therefore essential to grow zirconia crystals which retain cubic structure at room temperature in order to imitate optical properties of cubic diamond. It was found in 1930 that such material can be made by adding a few per cent of

oxides such as calcium oxide, magnesium oxide, or yttrium oxide. Almost as soon as it became generally available in 1976, the synthetic product cubic zirconia superseded all the previously popular diamond imitations such as YAG, GGG, and Strontium Titanate (Nassau, 1977).

Most of the detailed experimental data have still been kept in secret and some details of experimental growth of crystals of cubic zirconia of formula $(ZrO_2)_{0.875}(Y_2O_3)_{0.125}$ by a skull-type melting process were firstly described by Roulin et al. (1969). Although the phase diagram of ZrO_2-Y_2O_3 allows maximum of about 65 wt.% Y_2O_3 to be included in the cubic form zirconia, most cubic zirconia is being made using a littile less than 10 wt.% Y_2O_3 (Nassau, 1980).

In this paper, synthesis of yttria stabilized cubic zironia and investigation of its crystal structure will be described.

EXPERIMENTAL

Starting material ZrO_2 and stabilizer Y_2O_3 and decolorizing agent Nd_2O_3 were purchased from MEL, England. In order to find out the optimum amount of Y_2O_3 needed for the growth of ZrO_2, variable amounts of stabilizer i.e., 15, 20, 23, 25, 30 wt.% were added to the ZrO_2 powder. Nd_2O_3 of 0.03~0.05 wt.% were also added to them to remove yellow color of the product. Weighed amounts of three materials were thoroughly mixed and then put into cold containers of 105 mm inner diameter size. The skull is placed inside a copper coil which is connected to a LEPEL radio frequency generator of 50 kW and 2~5 MHz capacity.

RESULTS

Zirconia crystals grown in this study show slightly different color and diaphaneity depending on the amount of Y_2O_3 added. When 15 wt.% Y_2O_3 is applied, the crystal becomes cloudy and opaque. When 20 wt.% Y_2O_3 is added, most crystal is colorless and transparent. But some portion, especially grown near the inner wall of the crucible, remains cloudy. When 25 wt.% Y_2O_3 is added, the whole crystal is colorless and transparent. It be-

comes yellowish when 30 wt.% Y_2O_3 is included. It is thus concluded that the most optimum amount of stabilizer is 25 wt.%. The yttrium-stabilized cubic zirconia crystal (Fig. 1) has a composition $Zr_{0.73}Y_{0.27}O_{1.87}$ and shows a vitreous luster with a slight oily appearance. Under a polarizing microscope, the zirconia crystals show isotropic nature, almost entirely free from double refraction. Refractive index of the material is only determined to be larger than 1.81 by a standard gemological refractometer and Mohs hardness value is measured to be 8~8½ using the hardness pencils. Specific gravity is determined to be 5.85 by the hydrostataic weighing technique. A faint white glow appears under both the long- and short-wave ultraviolet light. No cleavage is seen, but conchoidal or uneven fracture is observed.

Small fragments of zirconia were ground into fine powder under acetone in an alumina mortar. The X-ray powder pattern (Fig. 2) of the zirconia was obtained by using a Rigaku Dmax II X-ray diffractometer with Ni-filtered CuKα (λ=1.5418Å) radiation. Lattice parameters for individual X-ray reflections were determined by the trial and error method (Table 1). The cell parameter, refined by a least-squares method using the present X-ray powder data, is a=5.157Å.

For a single crystal diffraction study, a single crystal of 0.4×0.2×0.2 mm, separated from a zir-

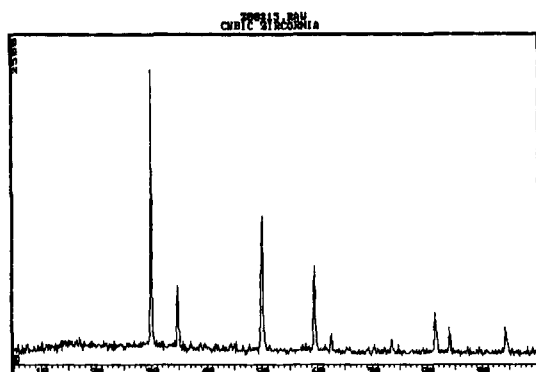**Fig. 1.** A separated column of yttria stabilized cubic zirconia.

Fig. 2. X-ray diffraction pattern of cubic zirconia.

Table 1. X-ray powder diffraction data of zirconia.

h	k	l	I/Io	do	dc
1	1	1	100	2.982	2.977
2	0	0	24	2.581	2.578
2	2	0	50	1.824	1.823
3	1	1	30	1.556	1.555
2	2	2	9	1.489	1.489
4	0	0	4	1.289	1.289
3	3	1	12	1.184	1.183
4	2	0	9	1.151	1.153
4	2	2	9	1.053	1.053

a=5.157Å. Ni-filtered Cukα (λ=1.5418Å) radiation used.

conia block, was mounted on CAD4 diffracto-meter. The orientation matrix determined by 21 in-itially collected reflections gave a triclinic system (a=3.6439(5)Å, b=3.6443(8)Å, c=3.6451(4)Å, α= 90.01(2)°, β=119.97(1)°, γ=119.98(1)°, V=34.25 (1) Å^3) for the compound. The triclinic structure can be successfully transformed into a cubic system with a=5.1568(6)Å, b=5.1540(14)Å, c=5.1547 (5) Å, α=89.99(1)°, β=89.99(1)°, γ=89.95(1)° and V= 137.00(5)Å^3 by using the BLIND program (Law-son and Jacobson, 1965) and the transformation matrix:

$$\begin{pmatrix} 2 & 1 & 1 \\ 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}$$

As recommended by Suh et al. (1977) an average value of a=5.1552(5)Å for the cubic system was taken.

397 reflections ($0 \le hkl \le 8$) were collected wit-hin the range of θ=2°~35° [(sin 35°/λ)$_{max}$=0.8007

Å^{-1}] using the ω/2θ scan method with a scan width of (0.8+0.34 tanθ)°. Lorentz and polarization corrections were applied to the intensity data (Enraf-Nonius, 1989), but no correction for ab-sorption was made due to almost isotropic nature of the crystal.

The reflection conditions (hkl: h+k, h+l, k+l=2n, 0 kl: k, l=2n, hhl: h+l=2n) indicated five possible space groups: #196 F23, #202 Fm$\overline{3}$, #209 F432, #216 F$\overline{4}$3m, #225 Fm$\overline{3}$m. The point group m$\overline{3}$m, confirmed by the intensity relation hkl=klh=lhk= khl=hlk=lkh, limited the space group to the last three. Therefore, the most symmetrical space group #225 Fm$\overline{3}$m was chosen for the compound.

The Zr atom was placed at the origin by ap-plication of the heavy atom methods and the po-sition 1/4 1/4 1/4 of an oxygen atom was located using standard least squares and Fourier tech-niques. Since Zr and O atoms occupied the special positions belonging to Wyckoff notation a and c (Hahn, 1992), the relations U_{11}=U_{22}=U_{33} and U_{12}= U_{23}=U_{13}=0 in anisotropic displacement factors held. Therefore they were refined isotropically using SHELX93 (Sheldrick, 1993). As 27 at.% of Zr a-toms were supposed to be replaced by Y atoms in the structure, Zr and Y atoms were assigned at the same origin, and refined with the same tem-perature factor and fixed occupancy factor of 3/4 and 1/4, respectively, the most optimum ratio cal-culated. Therefore there were only four variable parameters: scale factor, extinction factor, U_{11} for zirconium, and U_{11} for oxygen. 29 unique re-flections out of 397 measured gave the ratio 7.25 for reflections to refined parameters. There was no unobserved reflections for the criterion of F$_o$< 4σ (F$_o$). Final agreement values are R=0.0488 and ωR =0.1135 for all 29 unique reflections. Experimental details are given in Table 2 and atomic coor-dinates in Table 3. Software used to prepare mo-lecular graphics is ORTEPII (Johnson, 1976) in NRCVAX (Gabe et al., 1989).

In the zirconia structure, a molelcule consists of a Zr atom at 0 0 0, two O atoms at ±1/4 ±1/4 ± 1/4 (Table 2). The Zr atoms are arranged at the corners and face centers of a cubic unit cell and the oxygen atoms are at the centers of the eight cubelets into which the cell may be divided. Each

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Table 2. Summary of experimental details

Crystal data	
Chemical formula	$Zr_{0.73}Y_{0.27}O_{1.87}$
Chemical formula weight	120.51
Cell setting	Cubic
Space group	Fm3m
a (Å)	5.1552(5)
V (Å^3)	137.01(2)
Z	4
D (Mgm^3)	5.946
Radiation type	Mo K α
Wave length (Å)	0.71073
No. of reflection for cell parameter	21
θ range ($^\circ$)	11.22~17.93
μ (mm^{-1})	16.036
Temperature (K)	288
Crystal form	cube
Crystal size (mm)	$0.21 \times 0.20 \times 0.19$
Crystal color	colorless
Data collection	
Diffractometer	Enraf-Nonius CAD4
Cata collection method	ω-2θ scan
Absorption correction	None
T_{min}	
T_{max}	
No. of measured reflection	397
No. of independent reflections	29
No. of observed reflection	29
Criterion fro observed reflection	$F_o > 4\sigma$ (F_o)
R_{int}	1.0
θ_{max}	35
Range of h, k, l	$0 \rightarrow h \rightarrow 8$, $0 \rightarrow k \rightarrow 8$, $0 \rightarrow l \rightarrow 8$
No. of standard reflections	3
Frequency of standard reflections (min)	120
Intensity decay (%)	1.0
Refinement	
Refinement on	F
R	0.0488
ωR	0.1135
S	1.410
No. of reflections used in refinement	29
No. of parameters used	4
Weighting scheme	$\omega = 1/[\sigma^2$ $(F_o^2) + (0.0662P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\triangle/\sigma)_{max}$	0.000
$\triangle\rho_{max}$ (eÅ^{-3})	1.212
$\triangle\rho_{min}$ (eÅ^{-3})	-0.1499
Exftinction mode	SHELXL
Extinction coefficient	4.0935
Source of atomic scattering factors	SHELXL93

Table 3. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (A^{2}x10^3) for ZrO$_2$. U (eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

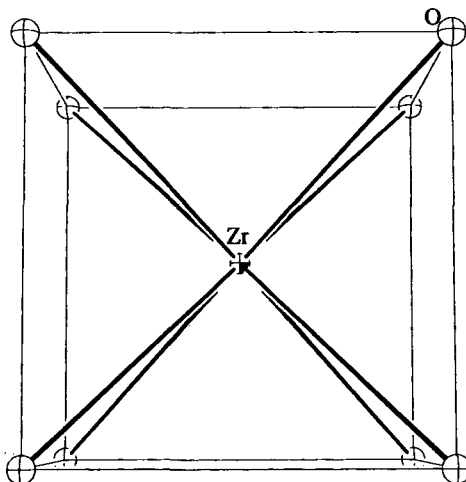|	x	y	z	Occup.		U (eq)
Zr	0	0	0	(4/192)	(3/4)	18 (6)
Y	0	0	0	(4/192)	(1/4)	18
O	2500	2500	2500	(8/192)		29 (5)

Fig. 3. A zirconium atom is coordinated by eight oxygen neighbours at the corners of a cube.
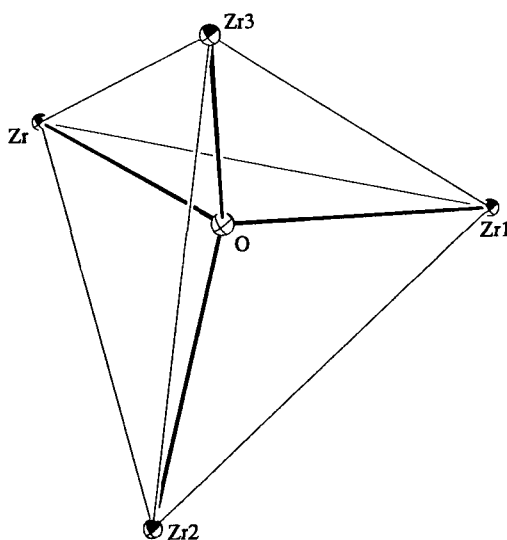

Fig. 4. An oxygen atom is at the center of a tetrahedron of Zr atoms.

Zr atom is therefore coordinated by eight oxygen neighbours at the corners of a cube (Fig. 3) with the distance of 2.2322(4)Å for Z-O and three dif-

Table 4. Bond lengths [A] and angles [deg] for ZrO_2

Zr-O	2.2323(2)	Zr-O#1	2.2323(2)
Zr-O#2	2.2323(2)	Zr-O#3	2.2323(2)
Zr-O#4	2.2323(2)	Zr-O#5	2.2323(2)
Zr-O#6	2.2323(2)	Zr-O#7	2.2323(2)
Zr-Zr#8	3.6453(4)	Zr-Zr#9	3.6453(4)
Zr-Zr#5	3.6453(4)	Zr-Zr#7	3.6453(4)
O-Zr#8	2.2323(2)	O-Zr#9	2.2323(2)
O-Zr#10	2.2323(2)		
O#1-Zr-O	180.0	O#1-Zr-O#2	109.5
O-Zr-O#2	70.5	O#1-Zr-O#3	109.5
O-Zr-O#3	70.5	O#2-Zr-O#3	109.5
O#1-Zr-O#4	109.5	O-Zr-O#4	70.5
O#2-Zr-O#4	109.5	O#3-Zr-O#4	109.5
O#1-Zr-O#5	70.5	O-Zr-O#5	109.5
O#2-Zr-O#5	180.0	O#3-Zr-O#5	70.5
O#4-Zr-O#5	70.5	O#1-Zr-O#6	70.5
O-Zr-O#6	109.5	O#2-Zr-O#6	70.5
O#3-Zr-O#6	180.0	O#4-Zr-O#6	70.5
O#5-Zr-O#6	109.5	O#1-Zr-O#7	70.5
O-Zr-O#7	109.5	O#2-Zr-O#7	70.5
O#3-Zr-O#7	70.5	O#4-Zr-O#7	180.0
O#5-Zr-O#7	109.5	O#6-Zr-O#7	109.5
Zr-O-Zr#8	109.5	Zr-O-Zr#9	109.5
Zr#8-O-Zr#9	109.5	Zr-O-Zr#10	109.5
Zr#8-O-Zr#10	109.5	Zr#9-O-Zr#10	109.5

*Geometric parameters for Y atom are same as those for Zr atom. Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z, #2 -x+1/2, -y+1/2, -z, #3 -x+1/2, -y, -z+1/2, #4 -x, -y+1/2, -z+1/2, #5 x-1/2, y-1/2, z, #6 x-1/2. y, z-1/2, #7 x, y-1/2, z-1/2, #8 x, y+1/2, z+1/2, #9 x+1/2, y, z+1/2, #10 x+1/2, Y+1/2, z.

ferent angles of 70.5°, 109.5°, and 180° for ∠O-Zr-O, while the Zr neighbours of an oxygen atom are four in number, disposed at the corners of a regular tetrahedron with the angle of 109.5° for ∠ Zr-O-Zr (Fig. 4 and Table 4). This is found to be the fluorite (CaF_2) structure in which 8:4 coordination (Evan, 1996) holds. The shortest distances for Zr-Zr (x, y+1/2, z+1/2) and for O-O (-x, 0.5-y, 0.5-z) are respectively 3.6453 (4)Å and 2.5776(3)Å.

CONCLUSION

Yttria stabilized cubic zirconia was synthesized and some physical and crystallographic data were determined. The best optimum amount of stabilizer Y_2O_3 to add was found to be 25 wt.%. To avoid yel-
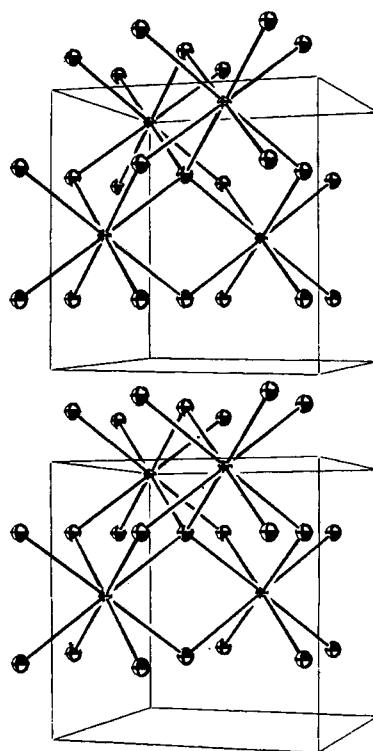

Fig. 5. Stereoview of the crystal packing of ZrO_2 with 8:4 coordination. Displacement ellipsoids are drawn at the 50% probability level.

lowish color of the crystal 0.03~0.05 wt.% Nd_2O_3 was employed. If none or more than 0.05 wt.% of Nd_2O_3 is added to the zirconia powder, color of the zirconia becomes yellow or violet. The cubic zirconia ($Zr_{0.73}Y_{0.27}O_{1.87}$), synthesized in this study, is colorless and transparent, showing vitreous luster. Optically it is nearly isotropic with no appreciable anisotropism. Mohs hardness and specific gravity values were determined to be 8~8½ and 5.85, respectively. Weak white glow is seen when ultraviolet light is illuminated. It does not have clavage but exhibits conchoidal to uneven fracture on the broken surface. Crystal structure of yttria stabilized zirconia has cubic symmetry, space group Fm3m (O^5_h) with a=5.1552(5)Å, V=136.99(5)Å^3, Z=4, and R=0.0488 for 29 unique reflections. Similar to the fluorite (CaF_2) structure, each zirconium atom is surrounded by eight oxygen atoms situated at a distance of 2.2322(4)Å. The shortest distances for Zr-Zr and for O-O are 3.6453(4)Å and 2.5776(3)Å, respectively. Stereoview of the crystal packing of zirconia with 8:

4 coordination, drawn at the 50% probability level, is shown in Fig. 5.

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