

Neutron Diffraction Study on the Crystal Structure of Yttria-Stabilized Zirconium Oxide

중성자회절법을 이용한 이트리아 저코니아의 결정구조 연구

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ABSTRACT : Neutron single crystal and powder diffraction techniques have been applied to the structure analysis of yttria-stabilized zirconia, $Zr_{0.73}Y_{0.27}O_{1.87}$, prepared by the skull-melting method. The crystal structure has been determined to be cubic symmetry, space group $Fm\bar{3}m(O_h^5)$ with $a=5.155(2)\text{\AA}$, $V=136.99(5)\text{\AA}^3$, $Z=4$, and $R(F)=5.65\%$, $\omega R(I)=10.57\%$ for 70 integrated intensities of Bragg peaks observed from single crystal of $Zr_{0.73}Y_{0.27}O_{1.87}$. The stabilizer atoms randomly occupy the zirconium sites and there are displacements of oxygen atoms with amplitudes of $\Delta/a\sim 0.033$ and 0.11 along $\langle 110 \rangle$ and $\langle 100 \rangle$ directions from the ideal positions of the fluorite structure, respectively. There are no significant differences in crystallographic data between the single crystal and powder studies. Diffraction pattern after Rietveld refinement, using neutron powder data, has shown the evidence of a tetragonal impurity phase, or a slight tetragonal distortion.

Keywords : neutron diffraction, zirconia, crystal structure, yttria, Rietveld refinement

요약 : 중성자 단결정 및 분말회절실험을 이용하여 이트리아를 첨가한 저코니아 (yttria-stabilized zirconia, $Zr_{0.73}Y_{0.27}O_{1.87}$) 결정의 구조 분석을 수행하였다. 시료는 입방정계로써, 공간군 $Fm\bar{3}m(O_h^5)$, $a=5.155(2)\text{\AA}$, $V=136.99(5)$, $Z=4$ 로 결정화되었고, 중성자 단결정 회절실험의 결과로 얻어진 70개의 브라그 회절반점을 이용한 최종신뢰도 $R(F)$ 및 $\omega R(I)$ 값은 각각 0.0576 , 0.1057 이었다. Zr과 Y 원자들은 이상적인 형석 (CaF₂) 구조의 cation 위치에 불규칙하게 배열되어 있었으며, 산소 원자들의 대부분 (95%)은 $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ 위치에서 $\langle 110 \rangle$ 방향으로 $\Delta/a\sim 0.033$ 의 크기만큼 이동하였고, 나머지 산소 원자들은 $\langle 100 \rangle$ 방향으로 $\Delta/a\sim 0.11$ 의 변위가 존재하였다. Rietveld 분석법을 이용한 중성자 분말회절실험의 결과는 단결정 회절실험에서 보여주었던 결정학적 정보와 모든 면에서 잘 일치하고 있었으며, 정방정계의 구조에서 기인되는 몇 개의 불순상의 존재가 최종 분석된 분말 회절상에서 확인되었다.

주요어 : 중성자회절, 저코니아, 결정구조, 이트리아, 리트벨트분석

Introduction

The zirconia, ZrO_2 , is known to have 3 polymorphs under atmospheric pressure condition. It is monoclinic at temperatures lower than $\sim 1440K$, and occurs in nature as mineral baddeleyite. It is tetragonal between ~ 1440 and $\sim 2640K$ and cubic between ~ 2640 and $\sim 2950K$. In view of the interest in yttria-stabilized zirconia as high performance ceramic and excellent conductor of O^{2-} ions at temperatures high than $900K$ and also diamond substitute yet produced, synthesis and crystal structure of zirconia have been attempted extensively by many workers including Vest and Tallan (1965), Anthony *et al.* (1966), Madeyski and Smeltzer (1968), Kumar *et al.* (1972), and Scott (1975). Recently Kim *et al.* (2000) firstly reported the details of growing technique of skull method to produce cubic form zirconia else where. According to them, the cubic crystal of pure zirconia was obtained by adding yttria as stabilizer. They also proposed that at least 7 mol% Y_2O_3 is required in order to stabilize the zirconia in the cubic phase.

The significant industrial and technological importance of this material has resulted in many attempts to provide a reliable and universal method (mostly using X-ray diffraction) for the determination of crystal structure and phase abundance information. Although zirconia is known to have fluorite structure, it occurs always as oxygen deficient phase from the stoichiometry. Therefore, oxygen distribution in the crystal structure had been of great interest in material science. In the literature, a few models for the possible distribution and displacement of oxygen atoms from the ideal fluorite sites have been proposed (Carter and Roth, 1968; Morinaga *et al.*, 1979; Parmigiani *et al.*, 1993).

In the earlier studies, powder method was principally employed, and there is a basic inadequacy of this method for accurate detection any displacements in this kind of materials. Above all, only a few peaks (often at low $\sin \theta / \lambda$) are generally used in structure refinement.

In general, neutron diffraction method is more advantageous over the X-ray diffraction for determining the oxygen behavior in the structures of yttria-stabilized zirconia, because the ratio of the scattering amplitude of O to Zr and Y is large (1 : 1.22 : 1.36) and absorption due to Zr and Y is less for the neutrons. Neutrons have been considered more useful than X-rays in structural analysis, because neutrons penetrate through the entire sample, whereas X-rays penetrate only tens of micrometers of the surface of the specimen. Steel and Fender (1974) investigated the $Zr(Y)O_{2-x}$, by neutron diffraction, and reported that a large proportion of the O atoms were displaced along the $\langle 100 \rangle$ direction by about 0.4 \AA , and that a small proportion are displaced along $\langle 111 \rangle$ by about 0.5 \AA from the ideal fluorite position. Horiuchi *et al.* (1984) later studied the structure of $Zr(Y)O_{1.862}$ using Time-of-Flight neutron diffraction and reported that the O atoms show displacements similar to those reported by Steel and Fender for $Zr(Y)O_{1.87}$.

Carter and Roth (1968) found similar phenomenon in the $Zr(Ca)O_{2-x}$, prepared from approximately $1670K$. They reported, by use of a neutron diffraction, displacement of the O atoms along $\langle 111 \rangle$ directions with magnitudes of $\sim 0.2-0.3 \text{ \AA}$. Howard *et al.* (1988) studied $Zr(Mg)O_{1.875}$ and observed a displacement of O atoms in the structure.

In the present paper, detailed information obtained from neutron single crystal diffraction and powder diffraction at room temperature for the yttria-stabilized zirconia ($Zr_{0.73}Y_{0.27}O_{1.87}$) are described.

Experimental

Sample preparation and some physical properties

Crystal structure of a cubic form zirconia crystal, prepared by skull-melting method (Kim *et al.*, 1997), was under investigation. The crystal showed slightly different colors and diap-

haneities depending on the amount of Y_2O_3 added. When 15wt.% 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, although some portion, grown especially near the inner wall of the crucible, remained cloudy. When 25 wt.% Y_2O_3 were added, the whole crystals became colorless and transparent. When 30 wt.% Y_2O_3 was included, it became yellowish. It was thus concluded that the highest optimum amount of the stabilizer was 25 wt.%. The colorless yttrium-stabilized cubic zirconia crystal shows a vitreous luster with an oily appearance. Under a polarizing microscope, the zirconia crystal shows isotropic nature, and is almost entirely free from double refraction. Refractive index of the material is greater than 1.81 by a standard gemological reflectometer. Mohs hardness value is measured to be $8-8\frac{1}{2}$ using the hardness pencils. Specific gravity is determined to be 5.85 by the hydrostatic weighing technique. A faint white glow is seen under both the long- and short-wave ultraviolet light. No cleavage is seen, but conchoidal or uneven fracture is observed.

Chemical analysis yielded the dopant concentration of yttrium, to be 24.6~25.9wt.%, suggesting a chemical formulae $Zr_{0.73}Y_{0.27}O_{1.87}$, assuming an oxygen-deficient structure. A single crystal of $0.8 \times 0.9 \times 10$ mm size, separated from the zirconia blocks, was used in our experiment. For neutron powder diffraction analysis, small fragments of zirconia were ground into fine powder under acetone in a alumina mortar. The lattice parameter determined using a CAD4 X-ray diffractometer with MoK α radiation, was $a=5.155(1)\text{\AA}$ (Kim *et al.*, 1997). It was chosen to be in accordance with the standard setting of the space group $Fm\bar{3}m$.

Neutron diffraction

Neutron diffraction studies were carried out at room temperature using the four circle diffractometer at the Korea Atomic Energy Re-

search Institute (KAERI)'s research reactor, HANARO. Neutrons of wavelength 1.0\AA , selected by the (331) plane of a germanium monochromator, were used. Two Bragg peaks were first indexed using lattice parameter determined previously by X-ray diffraction ($a=5.155\text{\AA}$). Preliminary orientation matrix was then obtained and was used to index the remaining Bragg peaks. Precise lattice parameters and an orientation matrix were determined by a least-squares fit of the observed peak positions. The lattice constant was $5.155(2)\text{\AA}$ for this experiment. 70 Bragg reflections up to a limit of $\sin \theta / \lambda = 0.57$ were measured by $\theta-2\theta$ step scans in increments of $0.1^\circ 2\theta$, counting 14s on each step. Lorentz correction was applied to the intensity data, but no correction for absorption was made due to isotropic nature of the crystal.

Powder diffraction data were recorded at room temperature on the thirty two counter, fixed-wavelength, high resolution powder diffractometer (HRPD) at KAERI. The data were recorded under monitor control at intervals of 0.05° to $160^\circ 2\theta$, using a wavelength of 1.844\AA .

Results and Discussion

Single crystal data

The least-square crystal structure and refinement were undertaken with the TRXFLS computer program, an updated version of ORFLS (Busing *et al.*, 1962). The scattering lengths used for zirconium, yttrium and oxygen were 6.9, 7.9 and 5.77fm , respectively. It was assumed that Zr and Y atoms were randomly occupied on cation sites and that the cation and anion temperature factors were isotropic. In the fluorite-type structure, the cation and anion sites are in the special position 4(a) and 8(c), respectively, of space group $Fm\bar{3}m(O_h^5)$. In order to elucidate the incorporation of yttrium and the oxygen atom motion, two models (with cation interstitials in $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites and with anion vacancies) were tested in this study. The least-

square refinement was carried out on the scale factor, an isotropic extinction parameter and individual isotropic temperature factors for the cations and anion atoms. Despite that the least-square refinement was processed well in anion vacancies, no satisfactory refinement was obtained for interstitial cations (indeed, unsatisfactory temperature factor and occupancy factor and high R values were consistently observed in this case). The reliability factor and temperature factor for a model with anion vacancies are as follows: $R(F)=5.72\%$, $wR(I)=10.79\%$, $B_c=1.8(3)\text{\AA}^2$ and $B_o=2.6(2)\text{\AA}^2$. The fact that temperature factor of oxygen atom is high when compared with that for the cations may suggest the possibility of a significant displacement of oxygen atoms away from the ideal fluorite 8(c) positions. To examine the magnitudes and directions of displacement for oxygen atoms, the least-squares refinement was carried out on the four variables (scale factor, extinction parameter and two isotropic temperature factors) for the slightly displaced positions of oxygen atoms along $\langle 100 \rangle$ or $\langle 111 \rangle$ direction. A refinement of the displacement of oxygen atoms along the $\langle 111 \rangle$ direction resulted in quite high temperature factors for all atoms and much poorer R value. A refinement for $\langle 100 \rangle$ displacement was also unsatisfactory; the oxygen temperature factor was somewhat reduced but R value was still high. Thus, we tested another possibility whether oxygen atoms were displaced along the $\langle 110 \rangle$ direction. A refinement on this model gave some improvement of the R value and the temperature factor of the oxygen atoms was reduced; $R(F)=5.98\%$, $wR(I)=10.64\%$ and $B_o=1.1(2)\text{\AA}^2$. Refinements of the displacement and occupancy number of oxygen atoms along $\langle 110 \rangle$ direction combined with the 8(c) position were also carried out, but the occupancy value resulted in zero and temperature factors become negative for the 8(c) position. Refinement of the displacement and occupancy of oxygen atoms along $\langle 100 \rangle$ direction were again tested, in addition to the $\langle 110 \rangle$ type displacements. The refinement reduced the agreement indices

and the oxygen atom thermal displacement parameter. The results are shown in Table 1. According to these data, displacements and occupancy numbers of oxygen atoms are compared well to those reported by Horiuchi *et al.* (1984) for $Zr(Y)O_{1.862}$ at 1040K. Horiuchi *et al.* (1984) indicated that 93% of total oxygen atoms were displaced along the $\langle 111 \rangle$ direction with magnitude of $\Delta/a \sim 0.022$ and the remaining 7% were displaced along $\langle 100 \rangle$ by $\Delta/a \sim 0.14$. Displacements of oxygen atoms along both the $\langle 110 \rangle$ and $\langle 111 \rangle$ were attempted but unsatisfactory results were observed.

The temperature factor of cations is larger than that of the similar materials reported in earlier works. The possibility for a small displacement of cations, suggested by Steele and Fender (1974), was tested, but could not be supported by unchanged R value, although the temperature factors of cations were reduced.

Powder data

The least-squares structure and profile refinements were undertaken with the Rietveld analy-

Table 1. Results of refinement using single crystal and powder diffraction methods.

		Single crystal work	Powder work
Zr(Y)	x	0.0	0.0
	y	0.0	0.0
	z	0.0	0.0
	$B(\text{\AA}^2)$	1.73(2)	1.18(3)
	Occupation	1.0	1.0
O (displaced along $\langle 110 \rangle$)	x	0.217(2)	0.217(5)
	y	0.250	0.250
	z	0.283(2)	0.283(5)
	$B(\text{\AA}^2)$	1.02(2)	0.90(5)
	Occupation	1.76	1.75
O (displaced along $\langle 100 \rangle$)	x	0.25	0.25
	y	0.36(4)	0.43(2)
	z	0.25	0.25
	$B(\text{\AA}^2)$	1.02(2)	0.90(5)
	Occupation	0.11	0.12
reliability indices(%)		$R(F)=5.65$, $wR(I)=10.57$	$Rf=2.67$, $\chi^2=2.94$

sis program Fullprof given by Rodriguez-Carvajal (1998). Starting values of the structure parameters (atomic coordinates, isotropic temperature factor and site occupancy parameters) were taken from the present results of single crystal analysis. Convergence is assumed to have been achieved when the parameter shifts in the final cycle of refinement are less than 10% of their associated estimated standard deviation (esd). The final values for the refinement agreement indices and a summary of the structure parameters are given in Table 1. Though relatively large (but reasonable) displacement of oxygen atom along the $\langle 100 \rangle$ direction were observed in neutron powder diffraction, the crystal structure parameters are essentially unchanged from those determined from single crystal neutron data. The presence of any displacement for the cations was not seen as well as a single crystal neutron diffraction studies.

The plot output from a Rietveld analysis is given in Fig. 1. It is noted that the diffraction pattern contains several very diffuse, low intensity peaks (Fig. 2) which are not explained by

the normal $Fm\bar{3}m(O_h^5)$ structure. A similar set of weak peaks was also reported by Steel and Fender (1974) and Howard *et al.* (1988). As worked by Howard *et al.* (1988), the additional peaks can be modelled equally well by a tetragonal-type distortion of the cubic structure or by a small amount of tetragonal material present as a second phase.

Conclusions

Crystal structure of yttria-stabilized zirconia, $Zr_{0.73}Y_{0.27}O_{1.87}$, synthesized by the skull-melting technique, has been determined to be cubic symmetry, space group $Fm\bar{3}m(O_h^5)$ with $a=5.155(2)\text{\AA}$, $V=136.99(5)\text{\AA}^3$, $Z=4$, and $R(F)=5.65\%$, $\omega R(I)=10.57\%$ for 70 integrated intensities of Bragg peaks. The stabilizer atoms randomly occupy the zirconium sites. The oxygen atoms are conias and some related phases. There is no evidence of the presence for displacement of cation atoms with the high temperatures. Additional peaks found in the powder pattern may

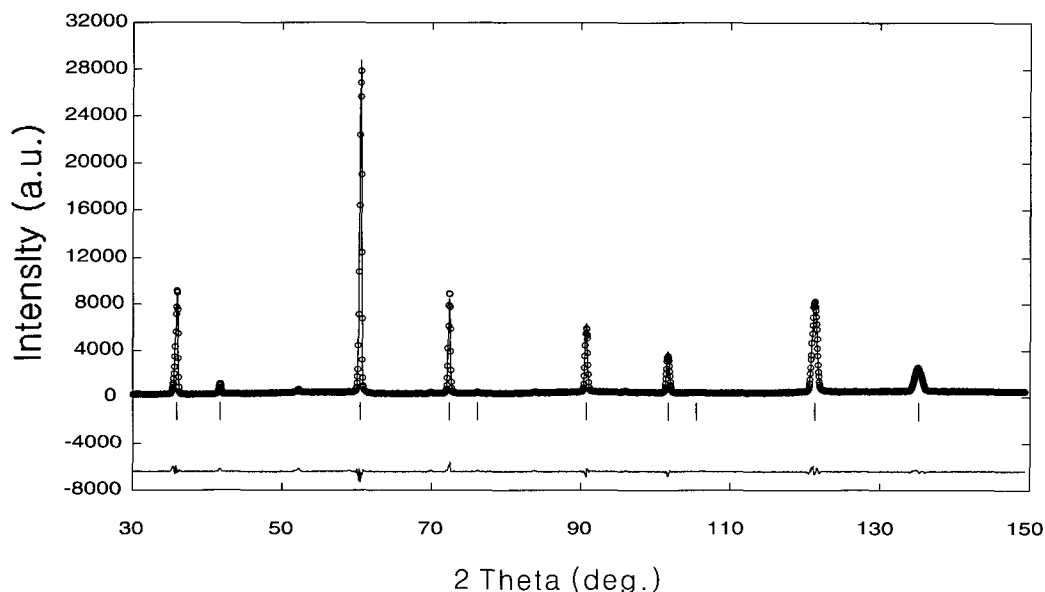


Fig. 1. Plot output from Rietveld analysis of the neutron diffraction pattern from yttria-stabilized zirconia, $Zr_{0.73}Y_{0.27}O_{1.87}$

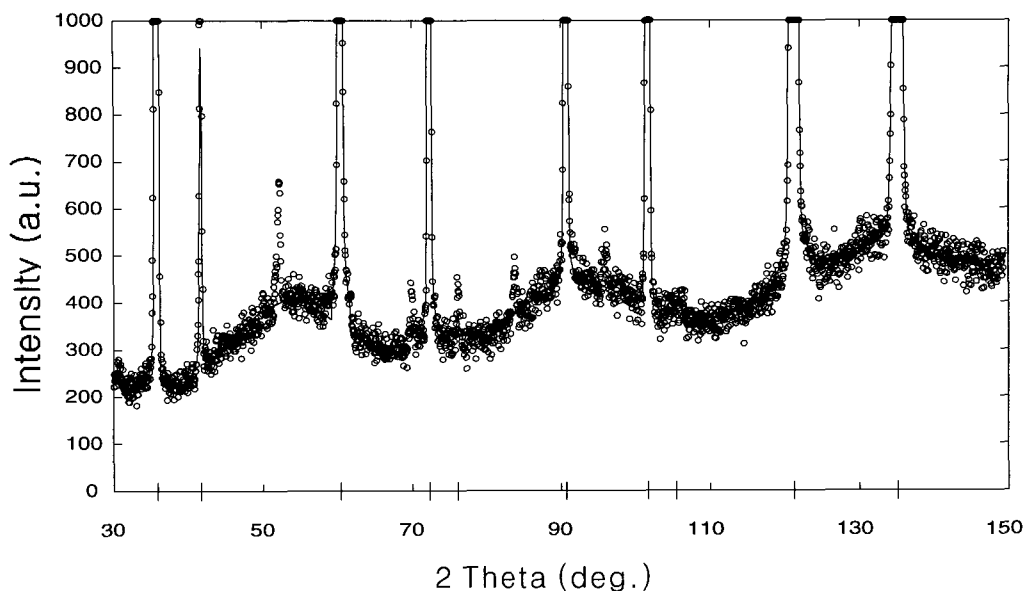


Fig. 2. Plot output from Rietveld analysis of $Zr_{0.73}Y_{0.27}O_{1.87}$ showing the very diffuse background.

suggest a slight tetragonal distortion of the cubic structure or a tetragonal phase present as a second phase.

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