

Synthesis of $Zr_{0.73}Y_{0.27}O_{1.87}$ Crystals by the Bridgman-Stockbager Method

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Abstract: A colorless and transparent zirconium oxide ($Zr_{0.73}Y_{0.27}O_{1.87}$) crystal has been synthesized by the Bridgman-Stockbager method. The gem-quality material is produced by adding 20 ~ 25 wt.% Y_2O_3 (stabilizer) and 0.04 wt.% Nd_2O_3 (decolorising agent) to the ZrO_2 powder. It shows a vitreous luster with a slight oily appearance. Under a polarizing microscope, it shows isotropic nature with no appreciable anisotropism. Mohs hardness value and specific gravity is measured to be $8 \sim 8\frac{1}{2}$ and 5.85, respectively. Under ultraviolet light it shows a faint white glow. The crystal structure of yttria-stabilized zirconia with 0.27 at.% Y has been re-investigated, using single crystal X-ray diffraction, and confirmed to be a cubic symmetry, space group $Fm\bar{3}m$ (O_h^3) with $a = 5.1552(5)$ Å, $V = 136.99(5)$ Å³, $Z = 4$. 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 $\langle 111 \rangle$ from the ideal positions of the fluorite structure, respectively.

Key words: cubic zirconia, zirconium oxide, synthesis, crystal structure, Bridge-Stockbager method, skull-melting

INTRODUCTION

Because the yttria-stabilized zirconia has been used as a high performance ceramic, attempts to synthesize zirconia have been carried out extensively. The zirconium oxide is known to have 3 polymorphs under atmospheric pressure condition. Experiments to determine its crystal structure have also been made by many workers including Vest and Tallan (1965), Anthony *et al.* (1966), Kumar *et al.* (1972), Scott (1975), and Aldebert and 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_2 . 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 pro-

duced. Such 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 oxy-acetylene furnace, and proposed that 16 ~ 30 mole % calcia or 16 ~ 25 mole % magnesia was required to stabilize zirconia into the cubic form (Duwez *et al.*, 1952). Reviewers of their manuscript, however, mentioned that 10 mole% calcia or 12 mole% magnesia was enough. 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). Scott (1975) suggested the most recent phase diagram (Fig. 1). Contrary to the fact that 7 mole % yttria was necessary to stabilize cubic zirconia as proposed by Duwez *et al.* (1951), Scott (1975) indicated that all

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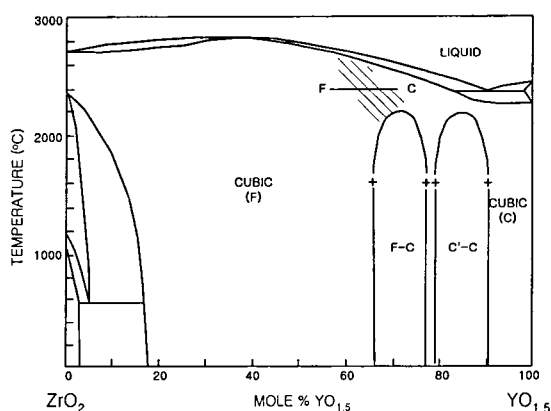


Fig. 1. Phase diagram for the zirconia-yttria system (Scott, 1975). Hatched region represents the apparently continuous fluorite-type C transition.

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. Steel and Fender (1974) synthesized three yttrium zirconia samples with composition $Zr_{0.82}Y_{0.18}O_{1.91}$, $Zr_{0.78}Y_{0.22}O_{1.89}$, and $Zr_{0.74}Y_{0.26}O_{1.87}$ by heating at $1800^\circ C$ under a 10^{-3} bar vacuum, for 15 minutes within an induction furnace. Yoshimura (1988) indicated hydrothermal technique was not useful due to formation of $Y(OH)_3$ and $YOOH$ and dissolution of H_2O into the solid solution. But, Takayuki *et al.* (1999) succeeded in synthesizing yttrium-doped zirconia $[(Zr,Y)O_2]$ crystalline powder by low-temperature hydrothermal method, in which $Zr(OH)_4$ and $Y(OH)_3$ were reacted in aqueous solution at $100^\circ C$ 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 zir-

conia is the coprecipitation/calcination/heat treatment process (Ramanathan *et al.*, 1992; Toraya, 1989) which uses yttria as stabilizer.

Nevertheless, all the materials prepared by the methods mentioned above were polycrystalline powders and of no use for gemological purpose. In order to use zirconia as diamond substitute, it is essential to grow a crystal large enough to fashion it into gemstone. Although the best technique for this purpose is known to be the Bridgman-Stockbager method (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 available (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 of experiment. Properties of diamond and its simulants are summarized in Table 1.

The purpose of this paper is, therefore, to synthesize colorless and transparent yttria-stabilized cubic zirconia crystals by the Bridgman-Stockbager method and to describe the detailed experimental results.

EXPERIMENTS AND RESULTS

Based on the phase diagram of the zirconia-yttria system (Fig. 1) and also the detailed phase relations of the zirconia-rich portion (Fig. 2), all given by Scott (1975), ZrO_2 (99.8% purity) and stabilizer Y_2O_3 (99.999% purity) were chosen as starting materials, and were purchased from MEL, England. Spectroscopic analyses of ZrO_2 and Y_2O_3 are given in Tables 2 and 3, respectively.

In order to find out the optimum condition for the growth of a colorless and transparent single

Table 1. Gemological properties of diamond imitations.

	Diamond	Quartz	Strontium titanate	YAG	GGG	Cubic zirconia	Moissanite
Chemical formula	C	SiO_2	$SrTiO_4$	$Y_3Al_5O_{12}$	$Gd_3Ga_5O_{12}$	ZrO_2	SiC
Hardness	10	7	5.5 ~ 6	8.5	7	8.5	9 ~ 9.5
Refractive index	2.417	1.54 ~ 1.55	2.41	1.83	1.97	2.17 ~ 2.18	2.65 ~ 2.69
Specific gravity	3.52	2.65	5.13	4.55	7.02	5.95	3.22
Dispersion power	0.044	0.013	0.190	0.028	0.045	0.060	0.014

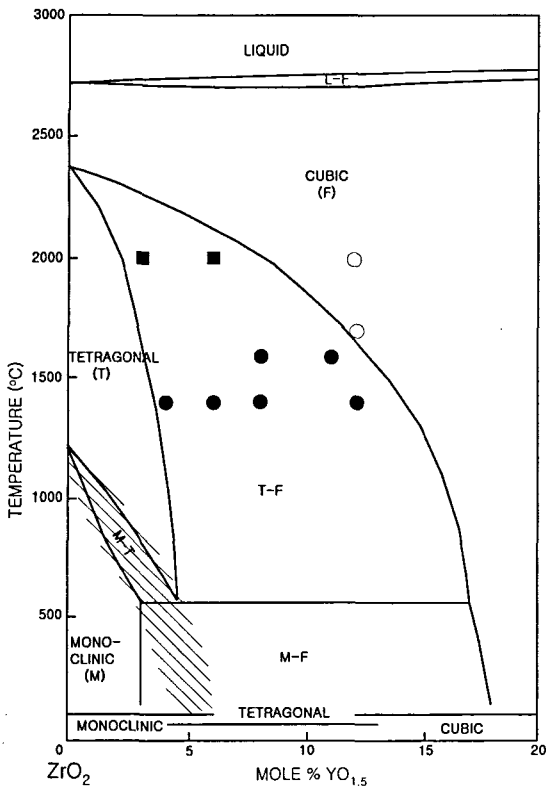


Fig. 2. Phase diagram of the zirconia-rich portion of the zirconia-yttria system. Non-equilibrium homogeneous phases are indicated at lower margin. Phases found at room temperature are indicated thus : Δ monoclinic, \square tetragonal, \circ cubic, \blacksquare monoclinic+tetragonal, \bullet monoclinic + cubic. Hatched region indicates non-equilibrium monoclinic-tetragonal transition (Scott, 1975).

crystal, variable amounts of Y_2O_3 , i.e., 15, 20, 25, and 30 wt.% were tested by adding o the ZrO_2 powder.

Weighed amounts of two chemicals were thor-

Table 2. Spectroscopic analyses of impurities of Y_2O_3 powder used in this study.

Elements	G60	G10
ZrO_2	99.4 wt%	99.8 wt%
SiO_2	0.20 wt%	0.05 wt%
TiO_2	0.15 wt%	0.07 wt%
Fe_2O_3	0.006 wt%	0.001 wt%
SO_3	0.25 wt%	0.07 wt%
Ni	< 1 ppm	< 1 ppm
Mn	< 5 ppm	< 5 ppm
Cn	< 2 ppm	< 2 ppm
Co	< 1 ppm	< 1 ppm
Cr	< 1 ppm	< 1 ppm

Table 3. Spectroscopic analyses (%) of Y_2O_3 used in this study.

Elements	
La_2O_3	< 5 ppm
Ce_2O	< 5 ppm
Pr_6O_{11}	< 5 ppm
Nd_2O_3	< 5 ppm
Sn_2O_3	< 5 ppm
Eu_2O_3	< 5 ppm
Gd_2O_3	< 5 ppm
Tb_4O_7	< 5 ppm
Dy_2O_3	< 5 ppm
Ho_2O_3	< 5 ppm
Er_2O_3	< 5 ppm
Tm_2O_3	< 5 ppm
Yb_2O_3	< 5 ppm
Lu_2O_3	< 5 ppm
Ca	6 ppm
Fe	< 5 ppm
Si	< 5 ppm

oughly mixed in a mechanical mixer for 5 hours and then put into a cold skull of 105 mm inner diameter and 135 mm height. A small piece of Zr metal was also included into the skull. 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 (Fig. 3). Shortly after



Fig. 3. A skull within RF electrical coils.

heating to 2900°C, the electric power was reduced slowly and the skull was lowered at various speed, i.e., 6 mm/hr, 10 mm/hr, 13 mm/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 mixes. 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.% or more than 0.05 wt.% was added, the crystal remained slightly yellow and purple, respectively, regardless of the amounts of Y_2O_3 in the mixes. Therefore, 0.04 wt.% of Nd_2O_3 were decided in this study to be added to all the mixes in the hope to grow colorless crystal. The crystal grown now showed different quality depending on the amount of Y_2O_3 added. When 15 wt.% Y_2O_3 was applied, the crystal became cloudy and opaque. When 20 wt.% Y_2O_3 was added, most crystals were turned out to be colorless and transparent. But some portion, grown especially near to the inner wall of the crucible, remained cloudy. When 25 wt.% Y_2O_3 was added, the whole crystal became colorless and transparent. When 30 wt.% Y_2O_3 was included, it became yellowish. It was, therefore, concluded that the highest optimum amount of the stabilizer and decolorizing agent were 20 ~ 25 wt.% and 0.04 wt.%, respectively.

Maximum yield (42%) was obtained when lowering rate of the skull was adjusted to be 16 mm/hr. However, various lowering rates performed in this experiment, 6, 8, 10, 13 mm/hr, 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

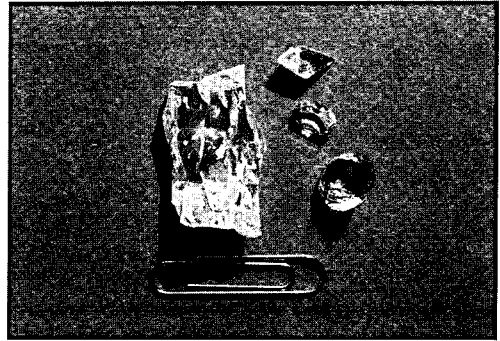


Fig. 4. The synthetic-yttria stabilized cubic zirconia crystal grown by the Bridgman-Stockbager method (left) and cut stones (right).

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 dimension of it was about 100 mm in diameter and 100 mm in height. It consisted of a number of columnar crystals of approximately $20 \times 15 \times 40$ mm in size (Fig. 4). It showed a vitreous luster with an oily appearance. It did not show cleavage but exhibited conchoidal or uneven fracture on the broken surface of the crystals. It was rather brittle and Mohs hardness value was measured to be $8 \sim 8\frac{1}{2}$ using the hardness pencils. Under a polarizing microscope, the zirconia crystal was optically isotropic, and was entirely free from normal or abnormal double refraction. Thus, it was assumed to be optically cubic. Refractive index of the material was determined to be 2.15 ~ 2.18 by a Brewster-angle refractometer. Critical angle of the material was calculated to be 27.37° . Faint white glow was seen under both the long- and short-wave ultraviolet light.

The chemical composition of the specimen, determined by a JEOL electron probe microanalyser, was 73.8 ~ 4.2 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 unable to determine precisely, mainly due to extremely small amount. For X-ray powder diffraction analysis, small fragment of zirconia was ground into fine powder under acetone in an alu-

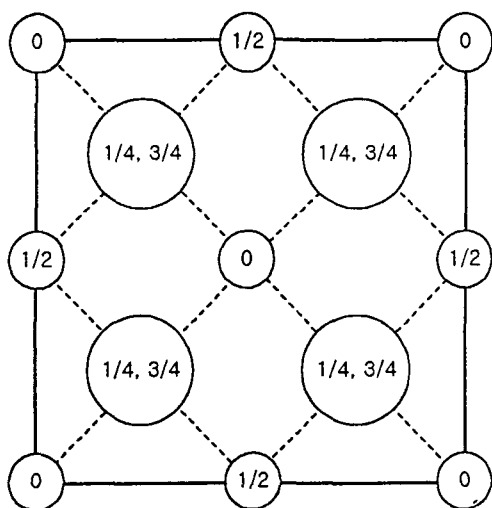


Fig. 5. The positions of the zirconium (larger) and oxygen (smaller) atoms within the unit cell of ZrO_2 structure, projected on a cube face.

mina mortar. A Rigaku Dmax II X-ray diffractometer with Ni-filtered $CuK\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation was used. Lattice indices for individual X-ray reflections were determined by the trial and error method and the refined cell parameters ($a = 5.157 \text{ \AA}$) were 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 $0.4 \times 0.2 \times 0.2 \text{ mm}$ in size, confirmed the cubic symmetry, space group $Fm\bar{3}m$ (O_h^5) with $a = 5.1552(5) \text{ \AA}$. The positions of atoms within the unit cell was shown in Fig. 5.

The cell parameters (a), 5.157 \AA and $5.1552(5) \text{ \AA}$ obtained respectively by X-ray powder diffraction and by single crystal diffraction were in good agreement with $a = 5.1562 \pm 0.0003 \text{ \AA}$ of Steel and 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 $Zr_{0.78}Y_{0.22}O_{1.89}$ (Steel and Fender, 1974), there was a good linear correlation between the cell parameters (a) and the amount of Y_2O_3 . i.e., cell parameters increase as the concentrations of Y_2O_3 increase (Fig. 6).

The specific gravity of cubic zirconia, synthesized in this study, was measured to be 5.85 by the

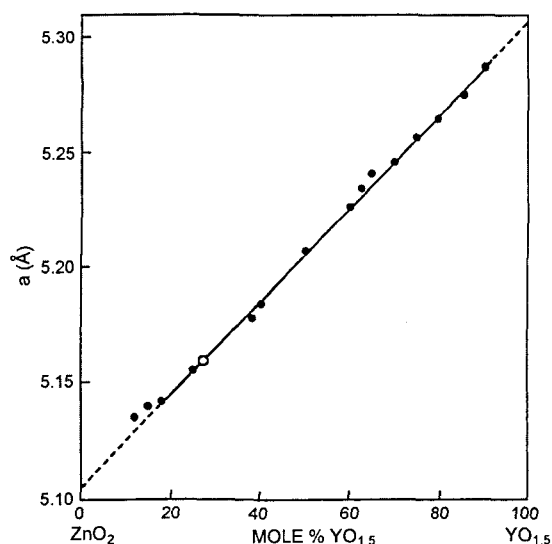


Fig. 6. Lattice parameters for homogeneous zirconia-yttria phases with 12 to 100 mol % of $YO_{1.5}$ (Scott, 1975). Circle represents the data obtained in this study. $Zr + 4 = 2.16 \text{ \AA}$, $Y + 3 = 2.27 \text{ \AA}$.

hydrostatic weighing technique, which was considerably lower than the calculated value of 5.946. This observation can be explained by the omission of the solid solution of the yttria-stabilised zirconia, as indicated by the chemical formula.

A single crystal neutron diffraction analysis was carried out at room temperature using the four circle diffractometer at the Korea Atomic Energy Research Institute's research reactor (HANARO). Neutrons of wavelength 1.0 \AA selected by a (331) planes of a germanium monochromator were used. Two Bragg peaks were first indexed using lattice parameter determined by X-ray diffraction ($a = 5.1552 \text{ \AA}$), and a preliminary orientation matrix was obtained and then used in indexing the remaining Bragg peaks. 70 Bragg reflections up to a limit of $\sin\theta/\lambda = 0.57$ were measured by θ - 2θ step scans in increments of $0.1^\circ 2\theta$. Lorentz correction was applied to the intensity data, but no correction for absorption.

In the fluorite-type structure, the cations and anion sites are in the special position 4(a) and 8(c), respectively, of space group $Fm\bar{3}m$. Carter and Roth (1968) suggested the displacements of the oxygen atoms along the $\langle 111 \rangle$ direction from the ideal $(1/4, 1/4,$

$1/4$) fluorine position. In contrast to those results, Steel and Fender (1974), Morinaga *et al.* (1979) and Horiuchi *et al.* (1984) reported that there were displacements of oxygen atoms along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. Howard *et al.* (1988) reported that the oxygen atoms showed the displacement mode similar to that suggested by Carter and Roth (1968).

For the structure analysis in this study, the least-square crystal structure and refinements were undertaken with the TRXFLS computer program (Busing *et al.*, 1960). 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. 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. The fact that the temperature factor of oxygen atom was high when compared with that for the cations suggested that there was a significant displacement of oxygen atoms away from the ideal fluorite 8(c) positions. As in previous works, various models for this displacement were tested and the best results are shown in Table 4. In these results, displacements and occupancy numbers of oxygen atoms are compared to those reported by Horiuchi *et al.* (1984) for $Zr(Y)O_{1.862}$ at 1040 K. They reported 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% are displaced along $\langle 100 \rangle$ by $\Delta/a \sim 0.14$. The temperature factor of cations is larger than that of a similar material reported in earlier works. The possibility

of a small displacement of cations, indicated by Steel and Fender (1974), were again investigated, but could not be supported by unchanged R value, although the temperature factors of cations was reduced. Attempts to locate the Zr in the interstitial site 4(a) at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ resulted in unsatisfactory temperature factors and occupancy factors, and also high R values.

CONCLUSION

1. Gem-quality colorless and transparent cubic zirconia crystals were successfully synthesized by the Bridgman-Stockbager method. The whole crystal block is approximately 100×100 mm in dimension and consists of a number of columnar crystals with approximately $20 \times 15 \times 40$ mm in size.

2. The cubic symmetry, the highest temperature structure of the 3 ZrO_2 polymorphs, can be maintained at room temperature by adding 20 ~ 25 wt.% Y_2O_3 to the ZrO_2 powder. Coloration of the crystals can be removed when 0.03 ~ 0.04 wt.% Nd_2O_3 was mixed together.

3. The crystals are 73.8 ~ 74.2 wt.% ZrO_2 and 24.6 ~ 25.9 wt.% Y_2O_3 in chemical composition, giving a chemical formulae $Zr_{0.73}Y_{0.27}O_{1.87}$. They show vitreous to resinous luster and are 2.15 ~ 2.18 in R.I., 8 ~ $8\frac{1}{2}$ in Mohs hardness, and 5.85 in S.G.

4. Crystal structure of them is confirmed to be cubic structure, space group $Fm\bar{3}m (O_h^5)$, cell parameters $a = 5.1552(5) \text{ \AA}$, $V = 136.99(5) \text{ \AA}^3$, and $Z = 4$.

5. The stabilizer atoms, Y, randomly occupy the zirconium sites and oxygen atoms are displaced with amplitudes of $\Delta/a \sim 0.033$ and 0.11 along $\langle 110 \rangle$ and $\langle 111 \rangle$ from the ideal positions of the fluorite structure, respectively.

Table 4. Results of refinement for $Zr_{0.73}Y_{0.27}O_{1.87}$.

Atom	Zr(Y)	O (displaced along $\langle 110 \rangle$)	O (displaced along $\langle 100 \rangle$)
x	0.0	0.217(2)	0.25
y	0.0	0.25	0.36(4)
z	0.0	0.283(2)	0.25
occupation	1.0	1.76	0.11
$B(\text{\AA}^2)$	1.7(3)	1.02(2)	
reliability indices (%)		$R(F) = 5.65$, $wR(I) = 10.57$	

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