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Structural Study on Low Symmetry Cassiterite

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1 Introduction

Cassiterite, SnO_2, is an important mineral as the material source of Sn. The crystal structure of cassiterite belongs to tetragonal symmetry with the space group of $P4_2/mnm$, but some of natural cassiterite samples show a lower symmetry than tetragonal symmetry under microscopic observation. There are few descriptions of the low-symmetry cassiterite. So, the crystal structure of such a low-symmetry cassiterite is still unknown in detail, and the reason for having lower symmetry is not clear. Recently, we found the cassiterite showing low symmetry from some mines in Japan. In this study, we have conducted single-crystal X-ray diffraction experiments using synchrotron radiation to investigate a low symmetry cassiterite, and to clarify the mechanism of symmetry reduction of cassiterite.

2 Experimental Procedure

The natural cassiterite used for this study was from the Ohtani Mine, Kyoto, Japan. We confirmed symmetry reduction and sector structures such as {231} and {111} sectors in this sample from microscopic observation of the thin section perpendicular to the *c*-axis. Before sample preparation for the X-ray diffraction experiments, chemical properties were checked from BSE-image using an SEM-EDS apparatus (JEOL, FE-SEM JSM-7001F; Oxford, EDS INCA), and we observed chemical zoning in each sector. The samples for X-ray diffraction experiments were carefully picked-up from the area showing no chemical zoning in each sector. The sample dimensions (μm) were as follows: 70 × 70 × 50 for a {231} sector and 90 × 90 × 70 for a {111} sector. The chemical compositions of the sample used for the X-ray diffraction study were measured using a WDS apparatus for the {231} and the {111} sectors (JEOL, JXA-8800M). The chemical formulae of the samples were determined as $Sn_{0.993}Ti_{0.007}O_2$ for the {231} and $Sn_{0.988}Ti_{0.012}O_2$ for {111} sector, respectively.

Single-crystal X-ray diffraction experiments were performed using an automated four-circle X-ray diffractometer installed at the beam line BL-10A, PF, KEK. The wavelength (λ = 0.70137 Å for the {231} sector and λ = 0.70116 Å for the {111} sector) of synchrotron radiation in each run was calibrated by the unit cell volume of the NIST standard ruby at ambient temperature. The X-ray diffraction intensity data were collected up to $2\theta_{max}$ = 96° for the {231} sector and $2\theta_{max}$ = 99° for the {111} sector, respectively by using the ω-scan method. Structural refinements for both samples were conducted using SHELX97 with WINGX software. The cell parameters for each sector were determined in our laboratory using an automated four-circle diffractometer (Rigaku, AFC-7S) with Mo$K\alpha$ radiation (λ = 0.71073 Å). The unit cell parameters of each samples were determined from the 54 centered reflections such as {310}, {220}, {301} and {231} of in the 2θ range between 23° and 35°.

3 Results and Discussion

The lattice constants of each sample are summarized in Table 1. The obtained cell parameters showed almost tetragonal symmetry. However, the systematic absence rule for the space group of $P4_2/mnm$ ($h + l = 2n$ for $h0l$, $k + l = 2n$ for $0kl$, $h = 2n$ for $h00$, $k = 2n$ for $0k0$ and $l = 2n$ for $00l$) was broken for both sectors from the analysis of the distribution of X-ray diffraction intensity data. We also checked these peaks breaking the rule using the psi-scan method, and confirmed that these peaks were not the results of multiple diffraction. The candidates for the space group of the cassiterite structure showing symmetry reduction can be considered as follows: $P2/m$, Pm, $P2$, $P1$ and $P\bar{1}$. In this report, the results of the structure refinement for the {231} sector was shown only. We conducted structure refinements for these all structural models for each sector. The results of structural refinements for these models were summarized in Table 2. The space group for the structure of {231} sector in the low symmetry cassiterite could be considered as $P2/m$.

Table 1. Cell parameters for each sectors

Sample	{231} sector	{111} sector
Triclinic setting		
a (Å)	4.7368 (5)	4.7368 (3)
b (Å)	4.7370 (4)	4.7371 (3)
c (Å)	3.1848 (4)	3.1848 (3)
α (°)	89.996 (8)	89.988 (6)
β (°)	90.001 (10)	89.99 (7)
γ (°)	89.993 (7)	90.008 (5)
V (Å^3)	71.46 (6)	71.46 (1)

Table 2. The information on the results of structural refinement for {231} sector

Space group	$P2/m$	Pm	$P2$	$P\bar{1}$	$P1$
No. of reflections mesured	3123	3123	3123	3123	3123
No. of unique reflections (Fo > 4σFo)	757	1471	1330	1331	2667
R(int) (%)	6.27	5.19	5.55	4.75	2.85
$R1$ (%)	2.66	3.16	2.93	3.17	3.84
$wR2$ (%)	7.12	8.37	7.82	7.98	12.39
Goodness of fit	1.147	1.044	1.113	1.132	1.204
No. of parameter	24	40	32	34	58

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