

RAPID COMMUNICATION

A New High-Temperature Cubic Fluorite-Type Phase $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ with a Rare Three-Dimensional Incommensurate ModulationM. Valldor,¹ S. Esmailzadeh, C. Pay-Gomez, and J. Grins

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Received February 22, 2000; accepted April 7, 2000

A new high-temperature phase $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ was obtained by quenching from 800°C. Its average structure is of the cubic $Fm\bar{3}m$ fluorite type with $a = 5.6478(1)$ Å and was refined from single-crystal Mo $K\alpha$ X-ray diffraction (XRD) data to a weighted R -value of 3.7% for 16 unique reflections and isotropic thermal displacement parameters refined for the metal atoms, $U_{\text{iso}} = 0.0564(4)$ Å², and the O atoms, $U_{\text{iso}} = 0.186(6)$ Å². The structure exhibits in addition a novel 3-D incommensurate modulation that was studied by electron diffraction and both powder and single crystal XRD. Extinction conditions indicate the symmetry $P:Fm\bar{3}m:Fm\bar{3}m$, which has previously only been reported once. The three q -vectors are along the unit cell axes and have lengths of 0.29256(6) unit cells in reciprocal space. The modulated structure is compared with the previously reported and similarly modulated structure of the solid solution $\text{Nb}_x\text{Bi}_{1-x}\text{O}_{1.5+x}$, with $0.12 \leq x \leq 0.46$ and symmetry $P:Fm\bar{3}m:Fd\bar{3}m$. © 2000 Academic Press

Key Words: Mo–Bi–O; fluorite type structure; incommensurate; 3D modulation.

INTRODUCTION

The high-temperature fluorite-type δ form of Bi_2O_3 is stable above 730°C up to its melting temperature 824°C and is one of the best oxygen ion conductors known (1). The pure Bi phase cannot be quenched to room temperature but closely related modifications can be stabilized at lower temperatures by addition of numerous cations (1), either isovalent (Y^{3+} , Ln^{3+}) or with smaller ionic radii and higher valence states (e.g., W^{6+} , Ta^{5+} , Mo^{6+} , Nb^{5+}). A number of Bi_2O_3 -based systems of the latter type are described by Ling *et al.* (2). In the Bi_2O_3 - MoO_3 system there exists a low-temperature phase $\text{Bi}_{38}\text{Mo}_7\text{O}_{78}$ having a metal composition around 15% Mo, reported previously also by Buttery

et al. (3). Its structure has so far not been determined, but it is fluorite-related with an orthorhombic unit cell with $a = 16.8065(2)$, $b = 28.6004(4)$, and $c = 16.8898(2)$ Å and the probable space group symmetry $Pccn$ (2,3). High-temperature fluorite-related Bi–Mo oxide phases have not been characterized in any detail. The synthesis and structural characterisation of the 6-D incommensurate structure of the phase $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ is reported here. The observed symmetry is rare and the existence of the phase is therefore of general interest for studies of aperiodic structures.

EXPERIMENTAL

The $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ phase was synthesized by melting a stoichiometric mixture of analytical grade Bi_2O_3 and MoO_3 in a Pt crucible at 950°C for a few minutes, cooling the sample to 800°C at a rate of 7.5°/min, and then removing it rapidly from the furnace. The obtained sample was homogeneous and contained large reddish-yellow and transparent crystals.

The unit cell parameter and q -vector length were determined from Guinier–Hägg film data, using Cu $K\alpha_1$ radiation and Si as internal standard. The films were evaluated with an LS-KEJ20 scanner (4). Powder XRD data were also recorded with a STOE STADI P diffractometer, with Cu $K\alpha_1$ radiation and the sample in symmetric transmission mode. Data were collected from 5–130° in 2θ in steps of 0.2° with a recording time of 350 seconds at each step. Single-crystal X-ray diffraction (XRD) data were obtained using a rotating anode Mo $K\alpha$ X-ray source and a STOE image plate detector system. The data set consisted of 100 diffraction images with the crystal rotated 2 degrees between every 5 min exposure. The intensities of the fluorite-type reflections were integrated using the STOE software and the X-RED (6)/X-SHAPE (7) programs used for an absorption correction. The JANA98 program (8) was used for the structure refinement. Electron diffraction (ED) patterns

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were obtained with a transmission electron microscope (TEM) JEOL 2000FX operating at a 200 kV accelerating voltage. The samples investigated were crushed and dispersed in butanol before they were placed on holey carbon-coated copper grids. Energy dispersive X-ray spectroscopy (EDS) analysis of the metal composition was made in a JEOL SEM820 scanning electron microscope (SEM) with a LINK AN10000 EDS system.

RESULTS

The synthesis yielded a homogeneous sample containing large single crystals. For the EDS analyses in the SEM a part of the material was molded in conducting plastic which was surface polished. The metal composition was determined from 20-point analyses to be Mo₁₆(1):Bi₈₄(1). The determined composition agrees very well with the nominal one and shows that no significant Bi₂O₃ loss by evaporation had occurred during the synthesis.

ED patterns, see Fig. 1, revealed satellite reflections, of several orders, to the basic fluorite reflections. The satellite reflections could be indexed using six indices $hklmnp$ and three \mathbf{q} -vectors along the unit cell axes with equal lengths of ca. $0.29a_f^*$ in reciprocal space. The presence of cross term reflections in all investigated crystallites excluded the possibility of twinning. Since the satellites are spaced equally along all space diagonals, it was concluded that the modulation is three-dimensional and does not break the cubic symmetry. The same systematic extinction conditions was observed for the satellites as for the main reflections, with hkl or mnp all odd or even. This, together with the fact that the point symmetry for the basic nonmodulated and modulated part of the structure must be equal, implies that the symmetry for both parts are $Fm\bar{3}m$. No satellites could furthermore be observed that connect the real space three dimensions with the three modulation dimensions, i.e., satellites to systematically absent basic reflections. This implies that the 6-D structure is primitive and that the symmetry is $P:Fm\bar{3}m:Fm\bar{3}m$. The strongest satellites are found in the $\langle 111 \rangle^*$ directions (type $hkl111$) and the next-strongest ones in the $\langle 200 \rangle^*$ directions (type $hkl200$).

The Guinier-Hagg film data yielded a unit cell parameter of $a = 5.6484(5) \text{ \AA}$, which equals that reported for pure $\delta\text{-Bi}_2\text{O}_3$, $a = 5.6485(6) \text{ \AA}$ (8). Using the approximate \mathbf{q} -vector length of $\varepsilon \approx 0.29a_f^*$, obtained from the ED patterns, it was possible to index several satellite Bragg peaks in the powder XRD pattern using six indices $hklmnp$, see Fig. 2, and thereby derive a better estimate of ε . Finally the unit cell parameter and ε were refined to $a = 5.6478(1) \text{ \AA}$ and $\varepsilon = 0.29256(6)a_f^* \text{ \AA}^{-1}$ from 37 reflections at $2\theta \leq 84^\circ$ by nonlinear least squares. The indexed powder pattern for the first 20 reflections is given in Table 1. The strongest and next-strongest satellite reflections are of the kind $hkl111$ and $hkl200$, in consistency with the ED data.

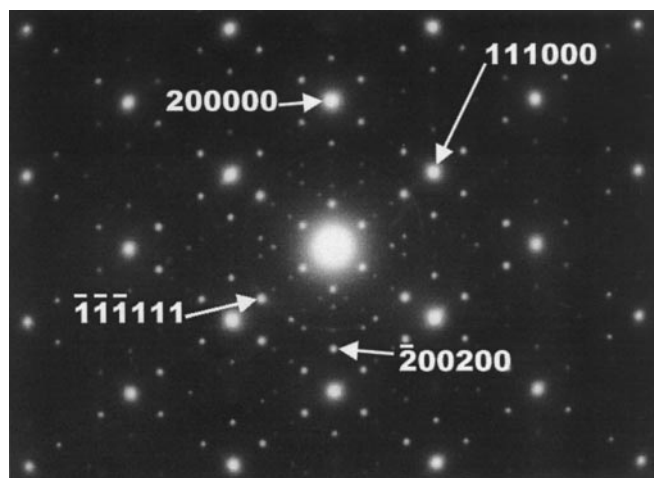


FIG. 1. ED pattern of Mo_{0.16}Bi_{0.84}O_{1.74} with zone axis $\langle 110 \rangle$. The image reveals both first- and second-order satellites along $\langle 111 \rangle^*$ as well as many cross terms reflections, e.g., $\bar{1}\bar{1}\bar{1}111$.

A crystal with an average dimension of 40–50 μm was investigated by single-crystal XRD. A section of the reciprocal space is given in Fig. 3 for comparison with the ED pattern in Fig. 1. The basic fluorite-type structure was refined to a weighted R -value of 0.037 using 16 unique basic reflections, an Mo/Bi ratio of 16:84 on the $4a$ sites (0, 0, 0) and $7/8$ (88%) of the $8c$ sites (1/4, 1/4, 1/4) occupied by O atoms, the latter occupancy calculated by charge balancing, assuming Mo⁶⁺ and Bi³⁺ ions. The only parameters refined were two isotropic thermal displacement for respectively the metal atoms, $U_{\text{iso}} = 0.0564(4) \text{ \AA}^2$, and the O atoms, $U_{\text{iso}} = 0.186(6) \text{ \AA}^2$. The refined values show that in the modulated structure the O atoms are significantly displaced but that the metal atoms are close to the positions in an ideal cubic fluorite-type structure.

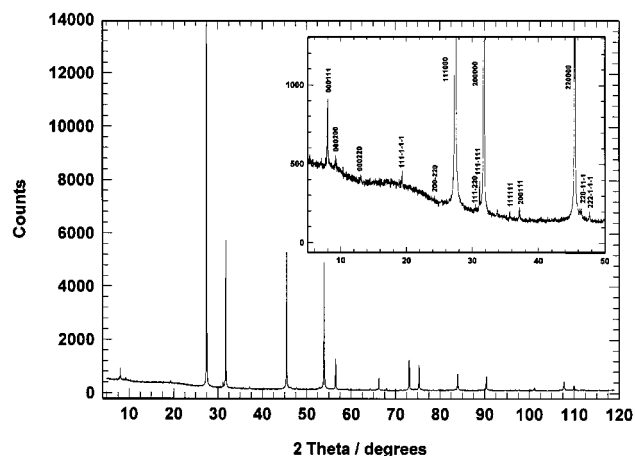


FIG. 2. Powder XRD pattern of Mo_{0.16}Bi_{0.84}O_{1.74} with indexed satellite reflections in the inset.

TABLE 1
Powder X-ray Diffraction Pattern of $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$

<i>hklmnp</i>	$2\theta_{\text{obs}}$	$\Delta 2\theta$	d_{obs} (Å)	I/I_0 (%)
000111	7.903	-0.017	11.17	36
000200	9.097	-0.051	9.71	6
000220	12.915	-0.041	6.849	1
200 $\bar{4}$ 00	12.997	0.005	6.806	2
111 $\bar{1}\bar{1}\bar{1}$	19.241	0.004	4.609	7
200 $\bar{2}$ 20	24.121	0.017	3.687	1
111000	27.319	-0.008	3.261	1000
111 $\bar{2}$ 20	30.538	0.005	2.941	1
111 $\bar{1}$ 11	31.005	-0.004	2.881	12
200000	31.653	-0.004	2.824	411
111111	35.562	0.006	2.5223	4
200111	37.041	-0.009	2.4250	6
220000	45.380	-0.001	1.9969	394
220 $\bar{1}\bar{1}\bar{1}$	46.139	-0.007	1.9657	5
222 $\bar{1}\bar{1}\bar{1}$	47.580	0.005	1.9095	6
311000	53.786	-0.003	1.7029	381
222000	56.385	-0.003	1.6304	90
331 $\bar{1}\bar{1}\bar{1}$	64.145	-0.008	1.4506	6
400000	66.128	0.003	1.4118	38
420 $\bar{1}\bar{1}$ 1	67.839	-0.014	1.3803	9

Note. $\Delta 2\theta = 2\theta_{\text{obs}} - 2\theta_{\text{calc}}$. $\lambda = 1.5406$ Å. $a = 5.6478(1)$ Å and $\varepsilon = 0.29256(6)$ Å⁻¹. Reflection intensities originate from diffractometer data.

DISCUSSION

The high-temperature phase $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ has not been reported previously. A well-crystallized sample of the orthorhombic low-temperature modification was obtained when remelting the quenched material at 1000°C and cooling the sample to 500°C at a rate of 5°/h.

Few 6-D structures are known and only a small number of them determined. The $P:Fm\bar{3}m:Fm\bar{3}m$ symmetry derived here for $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ has to our knowledge been observed previously only for $\text{Cu}_{5.378}\text{Bi}_{0.552}\text{S}_4$ (9) and not for any oxide compound. A similar 6-D solid solution phase is, however, found in the Nb–Bi–O system and a structure model has been proposed for it (10). Its composition is $\text{Nb}_x\text{Bi}_{1-x}\text{O}_{1.5+x}$, $0.12 \leq x \leq 0.46$, and the symmetry is $P:Fm\bar{3}m:Fd\bar{3}m$. The Nb and Mo phases have oxygen vacancy contents of 2–19% and 12.5%, respectively, and stabilizing metal atom concentrations of 6–23% and 16%, respectively. The \mathbf{q} -vector for the $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ phase spans in real space 3.418(1) unit cells or 19.307(4) Å, while the \mathbf{q} -vector for the Nb–Bi solid solution is significantly shorter, 15.6–14.6 Å. Further synthesis and structural work is evidently needed to evaluate the dependence of the modulations/diffuse scattering on added atom type and concentration. Possible displacive and occupational modulations have been discussed for the Nb–Bi solid solution (10). A few tentative inferences may however be made. In the case of $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$, the intensities of the satellite reflections,

for both ED and XRD, increase with 2θ angle in comparison with those of the main reflections. This indicates that the modulation has a substantial positional component that probably involves both metal and O atoms. The substitution of Bi^{3+} ions by the much smaller and higher charged Mo^{6+} ions should effect local metal–O configurations that differ considerably from those in the average structure, where each metal site is coordinated by eight O atoms at a distance of 2.45 Å. The local Mo–O distances in particular should be much shorter. When discussing the O atom positions in the phases it should, however, be realized that the O atom arrangement in $\delta\text{-Bi}_2\text{O}_3$ itself has been shown not to be like in an ideal cubic fluorite structure (11, 12). Since the scattering of X-rays and electrons are dominantly due to the metal atoms in the structure, little can be inferred from the present data about the behavior of the O atoms. It has, however, been shown from neutron powder diffraction data that for the Nb–Bi solid solution with composition $\text{Nb}_{0.18}\text{Bi}_{1.82}\text{O}_{1.68}$ the O atoms exhibit in addition to an occupational modulation also a displacive modulation along $[111]^*$ (10).

Attempts to determine the structure of $\text{Mo}_{0.16}\text{Bi}_{0.84}\text{O}_{1.74}$ from the collected single-crystal XRD data have so far not been successful, mainly due to difficulties to accurately integrate the intensities of the satellite reflections. The high symmetry of the structure makes, however, powder XRD data nearly equally useful for a structure determination due

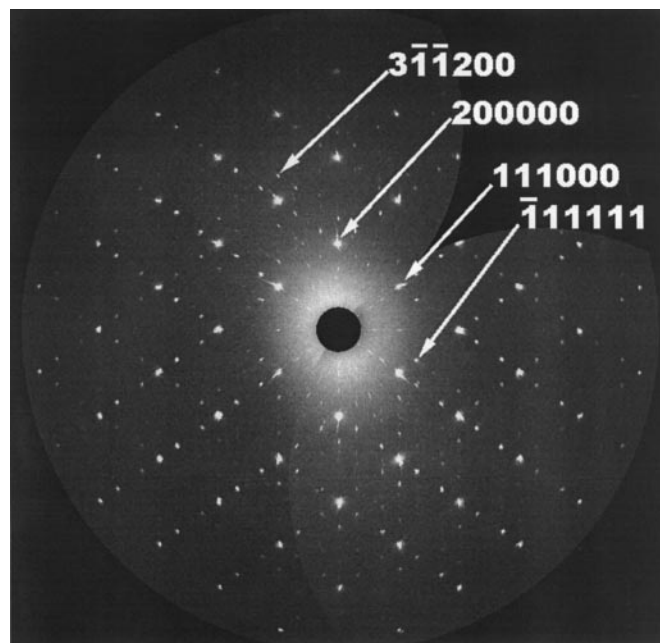


FIG. 3. A section of reciprocal space for single crystal XRD data in a $\{110\}$ plane, illustrating the intensity distribution for the basic fluorite type and satellite reflections. Up to second-order satellites and cross term satellite reflections in $\langle 200 \rangle^*$ directions are present.

to the fact that (i) peak overlap of reflections with different $hklmnp$ is small and (ii) that the multiplicity of satellite peaks is high, which provides for a good determination of their compounded intensities. A structure determination using X-ray and neutron powder diffraction data is scheduled.

ACKNOWLEDGMENTS

This study has been financially supported by the Swedish Natural Science Research Council.

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