JOURNAL OF SOLID STATE CHEMISTRY **108**, 250–252 (1994)

Neutron Diffraction Study of $Ca_{0.8}Bi_{1.2}O_{2.6}$ with Anti-α-AgI Structure

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Received February 19, 1993; in revised form May 19, 1993; accepted May 20, 1993

Powder neutron diffraction of $Ca_{0.8}Bi_{1.2}O_{2.6}$ at 8 K reveals a pseudocubic order–disorder structure, space group $R3m$, a = 424.6 pm and α = 90°. The average structure is of anti-α-AgI type, space group $Im3m$. Bismuth and calcium atoms are randomly distributed in (2a) with O,O,O, oxygen atoms in (24g) with x, 0, ½, x = 0.322. Antiglass disorder was established by high Debye–Waller parameters at low temperatures and extremely broad bands in the Raman spectrum.

INTRODUCTION

Ternary bismuth oxides of Ca (1), Sr, Ba (2), Cd (3), Pb (4), Na, and K (2) have small body-centered cubic cells containing two heavy atoms. In 1986, Graia *et al.* (3) determined the crystal structure of cadmium bismuth oxide as anti-α-AgI structure, space group $Im3m$, with bismuth and cadmium statistically distributed in (2a) with O,O,O, and oxygen in (12d) with ¼, 0, ½. They obtained for atoms in both positions rather high Debye–Waller parameters between 4 and 6 Å^2. Our assumption of antiglass disorder (5) was confirmed by Raman spectra of Sr, Ba (2), and Ca (6) bismutates with anti-α-AgI structure which showed a few bands only, extremely broadened by local violation of translational symmetry. We investigated $Ca_{0.8}Bi_{1.2}O_{2.6}$ by powder neutron diffraction at 8 K. With respect to antiglass disorder the characteristics of this phase are (1) nonstoichiometric composition, (2) high concentration of anion defects, (3) large irregular atomic displacements, and (4) statical disorder.

EXPERIMENTAL

Samples of $Ca_{0.8}Bi_{1.2}O_{2.6}$ were prepared by heating mixtures of $CaCO_3$ (99.9%, Merck) and Bi_2O_3 (99.9%, Janssen) for 2 hr. at 750°C, heating for 2–3 min at 1000°C and quenching by liquid nitrogen.

X-ray diffraction by a powder diffractometer Rigaku SG-9R, Ni-filtered Cu$K\alpha$ radiation, showed that the samples were cubic body-centered with a = 424.6(1) pm.

Neutron diffraction at 8 K was performed at the research reactor Orphée of the Laboratoire Léon Brillouin, Saclay, France, by a high resolution powder diffractometer with BF_3 detectors. The wavelength was 122.63 pm.

RESULTS

The neutron diffraction pattern of $Ca_{0.8}Bi_{1.2}O_{2.6}$ (Fig. 1), like the X-ray pattern, shows sharp Bragg reflections. Their intensities fall off rapidly with increasing scattering angle. A few broad reflections were first thought to be diffuse background scattering as in the neutron diffraction patterns of $Er_{0.4}Bi_{1.6}O_3$ (7) or $SrTe_5O_{11}$ (8) which are antiglass phases with fluorite defect structure.

From integrated intensities of the sharp Bragg reflections $|F_o|$ values were calculated. The average crystal structure was refined using The X-ray System (9) with scattering lengths from (10). Starting with the structure as determined by Graia *et al.* (3), the agreement between calculated and observed structure factors remained insufficient (R = 0.110 with $B_{(Bi,Ca)}$ = 7 Å^2, $B_{(O)}$ = 6 Å^2). It improved greatly to R = 0.043 when the oxygen atoms were refined in the position (24g), x, 0, ½, with x = 0.322(1), $B_{Bi,Ca}$ = 4.5(4) Å^2, B_O = 7(1) Å^2 (6). For observed and calculated structure factors see Table 1.

Following a suggestion by Dr. D. Hohlwein, Hahn-Meitner Institut Berlin, the maxima of background intensity were interpreted as Bragg reflections broadened by small particle size. Actually, their positions as far as they can be determined are close to the Bragg angles of 100, 111, 210, and 221/300 (see Fig. 1). We concluded that the arrangement of oxygen atoms is not body-centered but primitive, and after correction of background intensity, we determined intensities of these reflections. The noncentered space group with same general position as $Im3m$ is $P\bar{4}3m$. It was not feasible, however, to calculate adequate intensities assuming this space group. A trial and error-procedure (FORTRAN program TRITM which

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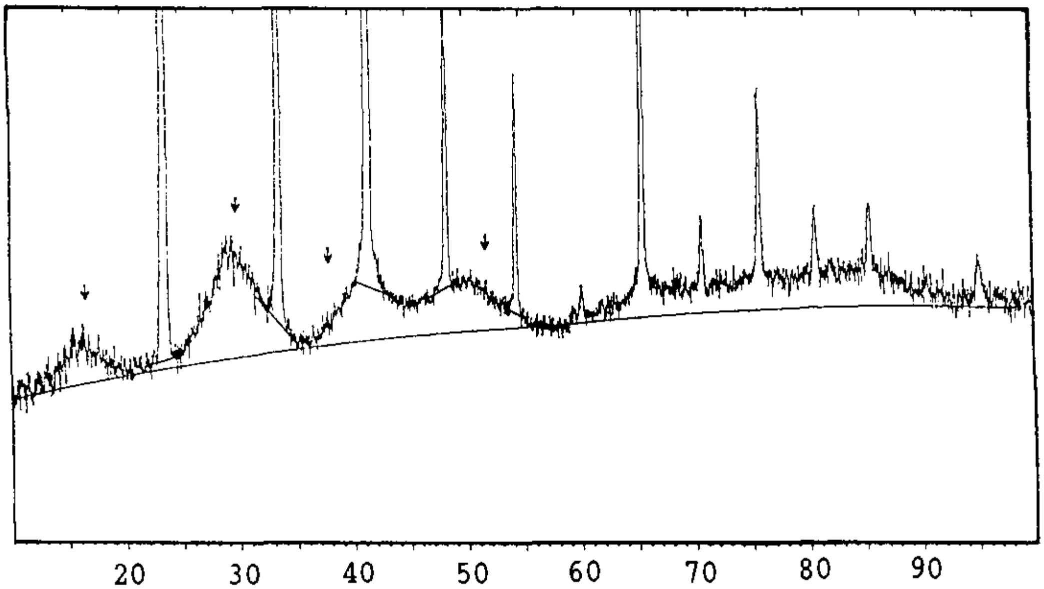

FIG. 1. Broadened reflections in neutron diffraction pattern of $Ca_{0.8}Bi_{1.2}O_{2.6}$ at 8 K (2θ-scale). Calculated positions of 100, 111, 210, and 221/300 are marked.

permits adaptation of parameters to the intensities of groups of reflections) in space group $P1$ showed that only six positions are occupied the coordinates of which are close to the positive permutations of x, y, z (with $y = 0$ and $z = \frac{1}{2}$). This is the general position of $R3m$. The structure can be described in this space group with the following parameters:

Atom	Position	x	y	z	B (Å^2)
Ca,Bi	(1*a*)	0	0	0	6.1(5)
Ca,Bi	(1*a*)	0.5	0.5	0.5	6.1(5)
O	(6*c*)	0.32(1)	0.96(2)	0.54(2)	3.1(8)

These calculations were performed with 18 reflection intensities instead of 10 F_o values (see Table 1), including those of the broadened reflections which can be estimated with low accuracy only. $R = \Sigma|\sqrt{I_c} - \sqrt{I_o}|/\Sigma\sqrt{I_o} = 0.069$, under these circumstances, seems satisfactory.

From the integral breadths, the diameters of the corresponding domains were estimated as 37 Å (100) and 17 Å (111) which indicates highly anisotropic domain shapes.

DISCUSSION

The average structure of $Ca_{0.8}Bi_{1.2}O_{2.6}$ is strictly spoken the anti-α-AgI type. In α-AgI, the silver atoms are distributed over the positions (24*g*) of $Im3m$ with x between 0.280 at 450°C and 0.308 at 180°C (11). The population parameter of oxygen atoms in this position in $Ca_{0.8}Bi_{1.2}O_{2.6}$ is very low (0.108) though somewhat higher than the one of silver atoms in α-AgI (0.083).

The different space groups of a (calcium + bismuth) framework ($Im3m$) and of oxygen blocks with partial occupancy ($R3m$) are a typical feature of order-disorder (OD) structures assembled from building units with partial symmetries (12). In space group $R3m$, within one cell are six oxygen positions. Not more than three of them can be occupied if oxygen–oxygen distances less than 200 pm are excluded. The actual mean occupancy in our specimen is 2.6 oxygen atoms per cell. Three oxygen atoms per cell

TABLE 1
Observed and Calculated Structure Factors and Intensities

hkl	$\|F_o\|$	F_c	I_o	I_c
100			10.0	10.0
110	8.5	8.6	60.4	72.7
111			54.9	39.5
200	16.8	16.8	63.2	71.2
210			17.6	14.5
211	13.2	12.5	100	99.7
220	8.5	8.9	17.4	16.3
221, 300			20.0	16.1
310	5.5	6.3	10.7	9.5
222	4.8	4.1	1.6	2.0
321	7.8	8.2	27.5	32.0
400	9.2	9.1	3.8	3.2
330, 411			11.0	12.2
420	5.6	5.4	3.8	3.1
332	5.5	5.4	4.8	4.5
422			1.1	1.1
510, 431			3.5	3.5
521			1.2	1.8

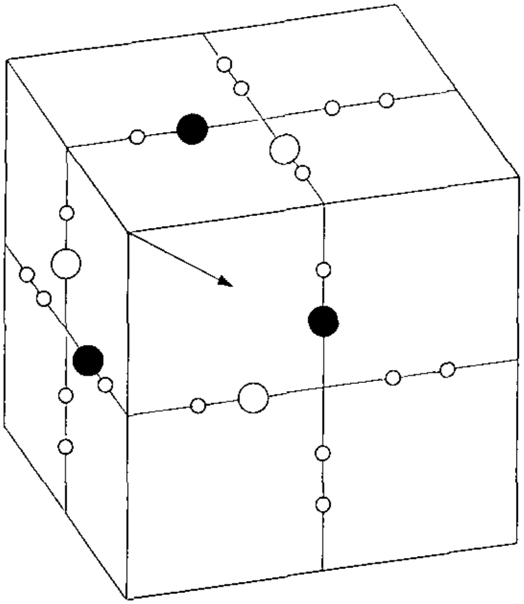

FIG. 2. Possible oxygen positions in the faces of cubic cell, space group *Im*3*m* (all circles). Large circles: Oxygen positions in *R*3*m*, split into two sets (●, ○) of three atoms each.

which must be present in at least 60% of all cells cannot be randomly distributed, however. Rather, two sets of three atoms each may be occupied alternatively (in Fig. 2 represented by large black and white circles). Their positions correspond to the general position of space group *R*3. In adjacent cells containing three oxygen atoms, this symmetry and the orientation of the polar trigonal axes (↑ in Fig. 2) may be maintained over each domain, and the different orientations of these axes (which correspond to the pseudocubic cell diagonals) will occur with equal frequency within the whole crystal.

The large irregular atomic displacements which are reflected by Debye–Waller parameters of 3–6 Å^2 are connected with varying coordination around all atoms, a characteristic of antiglass disorder. It cannot, at 8 K, be caused by thermal motion of the atoms. Disorder in $Ca_{0.8}Bi_{1.2}O_{2.6}$, therefore, is static as in other antiglass phases. In contrast, the disorder of α-AgI is dynamic at any temperature within its range of stability, and the Debye–Waller parameters are somewhat higher than in $Ca_{0.8}Bi_{1.2}O_{2.6}$ (7–15 Å^2, increasing with temperature). The electrical conductivity of ternary bismuth oxides with anti-α-AgI structure at elevated temperatures (compare (3)), caused by mobility of oxide ions, is the perfect counterpart to the conductivity due to mobile silver ions in α-AgI, and antiglass disorder can be understood as "frozen up" disorder of such ionic conductors (13).

ACKNOWLEDGMENTS

Our thanks are due to Dr. D. Hohlwein, Berlin, and Dr. A. Zedler, Frankfurt, for valuable discussions. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Bundesministerium für Forschung und Technologie (Bonn) under Grant 03-FU2DAR. Calculations were done at the Hochschulrechenzentrum Frankfurt.

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