JOURNAL OF SOLID STATE CHEMISTRY 63, 160–165 (1986)

Stability Range and Crystal Structure of the Oxygen-Deficient b.c.c. Solid Solution $Bi_{(1-x)}Cd_xO_{(1.5-x/2)}$$(0.11 < x < 0.25)$

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Received July 22, 1985; in revised form October 23, 1985

The composition range of the oxygen-deficient solid solution $Bi_{(1-x)}Cd_xO_{(1.5-x/2)}$ extends from $x > 0.11$ to $x < 0.25$ between 640–650 and 710–740°C. The b.c.c. structure can be preserved at room temperature by quenching for compositions ranging from $x = 0.14$ to $x = 0.23$. The crystal structure has been refined to $R = 0.037$ using automated diffractometer data collected on an air-quenched single crystal of composition $Bi_{0.79}Cd_{0.21}O_{1.395}$. The space group is *Im3m*, $a = 4.281(1)$ Å, $Z = 2$. Oxygen atoms are found in tetrahedral sites inside the b.c.c. cation framework.

In the last few years, a lot of work has been devoted to the oxygen conduction properties of bismuth and bismuth-based oxides (*1–3*). In our laboratory, it has been shown (*4*) that a highly conductive material, with a σ value as large as 1 $(\Omega \cdot cm)^{-1}$ at 600°C, could be prepared by the addition of lead oxide to bismuth oxide. High-temperature X-ray (*5*) and neutron powder diffraction experiments (*6*) revealed a body-centered cubic structure called β with two cations per unit cell. Unfortunately, this structure cannot be quenched: rapid cooling always results in two metastable phases with different structures, depending on the composition (*5*).

Isostructural phases have already been reported in other phase diagrams: Bi_2O_3–CaO (*7*) where the b.c.c. structure occurs in a limited range of composition and temperature; Bi_2O_3–SrO (*8*) where the observation of superlattice reflections indicates the occurrence of ordering among cations; finally Bi_2O_3–CdO where Sillen and Sillen (*9*) were able to obtain a nonstoichiometric phase with the b.c.c. structure by quenching from the melt.

In addition to this later work, several other investigations have been performed on bismuth oxide–cadmium oxide phases by means of X-ray diffraction, optical microscopy, and/or DTA. Levin and Roth (*10*) studied the Bi_2O_3-rich part while Kutvickij *et al.* (*11*) and, more recently, Jager and Kolar (*12*) investigated the whole system.

There are some discrepancies between the results of these various workers, although there is little doubt about the occurrence of two phases with a b.c.c. struc-

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0022-4596/86 $3.00

ture: a sillenite-type phase ($a \approx 10.2$ Å) and a β-type phase ($a \approx 4.2$ Å), in the low and medium cadmium oxide content regions, respectively.

Concerning electrical properties, Hauffe and Peters (*13*) measured, using ac techniques, the electrical conductivity of sintered pellets of mixtures of bismuth and cadmium oxides, between 300 and 500°C; their results showed an increase of conductivity of about two orders of magnitude in the region where the β phase is supposed to exist.

Takahashi *et al.* (*14*) indicated that, in contrast with strontium or calcium–bismuth mixed oxides which exhibit ionic conduction properties, cadmium–bismuth mixed oxides are predominantly electronic conductors.

In view of these somewhat contradictory results, we undertook investigations in the bismuth oxide–cadmium oxide system, with particular emphasis on the stability range of the β phase and on its electrical properties. This paper describes the formation conditions of this phase and its structure as determined from single-crystal X-ray data.

Experimental

The starting materials were bismuth oxide and cadmium oxide (Johnson Matthey grade 2). The appropriate quantities were thoroughly mixed in an agate mortar. The mixture was then heated for several days in a gold crucible at 700°C, i.e., about 25°C below the melting temperature. Heating was interrupted two or more times for homogenization by means of grinding.

Air-quenched samples were examined by X-ray diffraction at room temperature using a Guinier-De Wolf camera (Cu$K\alpha$). Powder spectra used for least-squares refinement of cell parameter were standardized against KCl.

High-temperature powder X-ray diffraction investigations were performed using a Guinier-Lenne camera with a gold sample holder. A Dupont 1090 thermal analyzer was used for DTA measurements. Single crystals were obtained either by melting followed by slow cooling or by heating during several days at about 20° below the melting temperature: the later method yielded crystals of better quality than the former.

Results

Composition and Stability Range of the b.c.c. Structure

Room-temperature X-ray examination of air-quenched samples disclosed the existence of a single-phase β domain with the b.c.c. structure in the composition range $0.30 < n < 0.375$ (n = molar fraction of CdO). The room-temperature parameter of the cubic cell slightly decreases as n increases, confirming that the phase is a solid solution (Table I).

However, it is a metastable solid solution: high-temperature X-ray investigations performed on quenched samples show that the b.c.c. structure is destroyed in the temperature range 400–450°C (heating rate 15°C · hr^{-1}) with appearance of a new phase of lower symmetry which, in turn, decomposes at 480–550°C into a mixture of a sillenite-type phase (a = 10.230(1) Å) and CdO. Further heating results in the forma-

TABLE I

n^a	a^b (Å)	d_{exp} (g · cm^{-3})	$d_{\text{th}}{}^c$ (g · cm^{-3})
0.30	4.293(1)	8.98(5)	9.01
0.35	4.281(1)	8.92(5)	8.94
0.375	4.272(1)	8.89(5)	8.90

[a] Molar fraction of CdO.

[b] Cubic cell parameter.

[c] The theoretical density was calculated with the hypothesis of an anion-deficient solid solution.

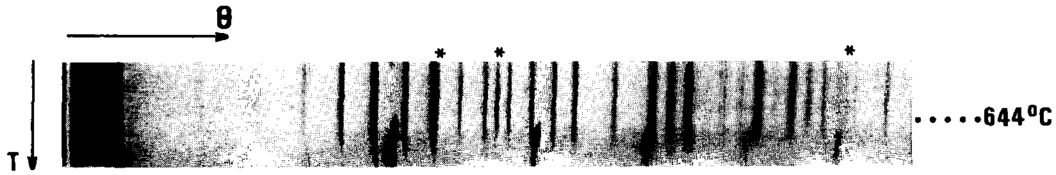

FIG. 1. High-temperature X-ray diffraction pattern of a sample $4Bi_2O_3$–PbO ($n = 0.20$) (* indicates lines due to CdO).

tion of a b.c.c. single-phased domain which is stable up to the melting temperature.

From examination of high-temperature X-ray photographs performed on samples of various compositions, it may be concluded that the b.c.c. composition range extends from $n \approx 0.20$ to $n \approx 0.40$. It is somewhat larger than the domain of the air-quenched b.c.c. phase and even larger than the values reported by Sillen and Sillen (9) ($0.27 < n < 0.42$) from samples quenched from the melt. Table II gives the temperatures of appearance (T_1) and fusion (T_2) of the b.c.c. solid solution, as determined from X-ray and DTA experiments.

In its high-temperature stability domain, the a parameter of the cubic cell slightly decreases as the cadmium content increases ($a = 4.355$ for $n = 0.25$; $a = 4.349$ for $n = 0.40$). This is well illustrated in Fig. 1 which represents a high-temperature X-ray pattern from a sample corresponding to $n = 0.20$. Up to 644°C the X-ray spectra mainly exhibit the sillenite phase reflexions. They coexist with some low-intensity diffraction lines (marked with an asterisk) corresponding to CdO. At 644°C the β b.c.c. phase appears for the first time. When the temperature raises the β cubic parameter clearly increases while the intensity of the sillenite reflexions gradually decreases and finally vanishes. The characteristic β parameter variation is then no longer observed.

As a consequence it may be concluded from these observations that a solid solution with a b.c.c. structure occurs over a large range of composition in the bismuth oxide–cadmium oxide system. It can be quenched within a small composition range.

Conversely, no significant parameter cell evolution can be observed in the case of the sillenite phase. This behavior indicates that this phase is a definite compound or may be a solid solution with a very narrow domain of existence.

Density measurements have been performed on β b.c.c. air-quenched samples (Table I). Experimental densities are in agreement with theoretical densities as computed from the model with two (Bi,Cd) ions in the cubic cell and a defective oxygen sublattice, according to the formula:

$$Bi_{1-x}Cd_xO_{1.5-x/2} \quad (0.11 < x < 0.25 \text{ at high temperature}) \quad (0.14 < x < 0.23 \text{ for air-quenched samples}).$$

TABLE II

STABILITY RANGE OF THE b.c.c. SOLID SOLUTION AT (a) TEMPERATURE OF APPEARANCE (°C), (b) MELTING TEMPERATURE (°C), AND (c) 710°C

n	$T_1^{(a)} \pm 5$	$T_2^{(b)} \pm 5$	Phases[(c)]
0.15	647	728	b.c.c. + sillenite
0.20	644	736	b.c.c.
0.225	646	737	b.c.c.
0.25	642	734	b.c.c.
0.30	649	728	b.c.c.
0.35	647	723	b.c.c.
0.375	651	720	b.c.c.
0.40	650	722	b.c.c.
0.45	652	711	b.c.c. + CdO

Structure Determination

A single crystal was isolated from a preparation with the nominal composition $13Bi_2O_3$, 7CdO ($n = 0.35$). The cell parameter value as computed from diffractometer data ($a = 4.281(1)$ Å) is in good agreement with the value given in Table I. It was therefore assumed that the cell contains two formulas $Bi_{0.79}Cd_{0.21}O_{1.395}$.

Intensity data were collected using the Philips PW 1100 automated diffractometer of the "Centre Commun de Mesures de l'Université des Sciences et Techniques de Lille" (Mo$K\alpha$ radiation, graphite monochromator). The intensities of 580 reflections were measured in a hemisphere of reciprocal space ($2° \leq \theta \leq 42°$). The only extinction condition was $h + k + l = 2n + 1$, indicating a body centered Bravais lattice. As a consequence, the structure was solved in the centrosymmetric space group $Im3m$. Atomic scattering factors for Bi and Cd were taken from Cromer and Waber (*15*); corrections for anomalous dispersion were applied using the data of Cromer and Liberman (*16*). Atomic scattering factors for oxygen were taken from Tokonami (*17*). Lorentz polarization corrections were then applied to intensities, resulting in 276 data with $I > 3\sigma(I)$ (where $\sigma(I)$ is the standard deviation on I).

To locate light elements (oxygen atoms) in the presence of heavy metals (cadmium and bismuth), it was necessary to apply absorption corrections. Owing to the difficulty of defining the geometrical characteristics of the crystal precisely, the analytical method of Tompa and De Meulenaer (*18*) did not give good results. Therefore, the empirical method of Walker and Stuart (*19*) was used : it gave more satisfactory results. The intensities of equivalent reflections were then averaged, giving 19 independent data. The corresponding R merging factor was equal to 0.1.

As no superstructure reflection could be detected, even on overexposed Weissenberg photographs, it was concluded that bismuth and cadmium atoms statistically occupy the 2(a) position of $Im3m$. Least-squares refinement of scale factor and isotropic thermal parameter yielded values of $R = |\Sigma F_{\text{obs}} - |F_{\text{cal}}||/\Sigma F_{\text{obs}}$ and B of 0.062 and 4.47 Å^2, respectively. This quite large B value could be due to the quenching performed to obtain the b.c.c. single crystals. This value is very close to that observed during a high-temperature neutron diffraction experiment on a β b.c.c. Bi_2O_3–PbO phase (*6*).

A difference map then revealed sharp maxima located on 12(d) positions ($\frac{1}{2}$, $\frac{1}{4}$, 0). It was assumed that these maxima correspond to oxygen atoms, i.e., 2.79 atoms per cell. Refinement of an isotropic thermal coefficient for these atoms led to a R value of 0.037, for B values of 4.47 and 5.46 Å^2 for the metals and oxygen, respectively.

TABLE III

COMPUTED AND OBSERVED STRUCTURE FACTORS FOR $Bi_{0.79}Cd_{0.21}O_{1.395}$

h	k	l	F_{obs}	F_{cal}
−1	−5	0	121.46	123.02
4	−4	0	75.43	84.08
2	−4	0	189.11	203.48
−4	0	0	294.04	292.93
−3	−3	0	220.28	228.00
−1	−3	0	439.98	439.78
2	−2	0	556.80	529.98
−2	0	0	844.78	823.90
−1	−1	0	886.91	927.66
0	−5	3	68.27	68.00
2	−5	1	91.29	94.53
−3	−4	1	112.29	123.59
−1	−4	1	232.72	229.24
2	−3	1	330.71	330.97
−1	−2	1	691.95	672.27
2	−4	2	133.43	142.84
−3	−3	2	151.98	174.36
2	−2	2	362.99	352.74
−4	3	3	82.07	68.00

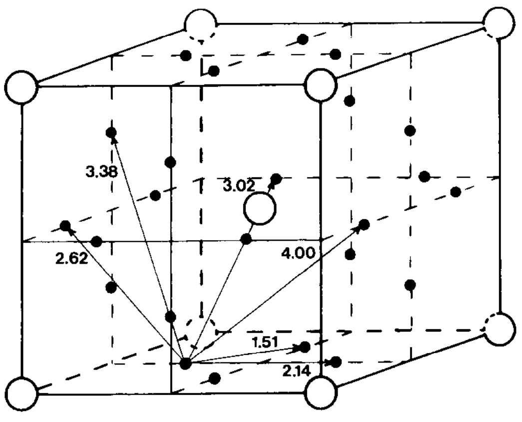

FIG. 2. Anti-α-AgI structure of $Bi_{1-x}Cd_xO_{(1.5-x/2)}$. Open circles : (Bi,Cd) ions; filled circles : oxygen positions.

Table III lists observed and computed structure factors.

Discussion

A three-dimensional view of the structure of $Bi_{0.79}Cd_{0.21}O_{1.395}$ is given in Fig. 2. This diagram is, in fact, a drawing of the structure of the high-temperature, high-conductivity phase of silver iodide. Since in the present case immobile framework ions are cations and mobile ions are anions, it can be described as an "anti-α-AgI" structure.

It is noteworthy that, of the positions which have been speculated in α-AgI, i.e., 12(*d*) (tetrahedral coordination), 24(*h*) (triangular coordination), and 6(*b*) (octahedral coordination), only the first set seems to be occupied in the mixed oxide. Although a direct confirmation is difficult to obtain from difference Fourier maps, this observation is supported by the fact that the thermal coefficient of 12(*d*) anions is only slightly larger than the thermal coefficient of 2(*a*) cations. Furthermore, tetrahedral rather than triangular or octahedral coordination is usual for oxygen in oxides.

The shortest (Bi,Cd)–O distance of 2.39 Å is only slightly larger than the mean Bi–O bond length (2.37 Å) as determined by Abrahams *et al.* (*20*); it is in good agreement with the distance which is computed from ionic radii values (*21*): 1.38 Å for oxygen in tetrahedral coordination and 1.01 Å for (0.79 Bi + 0.21 Cd) assuming that cation coordination is roughly octahedral.

The following distances (Å) between 12(*d*) equivalent positions are easily computed: $d_1 = 1.51$; $d_2 = 2.14$; $d_3 = 2.62$; $d_4 = 3.02$; $d_5 = 3.38$, and $d_6 = 4.00$ Å (see Fig. 2). Of course, only the positions which correspond to the last four distances can accommodate oxide ions.

The number of available sites for oxide ions is far greater than the effective number of these ions. Of course, there is never more than one ion on a cube face and, since the number of oxygen atoms in the cell is lower than three, some faces are empty.

It follows that the b.c.c. solid solution seems to fulfill some of the conditions that are required for fast ionic conduction: ionic disorder on a set of partially filled, crystallographically equivalent sites. However, we do not know if the anions are ordered or not.

Nevertheless, the bismuth oxide–cadmium oxide b.c.c. solid solution is a potential candidate for fast ionic transport of oxygen. In a later paper, we will describe and discuss its conduction and transport properties.

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