

Phase Relations in the System $\text{Bi}_2\text{O}_3\text{-CdO}$

ANTON JAGER AND DRAGO KOLAR

"J. Stefan" Institute, "E. Kardelj" University, Ljubljana, Yugoslavia

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Phase relations in the system $\text{Bi}_2\text{O}_3\text{-CdO}$ were studied in the composition range from 90-30 mole% Bi_2O_3 . A new phase, $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$, was found to exist up to 925 K. At this temperature it decomposes to form CdO and the $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ phase. The $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ phase is stable between 925 and 963 K and melts incongruently. Below 925 K it decomposes to $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ and $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$. The phase $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ has cubic symmetry. The Sillenite-type bcc phase $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ forms above 897 K from oxide mixtures in the solid state or from fused oxide mixtures, but the compound could never be prepared as a single phase.

Introduction

The phase diagram $\text{Bi}_2\text{O}_3\text{-CdO}$ has been investigated by Levin and Roth (1) in reference to the existence of a Sillenite-type phase, first reported by Sillen and Sillen (2). The term "Sillenite type-phase" designates a bcc form of Bi_2O_3 , stabilized by various oxides. It corresponds to $\gamma\text{-Bi}_2\text{O}_3$, which is metastable in pure form. The ideal Bi:Me ratio in the bcc structures is 12:1, however, various Bi:Me ratios were found in various systems. In the $\text{CdO-Bi}_2\text{O}_3$ system, Levin and Roth (1) reported two bcc phases with $\text{Bi}_2\text{O}_3:\text{CdO}$ ratios 15:2 and 6:1, respectively, which were found to be metastable. A third phase of unknown composition was also found, and was supposed to be one of Sillen's (2) reported $\text{Bi}_2\text{O}_3\text{-CdO}$ phases.

Kutvickij *et al.* (3) constructed a more complete $\text{Bi}_2\text{O}_3\text{-CdO}$ phase diagram up to 80 mole% CdO. Two stable compounds, i.e., $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ and $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ were identified. Both of them were found to undergo a polymorphic transition. The tetrag-

onal low-temperature phase $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ was reported to be stable up to 908 K. Above this temperature, the cubic form existed up to its incongruent melting point at 1018 K. The cubic low-temperature form $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ transformed at 918 K into another cubic one, which melted incongruently at 988 K. Both forms were found to have a bcc unit cell, with $a_0 = 10,20$ and $4,24 \text{ \AA}$, respectively. The third, unidentified compound, should exist on the cadmium-rich side.

The results published so far do not disclose all the characteristics of the $\text{Bi}_2\text{O}_3\text{-CdO}$ system. Our preliminary investigations threw doubt upon the existence of some compounds and their thermal stability. A reexamination of the phase equilibria, with particular emphasis on the middle part of the binary, was therefore undertaken.

Experimental

The starting materials were α -bismuth oxide (Meck, extra pure) and cadmium ox-

ide (Ventron, 99,9%). Powdered mixtures of various molar ratios were homogenized in an agate mortar and pelleted. Pellets were placed on platinum foil and heated in an electrical furnace several days and in some runs, several weeks. No significant change in weight was detected.

To accelerate the equilibration, the heating was interrupted several times; quenched pellets were crushed, homogenized, repressed, and subjected to further heating.

All the quenched samples were subjected to X-ray analysis using the Guinier powder technique with $\text{CuK}\alpha$ radiation. An optical microscope was used to examine polished sections. DTA measurements were made in air using platinum holders. Two samples were analyzed by high-temperature X-ray diffractometry.

Results and Discussion

It proved impossible to synthesize the reported low temperature $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase (3) from powder mixtures, even after prolonged heating of several weeks. All samples, prepared with compositions between 95 and 55 mole% Bi_2O_3 , when heated approximately between 773 and 903 K and quenched to ambient temperature or in ice-cold water, were identified as mixtures of $\alpha\text{-Bi}_2\text{O}_3$ with some unknown phase. Investigations of polished sections via the reflected-light microscope and X-ray powder analysis showed a decrease in the amount of $\alpha\text{-Bi}_2\text{O}_3$ as the content of cadmium oxide increased. $\alpha\text{-Bi}_2\text{O}_3$ disappeared in samples with 50 mole% CdO. The microstructure showed an increasing amount of the unknown phase until a monophasic picture was obtained at the 1:1 composition (Figs. 1 and 2). A new 1:1 phase was assumed to exist.

Attempts to prepare a homogeneous bcc 6:1 phase through reaction of bismuth and

cadmium oxides in the solid state above approximately 903 K were also unsuccessful. A cubic phase, having an X-ray pattern identical to that given by Kutvickij *et al.* for the high-temperature $6\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase (3), was formed, but every run yielded a two-phase sample. $\alpha\text{-Bi}_2\text{O}_3$ or 5:3 phase were present besides the Sillenite-type 6:1 phase. Once formed above approximately 897 K, the 6:1 phase did not completely transform or disappear even after prolonged heating below this temperature (One run of 2 weeks at 623 K.) Thus, it seems that the Sillenite-type 6:1 phase is in reality a stable rather than a metastable compound (1) above 897 K. The fact that the compound composition could never be obtained as a single phase, not even by slow cooling or rapid quenching and subsequent tempering of fused oxide mixtures, indicates that the reaction may depend on the oxygen partial pressure as well as on the temperature.

In such a case, even the stoichiometry may change. Recent crystallographic investigation of the bcc compound in $\text{ZnO-Bi}_2\text{O}_3$ system led the authors to propose the formula $\text{Bi}_{136}^{3+}\text{Bi}_{12}^{5+}\text{ZnO}_{60}$ instead of the previously proposed composition $7\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$ (5). Because of the chemical similarity between Cd and Zn, the possibility of formation of the isostructural compound $\text{Bi}_{136}^{3+}\text{Bi}_{12}^{5+}\text{CdO}_{60}$, instead of the 6:1 phase, may not be excluded.

On the other hand, if the 6:1 formula is correct, it seems likely that one out of every twelve Bi^{+3} ions must be oxidized to Bi^{5+} in order to satisfy the formula $\text{ZnBi}_{12}\text{O}_{20}$, isostructural with $\text{SiBi}_{12}\text{O}_{20}$ (6).

DTA measurements of seven samples with compositions between 80 and 50 mole% of Bi_2O_3 produced on heating, a strong endothermic peak at 897 ± 10 K. It practically vanished at the 50 mole% Bi_2O_3 composition. In most runs the samples used for DTA experiments were first heated for several days at approximately 934 K and then for several days at approximately 873

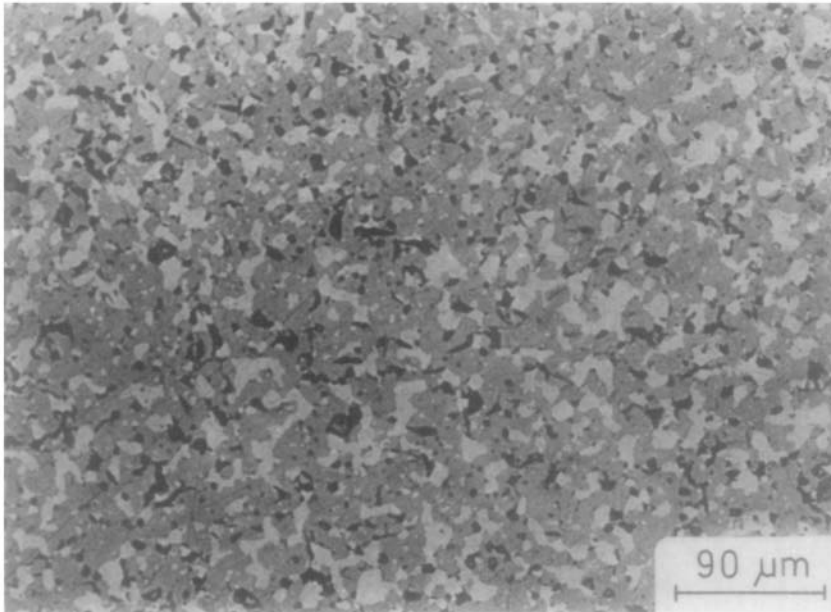


FIG. 1. Quenched sample with $\text{Bi}_2\text{O}_3 : \text{CdO} = 5 : 3$ after 192 hr annealing in air at 873 K, containing $\alpha\text{-Bi}_2\text{O}_3$ (light grey) and 1:1 phase (dark grey).

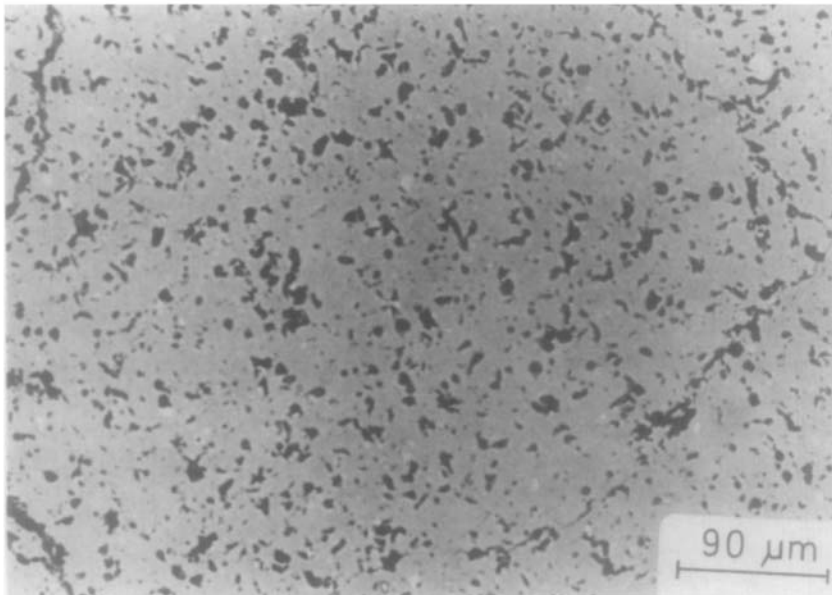


FIG. 2. Quenched sample of the 1:1 phase containing surplus $\alpha\text{-Bi}_2\text{O}_3$ (light grey) after 192 hr annealing at 873 K in air.

TABLE I
X-RAY POWDER DATA FOR THE
 $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ PHASE

hkl	d_{hkl}	hkl
100	3.02	100
39	2.14	110
72	1.743	111
16	1.510	200
12	1.350	210

K. The DTA peak at 897 K most probably indicates the temperature of formation of the bcc 6:1 phase. This means that the phase is metastable below 897 K. Its decomposition rate is slow, and there is no equivalent peak on cooling.

Samples of the compound of composition 5:3 which were examined suggest the existence of two phases in the temperature range up to 925 ± 10 K. The reported low-temperature phase, $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ (3), was

not formed through bismuth and cadmium oxide reaction in the solid state. Up to 897 K, samples were identified as mixtures of $\alpha\text{-Bi}_2\text{O}_3$ and 1:1 phase (Fig. 1). Between 897 and 925 K the bcc Sillenite-type phase was present, as well as the 1:1 compound. X-Ray analyses and polished section examinations showed the existence of a single phase above 925 K, i.e., the compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$. The X-ray pattern (Table I) is identical to that reported in Ref. (3), but the d -values that were found are consistent either with a primitive cubic unit cell with the lattice parameter $a_0 = 3.02 \text{ \AA}$, or with a body-centered cubic lattice, as stated in Ref. (3). In contrast to earlier findings, it is evident that only one polymorphic form of $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ exists, being stable between 925 and 963 K. In particular, the microstructural data confirm the incongruent melting of this compound (Fig. 4), at 963 ± 10 K. For instance, a sample close to the 5:3 composition on the bismuth-rich side (Fig. 3), on melting and slow cooling, pro-

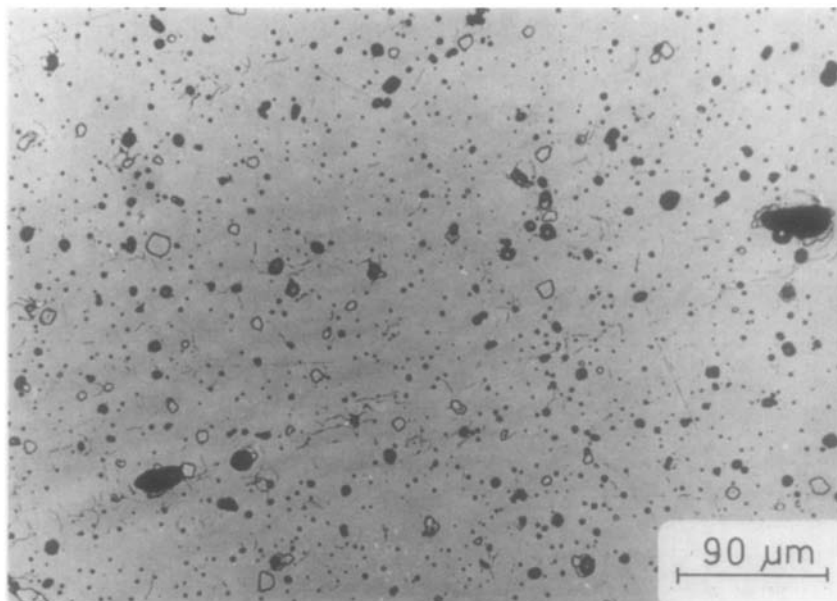


FIG. 3. Quenched sample of the 5:3 phase (matrix) containing surplus bismuth in the form of the Sillenite-type phase after 192 hr annealing in air at 953 K. Etched with dil. lactic acid.

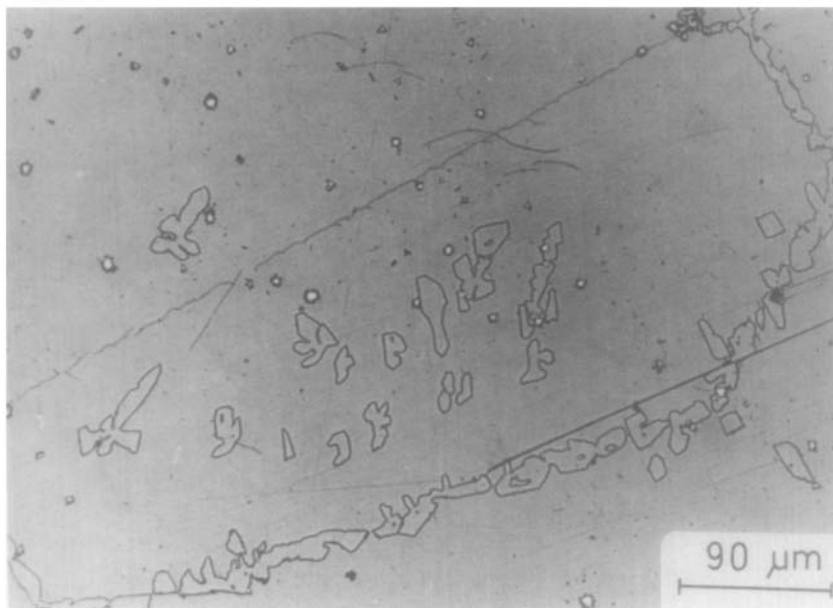


FIG. 4. Phase (5:3) containing surplus bismuth melted at 1023 K in air and slowly cooled to 873 K. Idiomorphic grains of the Sillenite-type phase in the matrix of 1:1 phase. Platinum inclusions (white).

duced idiomorphic crystal grains of the Sillenite-type phase.

Microstructural data of quenched samples along the $6\text{Bi}_2\text{O}_3 \cdot \text{CdO} - 5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ join showed some yet unidentified reaction within the temperature range of the 5:3 phase stability. There was, for instance, a clear difference in the microstructure of samples with 80 and 70 mole% Bi_2O_3 , heated at the same time at 943 K, both showing the same X-ray pattern. The microstructure of the sample with 80 mole% Bi_2O_3 behaved as if a considerable amount of liquid phase were present (Fig. 5), in contrast to the sample with 70 mole% Bi_2O_3 , which showed a microstructure characteristic of reaction in the solid state (Fig. 6). The binary eutectic at about 16 mole% Bi_2O_3 (1) might have been assumed to be due to this somewhat irregular behavior of the system.

A new compound $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ was identified. Samples with this composition appeared in all runs, after a few days heating

between approximately 823 and 873 K, to be present as a single phase. This phase is stable up to 925 ± 10 K, as determined by DTA, high-temperature X-ray analysis, and quenching experiments. The homogeneous phase $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ was heated stepwise from 903 to 943 K in 10 K steps. After being kept for 10 min. at the irrespective temperatures, the samples were quenched, X-rayed, and polished sections were examined with a reflected-light microscope. Between 925 and 935 K the decomposition of $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ to CdO and the $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ phase set in (Fig. 7). This temperature for the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ decomposition is in agreement with the temperature of formation of $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ as obtained by DTA measurements, as well as by high-temperature X-ray analysis.

DTA curves showed a peak at 925 ± 10 K, which indicates formation of the $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ phase, i.e., decomposition of the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase. On cooling at the rate of 10 K/min, this peak was not obtained be-

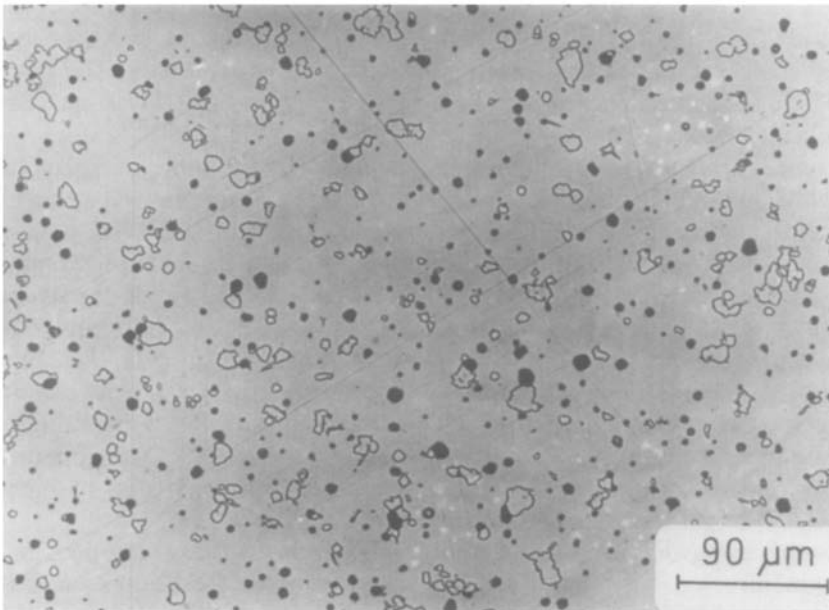


FIG. 5. Quenched sample with 80 mole% Bi_2O_3 showing idiomorphic grains of the Sillenite-type phase (light grey) in the matrix of needle-like crystals of the 5:3 phase after 72 hr annealing in air at 943 K. (Compare Fig. 6.) Etched with dil. lactic acid.

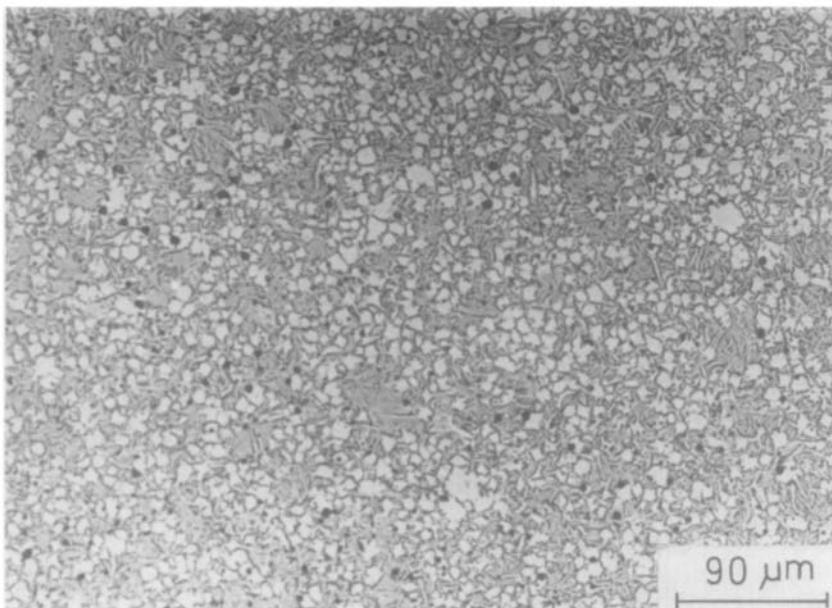


FIG. 6. Quenched sample with 70 mole% Bi_2O_3 showing grains of the Sillenite-type phase in a matrix of the 5:3 phase (compare Fig. 5). Etched with dil. lactic acid.

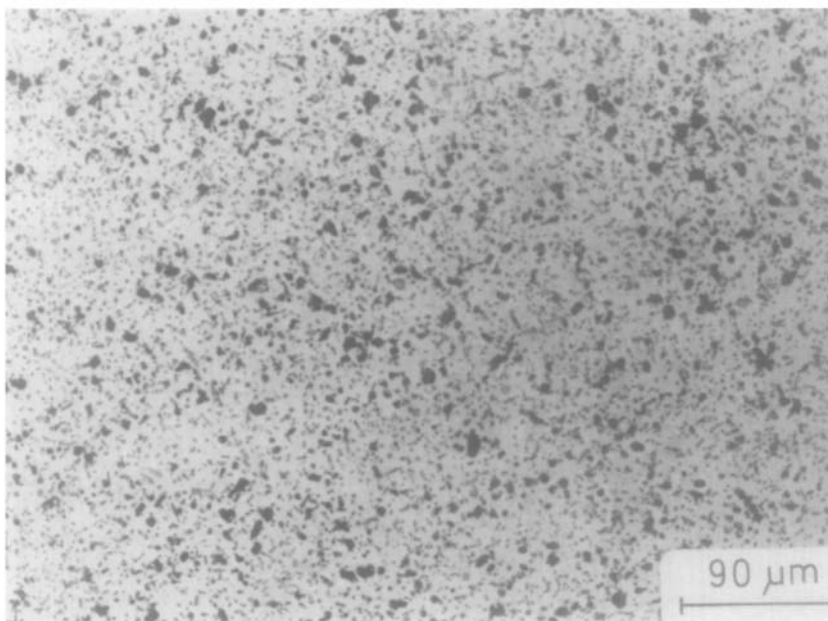


FIG. 7. Originally practically homogeneous 1 : 1 phase synthesized in air at 873 K (Fig. 2) after its decay to CdO (dark grey exsolutions) and 5 : 3 phase (matrix) at 933 K.

cause of the sluggish decomposition of the $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ phase.

Samples containing the rather homogeneous 1 : 1 phase or composed exclusively of this phase differed in color from samples containing surplus $\alpha\text{-Bi}_2\text{O}_3$ or CdO. The powdered 1 : 1 phase was beige while samples with several percent bismuth oxide in excess were yellow, and those with excess cadmium oxide, green. A discrete phase at the 1 : 1 oxide ratio was thus observable also with the naked eye.

The compounds $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ and $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ are essentially stoichiometric. No solid solution region was detected using our experimental technique. X-Ray powder data for the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase are presented in Table II.

High temperature X-ray analysis of two samples containing 65 and 55 mole% bismuth oxide, respectively, and composed of the Sillenite-type phase and the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase, displayed formation of the 5 : 3

phase and the disappearance of the 1 : 1 phase in the temperature range 918–928 K. Samples were X-rayed every 10 K, beginning at 873 K. The heating time was 20 min

TABLE II
X-RAY POWDER DATA FOR THE $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$
PHASE

hkl	d (Å)	hkl	d (Å)
7	7.53	7	2.2
7	7.25	10	2.13
10	5.39	19	2.09
32	3.71	8	2.07
25	3.66	16	2.01
94	3.30	30	1.07
41	4.06	9	1.87
100	2.77	12	1.83
78	2.75	9	1.82
22	2.63	55	1.78
16	2.57	44	1.73
19	2.43	29	1.71

for each temperature. The X-ray pattern of a sample containing 55 mole% Bi_2O_3 showed the existence of the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase and the Sillenite-type phase up to 918 K, where $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ began to appear. Above this temperature the 5:3 and 6:1 phases were identified. By quenching experiments it was shown that CdO exists with $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ in this composition and temperature range. Cadmium oxide, which was determined in quenched samples using the film technique, could not be detected by high-temperature X-ray analysis using the diffractometer method. The presence of three phases, i.e., 6:1, 5:3, and CdO , indicates some deviations in the binary system, as discussed below. After cooling to room temperature, the X-ray pattern still indicated the presence of the compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ and the bcc 6:1 phase. This preservation of $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$ to room temperature is in agreement with the results of DTA measurements, where the peak indicating the temperature of the 5:3 phase decomposition was absent. Samples with 65 mole% Bi_2O_3 yielded the same high-temperature X-ray patterns as the sample with 55 mole% Bi_2O_3 at the same temperature.

The Sillenite-type phase appears to disregard the phase rule. It was present in most runs together with cadmium oxide along the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ join. It is supposed that the composition of this phase could be slightly off the $\text{Bi}_2\text{O}_3\text{-CdO}$ join. The dependence of reactions within this systems on oxygen partial pressure and temperature may yield three instead of two phase assemblies, which were identified in several runs on the $\text{Bi}_2\text{O}_3\text{-CdO}$ join. The X-ray reflections, present in addition to those of $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ and CdO , were quite similar, if not identical, to those of the 6:1 phase.

No further phase could be determined along the $\text{Bi}_2\text{O}_3 \cdot \text{CdO}\text{-CdO}$ join. The $\text{Bi}_2\text{O}_3 \cdot \text{CdO}$ phase coexisted with a third phase, most probably the bcc 6:1 phase. No run produced an equilibrium two-phase sample

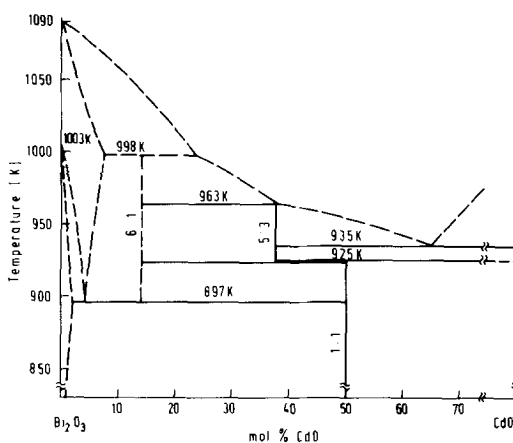


FIG. 8. Phase diagram $\text{Bi}_2\text{O}_3\text{-CdO}$. Maximum decomposition temperature of the 1:1 phase and the minimum decomposition temperature of the 5:3 phase were experimentally observed to occur at approximately the same temperature.

at or above the temperature of formation of the 6:1 phase. This means that the $\text{Bi}_2\text{O}_3\text{-CdO}$ phase diagram cannot be treated as a true binary diagram. Platinum, used as an inert vessel material, seems to play a more active role than previously supposed (4). The fact that the intermetal compound Bi_2Pt was detected by high-temperature X-ray analysis when oxide mixtures were melted on a platinum support, shows the great influence which Pt can have on the oxygen content, i.e., on the valence of bismuth in bismuth oxide.

DTA curves of samples containing more than 50 mole% CdO in most cases yielded a peak at 897 ± 10 K, most probably indicating the formation of the bcc 6:1 phase, also, a peak at 925 ± 10 K, indicating the decomposition of the 1:1 phase; also, a peak at 935 ± 10 K, indicating the appearance of the liquid phase ("binary" eutectic approximately between 60 and 70 mole% CdO), and finally, a peak at 963 ± 10 K, indicating the melting point of $5\text{Bi}_2\text{O}_3 \cdot 3\text{CdO}$.

The results are summarized in the phase diagram presented in Fig. 8.

Acknowledgment

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