

# Crystallographic state of the CdO lattice during sintering with added Bi<sub>2</sub>O<sub>3</sub>

ILIJA KRSTANOVIĆ, ALEKSANDRA RADAKOVIĆ, STAMENKA M. RADIĆ,  
MOMČILO M. RISTIĆ

Centre for Multidisciplinary Study of Belgrade University, and Institute of Technical Sciences  
of the Serbian Academy of the Sciences and Arts, Belgrade, Yugoslavia

In this paper the possibility of incorporation of Bi<sup>3+</sup> ions into CdO lattice, as well as the influence of this process on the very course of sintering of CdO, have been investigated. It was proved that Bi<sub>2</sub>O<sub>3</sub> added (up to 2 mol %) has a proportional influence on rise of the lattice parameter of CdO and that the density of sintered CdO increases exponentially.

## 1. Introduction

Kutvickii *et al.* [1] have thoroughly studied the Bi<sub>2</sub>O<sub>3</sub>-CdO system within the concentration limits 0 to 80 mol % Bi<sub>2</sub>O<sub>3</sub> and established the phase diagram for this field. Incorporation of additives (In<sup>3+</sup>, Ag<sup>1+</sup> or Na<sup>1+</sup>) into cadmium oxide has been studied here by precise measurements of the lattice parameter *a* [2]. Bearing in mind the fact that investigation of solid systems containing foreign atoms is of considerable interest for understanding the properties of a crystalline solid in terms of its defect structure, we have paid particular attention to an investigation of added Bi<sub>2</sub>O<sub>3</sub> on sintering of CdO while stress was laid on the establishment of the crystallographic state of the CdO lattice under stress.

## 2. Experimental details

Appropriate mixes of CdO and Bi<sub>2</sub>O<sub>3</sub> powders (1 to 2 and 1 μm particle size, respectively) were intensively homogenized by agate planetary milling, pressed as small tablets to ~100 mPa (density 4.07 ± 0.01 g cm<sup>-3</sup>), and sintered for 4 h in air at 850°C. The general characteristics are presented in Table I (Fig. 1).

All samples were analysed on an X-ray diffractometer using CuKα radiation and a graphite monochromator, and using spectrographically pure silicon as an external standard. The peak positions were measured at the mid-point of the so-called half-maximum width, all the peaks in the range between 14 to 100° 2θ were scanned manually at intervals of 0.02°.

TABLE I Influence of Bi<sub>2</sub>O<sub>3</sub> on sintering of CdO.

Bi <sub>2</sub> O <sub>3</sub> (mol %)	ρ <sub>s</sub> * (g cm <sup>-3</sup> )	ρ <sub>ST</sub> † (% TD)	α <sup>‡</sup> = $\frac{\rho_s - \rho_i^\ddagger}{\rho_t - \rho_i}$
0.0	7.21	90.12	0.7986
0.1	7.23	90.37	0.8041
0.5	7.27	90.88	0.8142
1.0	7.35	91.86	0.8321
2.0	7.55	94.38	0.8829

\*ρ<sub>s</sub>: density of the sintered sample.

†ρ<sub>ST</sub>: % of theoretical density (% TD).

‡ρ<sub>t</sub>: density of the pellet.

§α: densification parameter.

The values of *a* obtained for each reflection were least-square fitted to the cot θ cos<sup>2</sup>θ function. The resulting *a* parameters for Bi<sup>3+</sup> doped CdO are given in Table II.

## 3. Discussion

The influence of Bi<sub>2</sub>O<sub>3</sub> on sintering of CdO was investigated within the region in which, according to experimental evidence, the Bi<sup>3+</sup> ion is incorporated into the CdO lattice. Let us now consider the change occurring in degree of densification

$$\alpha = \frac{\rho_s - \rho_i}{\rho_t - \rho_i} \quad (1)$$

where ρ<sub>i</sub> is the pellet density; ρ<sub>s</sub> is the density of the sintered sample; and ρ<sub>t</sub> is the theoretical density of the relative material depending on the quantity of added Bi<sub>2</sub>O<sub>3</sub> (Fig. 2).

A rectilinear dependence having a general form as given below, is evident

$$\rho_s = \rho_i + (\rho_{s_0} - \rho_i) e^{kx}$$

where: ρ<sub>s<sub>0</sub></sub> is the density of the sintered sample having no additive; *k* is a constant; and *x* is the content of added oxide in mol %.

It is clear that the change in lattice constant and density of CdO is probably governed by the increase in concentration of point defects formed by Bi<sup>3+</sup> ions in solid solution (Table II). Brownlee and Mitchell [3] reported almost identical variations for semiconductors such as NiO(Li<sup>+</sup>) (and also Fe<sub>2</sub>O<sub>3</sub> (Ti<sup>4+</sup>)) with *a*

TABLE II Lattice *a* parameters (nm) for CdO containing Bi<sup>3+</sup> at 23 ± 2°C. The values are derived from (111), (200), (220), (311), (222), (400), (420) reflections

mol % Bi <sub>2</sub> O <sub>3</sub> in CdO	<i>a</i> (nm)	Δ <i>a</i> = <i>a</i> <sub>0</sub> - <i>a</i> <sub>i</sub>	$\frac{\Delta a}{a_i}$ (× 10 <sup>-3</sup> )
0	<i>a</i> <sub>0</sub> = 0.46957	0	0
0.1	<i>a</i> <sub>1</sub> = 0.46963	0.006	1.278
0.5	<i>a</i> <sub>2</sub> = 0.46983	0.026	5.540
1.0	<i>a</i> <sub>3</sub> = 0.47010	0.053	11.287
2.0	<i>a</i> <sub>4</sub> = 0.47065	0.108	23.000

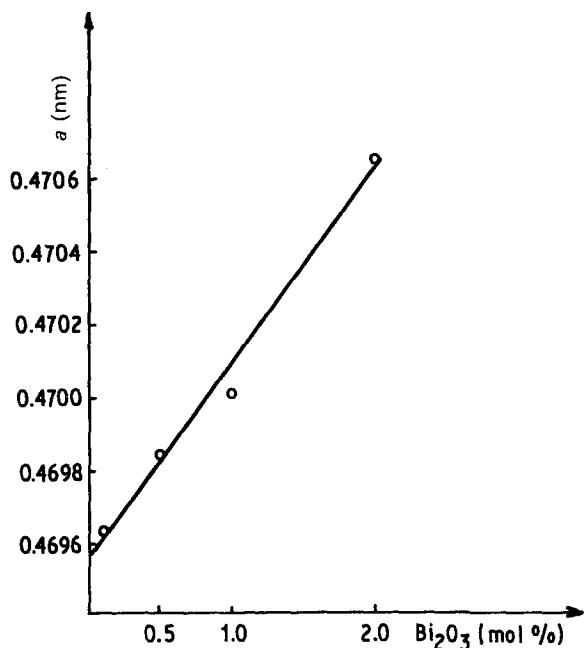


Figure 1 Lattice parameter of cadmium oxide containing of bismuth ions.

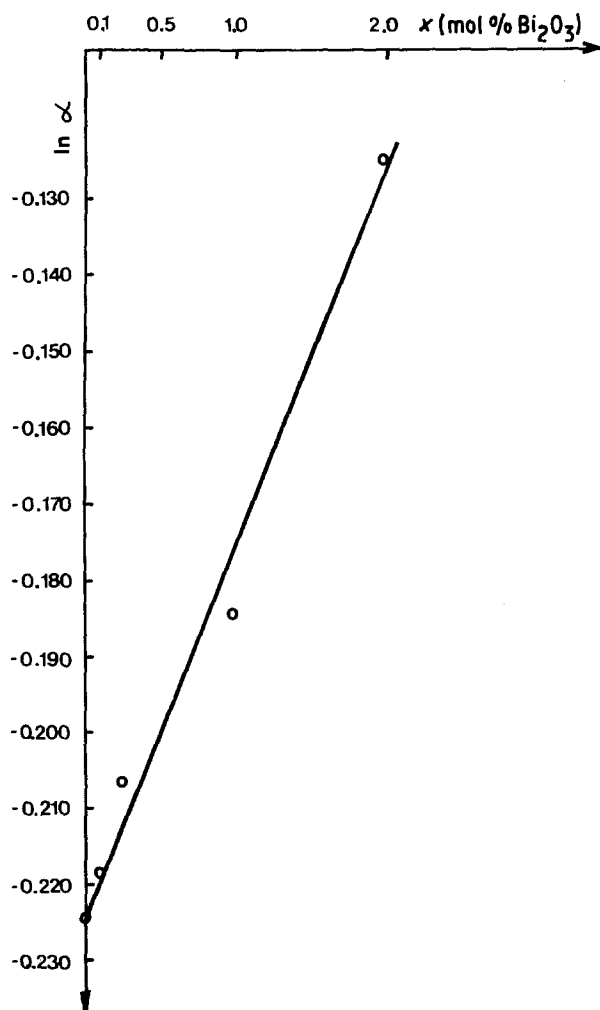


Figure 2 Degree of densification of CdO as a function of Bi<sub>2</sub>O<sub>3</sub> content.

TABLE III Lattice parameters of CdO

mol %	$a_0$ (nm)	
	In (in CdO)	Bi (in CdO)
0.1	0.46948	0.46963
0.5	0.46954	0.46983
1.0	0.46958	0.47010
2.0	0.46959	0.47065

varying linearly with the cube root of the Li<sup>+</sup> concentration, as also does [2]  $a_{\text{CdO}}$  with the cube root of In<sup>3+</sup> concentration.

It is interesting to compare the values of lattice parameters of CdO samples containing In<sup>3+</sup> [1] with Bi<sup>2+</sup> ions (Table III).

The most obvious point to note is that Bi<sup>3+</sup> ions have a greater effect than In<sup>3+</sup> ions on the CdO lattice on account of their larger ionic radius (0.116 compared to 0.081 nm).

One also needs to propose a substitution scheme which takes into account the differing changes on the guest (Bi<sup>3+</sup>) and host (Cd<sup>2+</sup>) ions. If the substitution of Cd<sup>2+</sup> by Bi<sup>3+</sup> is charge-compensated by an equal change of Cd<sup>2+</sup> to Cd<sup>+</sup>, the lattice parameter will expand due to the larger radius of ions with smaller charge: this is in addition to the effect of the increased ionic radius of Bi<sup>3+</sup> (0.099 nm) compared to Cd<sup>2+</sup> (0.078 nm) (Fig. 3).

Bearing all these points in mind, it would now seem reasonable to believe that the positive effect of Bi<sup>3+</sup> on CdO sintering is a consequence of the non-equilibrium state of the CdO lattice containing Bi<sup>3+</sup>.

### Conclusions

The influence of Bi<sub>2</sub>O<sub>3</sub> (0.1 to 2 mol %) on lattice parameters and sintering (850°C in air) of CdO has been investigated. This established that Bi<sup>3+</sup> ions are incorporated into the CdO lattice thus increasing its lattice ( $a$ ) parameter in direct proportion to the concentration of added Bi<sub>2</sub>O<sub>3</sub>.

### Acknowledgements

The authors would like to thank the Bismuth Institute for providing them with the Bi<sub>2</sub>O<sub>3</sub> powder and thus enabling the experimental work to be carried out.

This paper was performed within the framework of the scientific programme that was financially supported by the Serbian Academy of the Science and Art

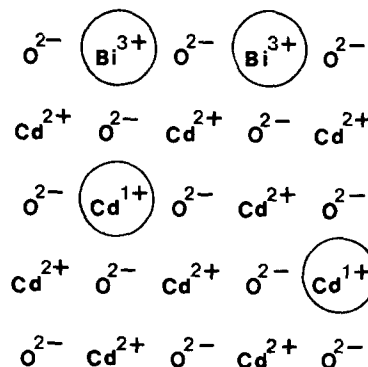


Figure 3 Incorporation of Bi<sub>2</sub>O<sub>3</sub> in CdO.

(Belgrade, Yugoslavia) and the Republic Committee of Science.

### References

1. V. A. KUTVICKII, A. V. KOSOV, V. M. SKORIKOV and T. I. KORYAGINA, *Neorg. Materialy* **11** (1975) 2119 (in Russian).

2. A. CIMINO and M. MAREZIO, *J. Chem. Chem. Solids* **17** (1960) 57.
3. L. D. BROWNLEE and E. W. J. MITCHELL, *Proc. Phys. Soc.* **65** (1952) 710.

*Received 18 July 1985  
and accepted 11 February 1986*