EPR AND X-RAY ANALYSIS OF THE VARIATION OF ZnO-Bi_2O_3 SYSTEM ($ZnO \geqslant 95$ mol%, $Bi_2O_3 \leqslant 5$ mol%) STRUCTURAL PARAMETERS

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Abstract

The efect of ZnO on the phase transformation of polimorfic Bi_2O_3 in the ($ZnO \geqslant 95$ mol%, $Bi_2O_3 \leqslant 5$ mol%) system was studied. The ZnO-Bi_2O_3 specimens were sintered at 973 to 1173 K for 120 minutes. The X-ray diffractograms indicate the presence of a phase γ-Bi_2O_3, ZnO and identified a new phase — the $6 \cdot Bi_2O_3 \cdot ZnO$. Two kinds of signals: I at $g = 1957$ and $\Delta H = 10$ Gs and II ar $g = 2002$ and $\Delta H = 10$ Gs may observed for the system by EPR.

EXPERIMENTAL

The ZnO-Bi_2O_3 specimens were made from ZnO („Herman Starch") and Bi_2O_3 („Bismut Institute") 99,999% pure powder. The zinc oxide and bismuth oxide powder mixtures studied are given in Table I.

Table I. The examined ZnO and Bi_2O_3 powder mixtures

Semple designation	ZnO Bi_2O_3 (%)
ZB – 9505	95 : 05
ZB – 9802	98 : 02
ZB – 9901	99 : 01

The obtained mixtures were subjected to a pressure of 2MP and sintered in a resistere oven at 973 – 1173 K in air for 120 minutes. The ZnO-Bi_2O_3 specimens were

analysed using a „Philips PW 1051" powder diffractometer under Cu anticathode illumination and with a graphite monochromator. The X-ray tube voltage was V = 45 kV, the curent I = 25 A, the goniometer speed $v_g = 1^\circ$ 20/min and time constant $R_c = 2$ sec.

The diffraction maxima were measured peak to peak and the angles were reduced to the interplane distance d. The ratio of the intensities and d were used to identify the phases present in the system [1]. The observed X-ray diffractogram for the ZB – 9505 specimen is shown in Fig. 1.

The phases observed by X-ray structural analysis methods for the ZnO-Bi_2O_3 system specimens are presented in Table II.

Table II. Observed sintered ZnO-Bi_2O_3 phases sintering

Sample	temperature	Bi_2O_3	ZnO	compound
ZB – 9505	973	+	+	–
ZB – 9802	973	–	+	–
ZB – 9801	973	–	+	–
ZB – 9505	1023	+	+	–
ZB – 9802	1023	–	+	–
ZB – 9901	1023	–	+	–
ZB – 9505	1073	+	+	–
ZB – 9302	1073	–	+	–
ZB – 9801	1073	–	+	–
ZB – 9505	1173	+	+	+
ZB – 9802	1173	–	+	–
ZB – 9901	1173	–	+	–

The ZB – 9505, ZB – 9802 and ZB – 9901 sintered specimens were characterized by EPR on a „R 1306 Radiospectrometer" at the liquid nitrogen point. The two EPR signal types observed (I g = 1973, H = 10 Gs and II g = 2002, H = 10 Gs) my be explained in terms of two kinds of paramagnetic centers.

RESULT AND DISCUSSION

The detailed analysis of the observed X-ray spectra [2] of ≤ 5 mol% Bi_2O_3 specimens sintered at 1023, 1073 and 1173 K conducted in accordance with [3, 4] indicates with certainly the presence of 2n0, $\gamma - Bi_2O_3$ and a phase with lattice parameters akin to $6 \cdot Bi_2O_3 \cdot$ ZnO parameters Fig. 1. The X-ray structura analyses of the ZB – 9901, ZB – 9802 and ZB – 9505 specimens (Tab. II and Tab. III) indicate a crystal lattice contraction upon sintering for the first of the three specime and expansion in the latter two.

Table III. X-ray analysis of semples sintered at 1173 K, 120 min.

Sample	lattice	parameter	Bi_2O_3
Pure ZnO	a = 3,24966	c = 5,2053	–
ZB – 9901	a = 3,24846	c = 5,20436	–
ZB – 9802	a = 3,24933	c = 5,20665	–
ZB – 9505	a = 3,2498	c = 5,20445	+

The introduction of bismuth ions into the ZnO lattice may in principle be explained by the fact that Bi_2O_3 exchibits a significant decomposition pressure at higher temperatures. That is conductive to the introduction.

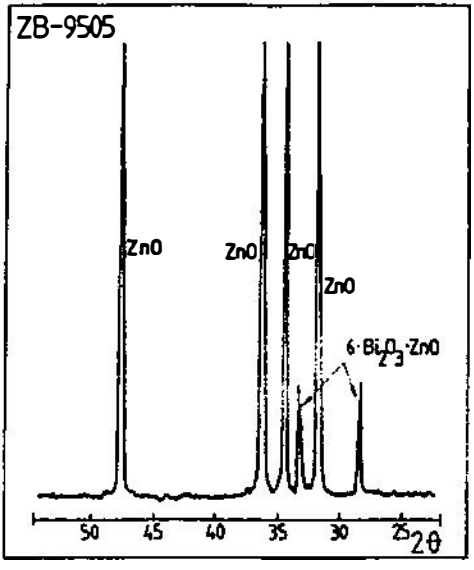

Fig. 1. X-ray diffraction specctra for the ZnO Bi_2O_3 system sintered at 1173 K

We are of the apinion that lattice contraction and the subsequent ZnO expansion may be explained in terms of the conclusions of E. Cimino and E. Morezio |5| who studied the effect of ions of different valence on sintered CdO. The two bismuth ions oxidation number 3^+ and 5^+ alow us to consider the introduction into the ZnO lattice the ion radii of all the ions partaking in the process are given in Table IV.

If we refer to Tab. IV, we may conclude that the Bi^{5+} ion upon their introduction into the ZnO lattice lead to its contraction at 1 mol% Bi_2O_3. When a Bi^{3+} ion is introduced into the ZnO lattice expansion ensures, as evidenced by the ZB – 9802 and ZB – 9505 specimens. It should be noted that our results agre with |6|, investigation bring conducted in the temperature range within wich the ZnO lattice expandi but no evaporation takes place. EPR analysis of the ZB – 9901, ZB – 9802 and ZB – 9505 specimens, as has already been mentioned, yields two types signals for $g_{||}$ = 2002 and $g_{|}$ = 1957. The I and ΔH us Bi_2O_3 concentration curves are given in Fig. 2. The $g_{||}$ = = 2002 signal is similar to the signals observed at ZnO |6| alloying and are due to the donor center formation. The analysis of the $g_{|}$ and $g_{||}$ signals, their variation and intensity indicates that the maximum concentration does not exceed 10^{17} cm^3. The significant variation of I and ΔH may be observed in the spectra of the ZB – 9505 samples sintered at 1073 and 1173 (Fig. 2.). This may be explained by the formation of $Zn^{2+} - Bi^{3+}$ type centers.

Table IV – Bismuth and Zinc radii

ion	Radius (μm)
Bi^{3+}	1,03
Bi^{5+}	0,70
Zn^{2+}	0,74

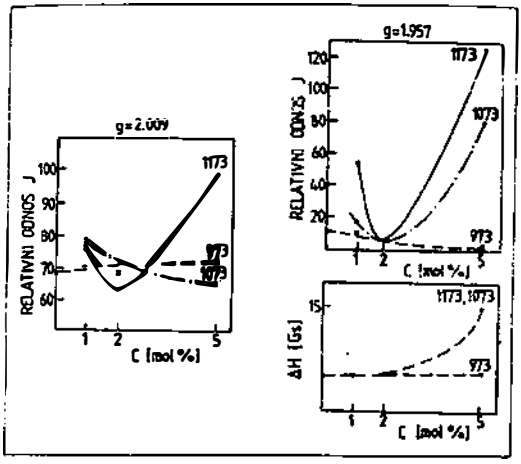

Fig. 2. EPR Parameters of ZnO-Bi_2O_3 specimens as a function of mol% Bi_2O_3 (c mol%)

CONCLUSIONS

X-ray analysis indicates that bismuth ions are introduced into the ZnO lattice at Bi_2O_3 concentrations of 1 and 2 mol%. At 1 mol% Bi_2O_3 the ZnO lattice contracts during sintering while for 2 mol% Bi_2O_3 it expands. At 5 mol% Bi_2O_3, in addition to the solid solution a phase identified as 6 Bi_2O_3 ZnO appears at the ZnO/Bi_2O_3 interface.

The EPR measurements are in agreement with above, as they yield signals at $g_{\perp}$ = 1957 and $g_{\parallel}$ = 2002 that indicate $Zn^{2+} - Bi^{3+}$ type paramagnetic centers and formed.

REFERENCES

1. G. Stanišić, I. Krstanović, M. M. Ristić, Science of Ceramics, **12** (1984) 209.
2. G. Stanišić, Dr thesis, CMS Belgrade university, Belgrad 1985.
3. G. Stanišić, Science of Sintering, **16** No. 2 (1984) 121.
4. J. Wong, J. Amer. Ceram. Soc., **57** (1974) 357.
5. A. Cimino, M. Marezio, J. Phys. Chem. Solids, **17** (1969) 57.
6. J. Krstanović, A. Radaković, M. M. Ristić, The Chemistry of Materials (in press).