

## On the possible formation of Aurivillius phases in the oxide system $\text{Bi}_2\text{O}_3\text{--ZnO--Nb}_2\text{O}_5$

IULIAN RUSU<sup>1\*</sup>, MIHAIL-LIVIU CRAUS<sup>2</sup>, DANIEL SUTIMAN<sup>1</sup> and ALICE RUSU<sup>1</sup>

<sup>1</sup>Technical University “Gh. Asachi”, Faculty of Industrial Chemistry, Bd. D. Mangeron 71, Iasi 6600 and

<sup>2</sup>National Institute for Technical Physics, Bd. D. Mangeron 47, Iasi 6600, Romania  
(e-mail: rusu\_iulian@hotmail.com)

(Received 7 March, revised 8 August 2003)

*Abstract:* This paper presents results concerning the possible synthesis of double perovskite and Aurivillius phases in the BZN system. A crystal chemical criterion based on an elastic model for the structure was used in order to determine if the formation of layered bismuth compounds is favoured in the above system. The temperature seems to be the decisive factor influencing Aurivillius phase formation.

*Keywords:* synthesis, phase transition, thermal analysis, XRD.

### INTRODUCTION

The oxide system  $\text{Bi}_2\text{O}_3\text{--ZnO--Nb}_2\text{O}_5$  (BZN) has received special attention from researchers in the last decade due to the high dielectric constant, high Q and controllable temperature coefficient of the capacitance that make it very appealing for the manufacture of high frequency multilayer devices.<sup>1–7</sup> The compounds from the BZN system have been observed to form pyrochlore structures in most cases over a large range of variable compositions.<sup>2,8</sup>

On the other hand, for  $\text{Bi}_2\text{O}_3\text{--AO--Nb}_2\text{O}_5$  oxide systems, where A is a divalent metallic cation, the formation of both double perovskites  $\text{A}_2\text{BiNbO}_6$ <sup>9</sup> and Aurivillius phases  $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{Nb}_n\text{O}_{3n+1})$ ,<sup>10–13</sup> with possible applications in high temperature superconductivity, has been reported. The aim of the present work was to evaluate the possibility of the formation of these phases in the BZN system and of the synthesis conditions where appropriate.

### EXPERIMENTAL

The following high purity materials were used as reagents for the solid-state synthesis:  $\text{Nb}_2\text{O}_5$ , Zn and Bi. These materials were intimately mixed in the stoichiometric ratio corresponding to the nominal composition  $\text{Zn}_2\text{BiNbO}_6$ , pressed into pellets and submitted to different thermal treatments in air.

\* Corresponding author.

The synthesis was monitored by thermal analysis and XRD. A MOM-Budapest derivatograph, for the concomitant recording of T, TG, DTG and DTA curves, was used. In all cases, the same sample weight (100 mg) and standard substance ( $\text{Al}_2\text{O}_3$ ) were maintained. The analysis were performed in air up to 1000 °C at a heating rate of 10 °C/min.

The evolution of the reactions and the formation of the final products were studied by means of the powder diffraction method, using a DRON-2 diffractometer with  $\text{FeK}\alpha$  radiation. The diffractometer was calibrated using standard samples of silicon dioxide. The data were processed using TREOR and DICVOL software.<sup>14,15</sup>

## RESULTS AND DISCUSSION

Based on the ionic radii<sup>16</sup> and using the hard sphere approximation,<sup>17</sup> the theoretical average lattice parameter for the  $\text{Zn}_2\text{BiNbO}_6$  material were calculated as follows:

$$a_A = 2(R_{\text{Zn}} + R_{\text{O}})/\sqrt{2} \quad (1)$$

$$a_B = R_{\text{Bi}} + R_{\text{Nb}} + 2R_{\text{O}} \quad (2)$$

$$a_{\text{calc}} = (a_A + a_B)/2 \quad (3)$$

where  $R$  are the ionic radii of each ion involved in the structure,  $a_A$  and  $a_B$  are the calculated lattice parameters based on A (*i.e.*,  $\text{Zn}^{2+}$ ) and B (*i.e.*,  $\text{Bi}^{3+}$  and  $\text{Nb}^{5+}$ ) cations, and  $a_{\text{calc}}$  is the average calculated lattice parameter. Accordingly, the expected value of the pseudo-cubic lattice parameter for the above material would be 7.49 Å.

The use of metallic zinc and bismuth as reaction precursors was preferred in order to obtain *in situ* the corresponding oxides and implicitly a higher reactivity on their part. The thermogravimetric data for the reagents and for a reaction intermediary are presented in Table I.

According to the thermogravimetric results, it was decided to perform a pre-sinterisation of the reaction mixture for eight hours at 800 °C. The temperature was chosen in order to avoid both the possible reduction of niobium and the volatilisation of bismuth, being known that some non-volatile bismuth niobates are formed in the temperature range 600–900 °C.<sup>19</sup> On the other hand, the exothermic effect of zinc oxidation disappeared from the DTA curve of the reaction mixture indicating a possible incorporation of a mixed oxide in the lattice.

The pre-sintered sample had a multiphase structure and was analysed again by means of thermal analysis in order to determine its stability at higher temperatures. As shown in Table I, the recording did not indicate any weight changes or thermal effects up to 1000 °C. Consequently, the sample was ground, pressed again and submitted to a new thermal treatment for nine hours at 1000 °C.

The as processed sample continued to have a macroscopic multiphase structure a fact confirmed by XRD, the most important secondary phases being ZnO (PDF 75-0576)<sup>20</sup> and  $\text{Bi}_{1.7}\text{Nb}_{0.3}\text{O}_{3.3}$  (PDF 33-0210)<sup>20</sup> (see Fig. 1). The main phase has a tetragonal distorted pyrochlore structure with the unit cell parameters  $a = b = 10.48$  Å

TABLE I. Thermogravimetric data for the reagents and intermediates

| No. | Substance                                     | Weight variation/% |              | Temperature field / °C | Observations  |
|-----|---|--------------------|--------------|------------------------|---|
|     |   | Calc.              | Found        |                        |   |
| 1.  | Nb <sub>2</sub> O <sub>5</sub>                | –                  | –2           | 840–1000               | The partial reduction to NbO <sub>2</sub> occurs <sup>18</sup>  |
| 2.  | Bi  | +11.48             | +11.5/850 °C | 690–720                | In the temperature range 247–270 °C, an endothermic effect due to the bismuth melting is noticed. The weight increase is due to the formation of Bi <sub>2</sub> O <sub>3</sub> , a fact that is also evidenced by a corresponding exothermic effect. At temperatures over 850 °C, a part of the resulting oxide volatilises. |
| 3.  | Zn  | +24.48             | +23.53       | 425–665                | In the temperature range 386–416 °C, an endothermic effect due to the zinc melting is noticed. The weight increase is due to the formation of ZnO a fact that is also evidenced by a corresponding exothermic effect.   |
| 4.  | 2Zn + Bi + 1/2 Nb <sub>2</sub> O <sub>5</sub> | +11.85             | +10          | 670–692                | The endothermic effects of bismuth (240–260 °C) and zinc melting (383–405 °C) were observed. The exothermic effect of bismuth oxidation remains but not that of zinc oxidation  |
| 5.  | Presented sample 8 h/800 °C                   | –                  | –            | –                      | There are no weight changes or thermal effects.   |

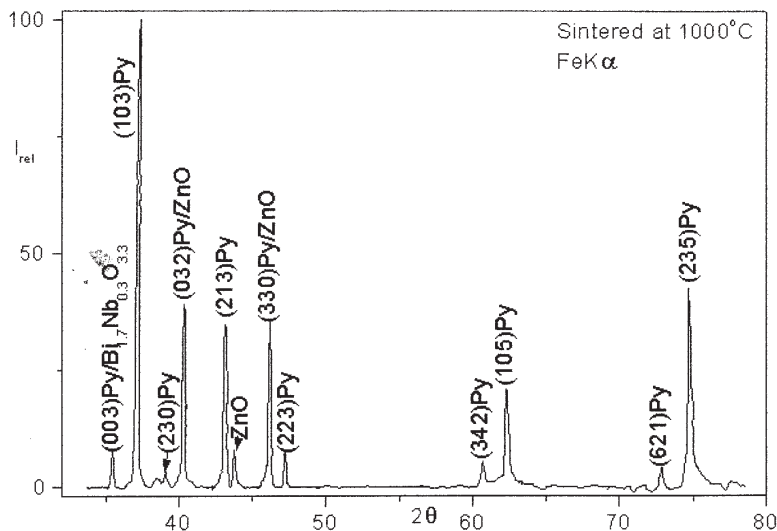


Fig. 1. XRD Spectrum of the sample sintered at 1000 °C, Py – pyrochlore phase.

and  $c = 9.524 \text{ \AA}$  (merit Figure =  $13^{21}$ ). Some of the lines of the main phase and secondary phases are superimposed.

Therefore, the sample was ground again, pressed and heated for two hours at 1200 °C. The structure of the sample after cooling indicated that it had melted during the processing but that the weight loss was only 0.1 %. The diffraction spectrum revealed the presence of a small quantity of  $\text{BiNbO}_4$  (PDF 82-0348)<sup>20</sup> (see Fig. 2). The three main lines of ZnO were also present but their relative intensities are not in agreement with the corresponding JCPDF file (75-0576). This suggests the overlapping of the first two lines with the lines of the main phase. No other secondary phases were identified in the spectrum.

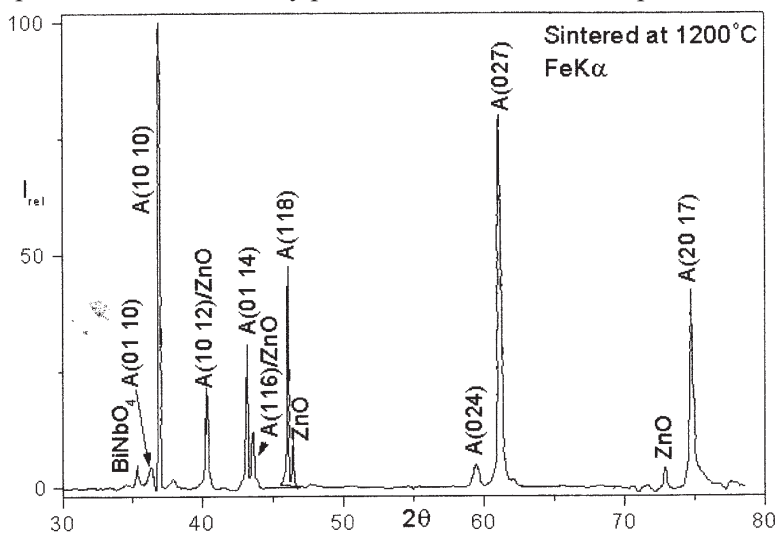


Fig. 2. XRD Spectrum of the sample sintered at 1200 °C, A – Aurivillius phase.

Attempts to index the diffraction lines of the obtained compound in a pyrochlore or a double perovskite structure (cubic or pseudo-cubic with  $a \approx 7.5$  Å) failed. The indexing with the best fit value (8.3)<sup>21</sup> corresponds to an orthorhombic unit cell with  $a = 3.813$  Å,  $b = 3.934$  Å and  $c = 49.485$  Å. These dimensions are in good agreement with those of an Aurivillius type compound with  $n = 5$  (i.e., Zn<sub>4</sub>Bi<sub>2</sub>Nb<sub>5</sub>O<sub>18</sub>).<sup>22</sup>

Dispite the fact that this result is quite unexpected, a possible confirmation can be found in the literature. Namely, Jeanne and co-workers<sup>8</sup> evidenced in the system Bi<sub>2</sub>O<sub>3</sub>-ZnO-M<sub>2</sub>O<sub>5</sub> (M = Nb, Ta) the formation of a phase over 1000 °C that cannot be indexed as a simple pyrochlore structure. In addition, our previous studies on the system Bi<sub>2</sub>O<sub>3</sub>-CdO-M<sub>2</sub>O<sub>5</sub> indicated the transition from pyrochlore to Aurivillius structures during the synthesis.<sup>10-13</sup>

Kikuchi developed a relation between the stability of Aurivillius type compounds and the structural mismatch in order to understand the criteria favourable for the formation of these compounds.<sup>23</sup> The study, performed on a large number of compounds, revealed that the formation of Aurivillius phases was restricted not by the size of the estimated lattice parameters but by the  $\Delta V$ -values (see Eq. (4)). According to this, the  $\Delta V$ -values of real compounds were almost all in the range smaller than 0.4 Å<sup>3</sup>.

$$\Delta V = V_{B'} [1 - (a/a_{B'})^2]^2 + nKa_p^3 [1 - (a/a_p')^2]^2 \quad (4)$$

$$a_p' = 1.33 R_{Nb} + 0.6 R_{Zn} + 2.36 \quad (5)$$

$$a = (a_{\text{orth}} + b_{\text{orth}})/2 \quad (6)$$

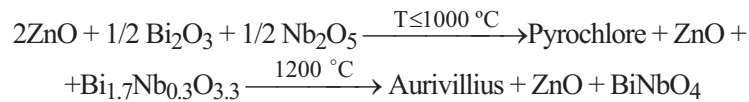
$$K = - [1 - (a/a_{B'})^2] / n [1 - (a/a_p')^2] \quad (7)$$

where  $n = 5$  (the number of perovskite layers),  $a_{B'}$  is the lattice parameter of the unconstrained Bi<sub>2</sub>O<sub>2</sub> sub-cell (3.78 Å),<sup>24</sup>  $a_p'$  is the lattice parameter of the unconstrained perovskite sub-cell (4.02 Å see Eq. (5)),  $a$  is the lattice parameter of the pseudo-tetragonal cell (3.87 Å see Eq. (6)),  $V_{B'}$  is the volume of the unconstrained Bi<sub>2</sub>O<sub>2</sub> unit (65.4 Å<sup>3</sup>).<sup>22</sup>

Performing the same calculation (see Eqs. (4-7)) for the assumed Aurivillius compound, a  $\Delta V$  value of 0.39 Å<sup>3</sup> was obtained which suggests the possibility of the existence of such a phase.

#### CONCLUSIONS

The evolution of the process may be described simply by the following scheme:



The precursors and synthesis conditions up to 1000 °C do not change dramatically the evolution of the system to the pyrochlore structure. In the temperature range 1000 –

1200 °C, a phase transition from pyrochlore to Aurivillius occurs with the congruent melting of the material. The double perovskite structure is not likely to be formed. Further studies must to be performed in order to obtain full confirmation of the formation of an Aurivillius phase in the BZN system.

## ИЗВОД

О МОГУЋНОСТИ СТВАРАЊА AURIVILLIUS-ОВИХ ФАЗА У ОКСИДНОМ СИСТЕМУ  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_3$ IULIAN RUSU<sup>1</sup>, MIHAIL-LIVIU CRAUS<sup>2</sup>, DANIEL SUTIMAN<sup>1</sup> and ALICE RUSU<sup>1</sup>

<sup>1</sup>Technical University "Gh. Asachi", Faculty of Industrial Chemistry, Bd. D. Mangeron 71, Iasi 6600 and <sup>2</sup>National Institute for Technical Physics, Bd. D. Mangeron 47, Iasi 6600, Romania

У раду се приказују резултати који се односе на могућност синтезе двоструких перовскита Aurivillius-ових фаза у систему BZN. Критеријум заснован на еластичном моделу структуре коришћен је при оцени да ли је фаворизовано стварање слојевитог једињења бизмута у посматраном систему. Изгледа да је температура одлучујући фактор при стварању Aurivillius-ове фазе.

(Примљено 7. марта, ревидирано 8. августа 2003)

## REFERENCES

1. H. C. Ling, M. F. Yan, W. W. Rhodes, *J. Mater. Res.* **5** (1990) 1752
2. D. Liu, Y. Liu, S. Q. Huang, X. Yao, *J. Am. Ceram. Soc.* **76** (1993) 2129
3. M. F. Fang, H. C. Ling, *Mater. Chem. Phys.* **44** (1996) 37
4. D. P. Cann, C. A. Randall, T. R. Shrout, *Solid State Commun.* **100** (1996) 529
5. X. Wang, H. Wang, X. Yao, *J. Am. Ceram. Soc.* **80** (1997) 2745
6. J. C. Nino, M. T. Lanagan, C. A. Randall, *J. Appl. Phys.* **89** (2001) 4512
7. Y. Hu, C. L. Huang, *Mater. Chem. Phys.* **72** (2001) 60
8. G. Jeanne, G. Desgardin, B. Raveau, *Mat. Res. Bull.* **9** (1974) 1321
9. H. Brusset, H. Gillier-Pandraud, P. Rajaonera, *Mat. Res. Bull.* **10** (1975) 209
10. I. Rusu, M. L. Craus, I. Rosca, E. Condiffe, M. J. Smith, D. Sutiman, M. Palamaru, A. Cailean, N. Apostolescu, *Proc. ISE 10*, IEEE, Piscataway, 1999, p. 325
11. I. Rusu, M. L. Craus, *Bull. IPI Chem. & Chem. Eng.* **3/4** (2000) 17
12. M. L. Craus, I. Rusu, A. Rusu, N. Apostolescu, *J. Phys. IV* **90** (2001) 109
13. M. L. Craus, I. Rusu, A. Rusu, *Proc. JEEP XXVII*, R. M. Marin-Ayral & M.C. Record, Eds., Montpellier, 2001, p. 103
14. P. E. Werner, *Z. Krist.* **120** (1964) 375
15. A. Boulitf, D. Louer, *J. Appl. Cryst.* **24** (1991) 987
16. R. D. Shannon, C. T. Prewitt, *Acta Cryst.* **B25** (1969) 925
17. C. D. Brandle, V. J. Fratello, *J. Mater. Res.* **5** (1990) 2160
18. *Nouveau Traite de Chimie Minerale*, P. Pascal, Ed., Masson et C<sup>ie</sup>, Paris, 1958, p. 449
19. V. G. Osipian, S. A. Igaune, I. A. Vitinia, E. J. Freidenfeld, *Zh. Neorg. Khim.* **27** (1982) 299
20. PCPDFWIN Version 2.0, JCPDS-ICDD, August 1998
21. P. M. De Wolff, *J. Appl. Cryst.* **1** (1968) 108
22. B. Aurivillius, P. H. Phang, *Phys. Rev.* **126** (1962) 893
23. T. Kikuchi, *Mat. Res. Bull.* **14** (1979) 1561
24. R. A. Armstrong, R. E. Newnham, *Mat. Res. Bull.* **7** (1972) 1025.