Available online at www.sciencedirect.com

Thermochimica Acta 428 (2005) 51–55

thermochimica acta

www.elsevier.com/locate/tca

Phase relations in the system $ZnO–BiVO_4$: the synthesis and properties of $BiZn_2VO_6$

M. Bosacka[*], M. Kurzawa, I. Rychlowska-Himmel, I. Szkoda

Department of Inorganic and Analytical Chemistry, Technical University of Szczecin, al. Piastow 42, 71-065 Szczecin, Poland

Received 12 July 2004; received in revised form 10 September 2004; accepted 27 September 2004

Abstract

As a result of solid-state reactions between ZnO and $BiVO_4$, mixed at a molar ratio of 2:1, or among ZnO, V_2O_5 and Bi_2O_3, mixed at a molar ratio of 4:1:1, a new double vanadate $BiZn_2VO_6$ has been obtained. Its crystallographic system was determined, its unit cell parameters were calculated and its incongruent melting temperature was established. The phase equilibria being established in the system $ZnO–BiVO_4$ over the whole components concentration range up to 1273 K were described.

Keywords: Double vanadate; Bismuth(III) zinc vanadate; Phase equilibria; X-ray diffraction; Thermal analysis

1. Introduction

Oxo salts of bismuth(III) exhibit interesting properties as ionic conductors, yellow pigments and catalysts for selective oxidation of propene and butene [1–3]. These compounds are also interesting with respect to their ferroelectric and ferroelastic properties [4].

It is known from literature review that bismuth forms with divalent and pentavalent elements a great family of compounds with their general formula BiA_2MO_6, where A is the divalent cation, and M the pentavalent cation. This family comprises: arsenates (A = Ca, Cd, Cu, Mg, Mn, Pb) [5–7], phosphates (A = Ca, Cd, Cu, Mg, Mn, Pb, Zn) [5,7,8] and vanadates (A = Ca, Cd, Cu, Mg, Mn, Pb) [4,5,9–12]. Almost all the above-mentioned compounds were obtained in the atmosphere of air, only the syntheses of $BiMn_2MO_6$ (M = As, P, V) were conducted in an inert atmosphere [5].

Majority of those compounds are isostructural, crystallize in the orthorhombic system, $Z = 4$, space group *Pmna* [5,6,8,11,14], *Cmcm* [7–9], *Cmc2₁* [4], *P2₁/n* [10,13], *Amma* [11] or *Pnma* [15], and their structures are described in the works [4–8,10,13–15]. These structures contain the chains BiO_2^{-}, the tetrahedra MO_4^{3-} and the cations A^{2+}, resulting in the structural formula $A_2[BiO_2][MO_4]$ [5,6]. Main differences in the structure details of the individual compounds consist in a variable orientation of the tetrahedra MO_4 and in a different coordination of the cations M^{2+} that varies with an increase of ionic radius of the cation assuming the values from 5 to 7 [10].

The aim of this work was determining the phase relations in the system $ZnO–BiVO_4$ and checking whether a compound belonging to the family BiA_2MO_6 is formed in the investigated system.

The components of the system $ZnO–BiVO_4$ are well known. ZnO crystallizes in the hexagonal system, space group *P6₃mc*. Its unit cell parameters are: $a = b = 0.3250$ nm, $c = 0.5207$ nm [16]. Zinc oxide does not form polymorphic modifications [16].

Bismuth(III) orthovanadate(V) occurs in nature as a mineral named pucherite, crystallizing in the orthorhombic system [17]. This polymorph has never been obtained in laboratory conditions. As a result of the synthesis of this compound, conducted under laboratory conditions at low temperatures, a tetragonal polymorph of $BiVO_4$

---

[*] Corresponding author. Tel.: +48 91 449 45 63; fax: +48 91 449 46 36.
E-mail address: bossm@ps.pl (M. Bosacka).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.09.025

is obtained, possessing a zircon-type structure [18,19]. This polymorphic modification of $BiVO_4$ undergoes at 623–723 K an irreversible transformation to a monoclinic polymorph with a fergusonite-type structure [18,19]. The monoclinic modification is also obtained by conducting the synthesis at temperatures above 873 K [20]. At 528 K a reversible second-kind transformation of monoclinic $BiVO_4$ to the tetragonal sheelite-type form occurs [18,19]. $BiVO_4$ melts congruently at 1213 K [18].

2. Experimental

The reagents used for the syntheses were: ZnO (a.p., Ubichem, UK), V_2O_5 (a.p., Riedel-de Haën, Germany) and Bi_2O_3 (a.p., POCh, Gliwice, Poland), as well as $BiVO_4$ obtained as a result of heating an equimolar mixture of V_2O_5 and Bi_2O_3 in the cycles: 873 K (24 h) + 923 K (24 h) + 973 K (24 h).

For the research on the phase relations being established in the system ZnO–$BiVO_4$ 12 samples were prepared from $BiVO_4$ and ZnO. The reacting substances were weighed in appropriate portions, homogenised by grinding and next pressed into pellets and heated in a resistance furnace. After each heating cycle the pellets were ground and subject to XRD and DTA investigations. All samples were heated in three 12 h cycles at the temperatures of: 873, 923 and 973 K.

The kind of phases occurring in the individual samples was determined by XRD. The powder diffraction patterns were obtained with the use of an X-ray diffractometer of the Philips type (X′Pert PRO) applying the radiation Co Kα and the filter Fe. The identification of individual phases was conducted on the base of X-ray diffraction characteristics contained in the PDF cards [21].

In order to determine the kind of phases co-existing with liquid, some selected samples were additionally heated at temperatures above the solidus line, i.e. 1053, 1093, 1113, 1123 and 1143 K for 2 h. These samples were rapidly cooled to ambient temperature and their composition was determined by XRD.

The DTA investigations were carried out by means of a derivatograph of F. Paulik–J. Paulik–L. Erdey type (MOM, Budapest, Hungary). All measurements were conducted in the atmosphere of air, in the temperature range 293–1273 K at a heating rate of 10 K/min. The samples subjected to the measurements weighed 1000 mg and were placed in quartz crucibles.

The unit cell parameters of the obtained compound were calculated by using the program POWDER [22] belonging to the crystallographic programs package X-Ray System 70. Exact positions of the diffraction lines were determined by the internal standard method. The internal standard used was KCl (space group *Fm3m*, $a = 0.6293$ nm).

The density of the compound was determined by the method described in the work [23].

3. Results and discussion

The work was begun with an attempt to synthesize the compound $BiZn_2VO_6$. For this purpose a sample was prepared at the composition 33.33 mol% $BiVO_4$ and 66.67 mol% ZnO, that was heated in three stages: 873 K (24 h) + 923 K (24 h) + 973 K (24 h). In the powder diffraction pattern of this sample, recorded after the last heating stage, no lines were identified characteristic for any known phases belonging to the ternary system ZnO–Bi_2O_3–V_2O_5. This diffractogram did not show either any similarity to the diffractograms of other BiA_2MO_6-type phases, where A = divalent cation, M = pentavalent cation, described in literature [4,5,9–11]. Fig. 1 presents the powder diffraction pattern of the investigated sample and of the initial mixture. We thus concluded that a new compound was obtained with its formula $BiZn_2VO_6$, being formed according to the reaction (1)

$$2ZnO_{(s)} + BiVO_{4(s)} = BiZn_2VO_{6(s)} \tag{1}$$

however this compound is not isostructural with other compounds of the type BiA_2MO_6 described in literature [4,5,9–11].

In other attempt to obtain $BiZn_2VO_6$ the reactants were ZnO, Bi_2O_3 and V_2O_5 mixed at a molar ratio of 4:1:1. This mixture was heated analogously to the mixture of ZnO with $BiVO_4$. The diffractogram recorded after the last heating stage of this mixture revealed a set of diffraction lines with both their positions and intensities being identical with those recorded in the diffractogram of $BiZn_2VO_6$ obtained from $BiVO_4$ and ZnO (reaction 1). It was concluded that $BiZn_2VO_6$ can also be obtained as a result of a reaction occurring in accordance with the equation:

$$4ZnO_{(s)} + Bi_2O_{3(s)} + V_2O_{5(s)} = 2BiZn_2VO_{6(s)} \tag{2}$$

$BiZn_2VO_6$ is yellow and melts incongruently at 1078 K with a separation of solid ZnO. The DTA curve of $BiZn_2VO_6$ is presented in Fig. 2.

The powder diffraction pattern of the obtained $BiZn_2VO_6$ was indexed and the received results are presented in Table 1. The triclinic unit cell parameters of $BiZn_2VO_6$ are the following: $a = 0.6879(5)$ nm, $b = 0.5725(3)$ nm, $c = 0.8903(3)$ nm, $\alpha = 91.0°$, $\beta = 130.1°$, $\gamma = 99.5°$, $Z = 2$. The X-ray calculated

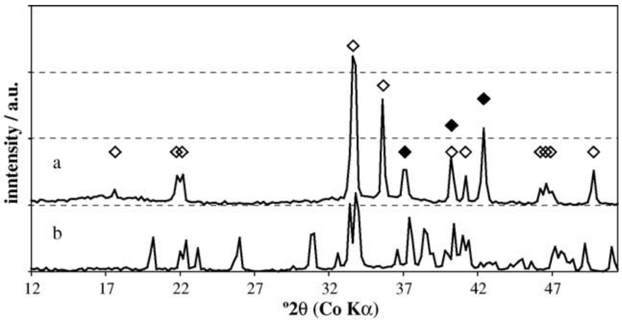

Fig. 1. Powder diffraction patterns of: (a) ZnO + $BiVO_4$ mixture and (b) Zn_2BiVO_6, where (◊) ZnO (PDF: 36-1451), (♦) $BiVO_4$ (PDF: 14-688).

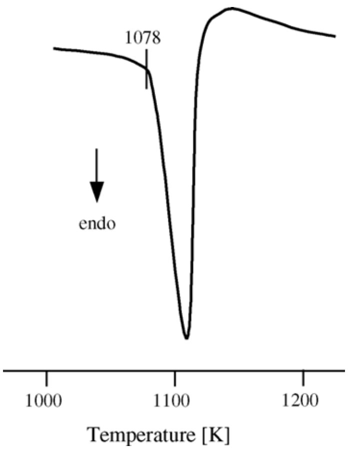

Fig. 2. DTA curve of Zn_2BiVO_6.

density amounts to $d_{\mathrm{rtg}} = 6.20\,\mathrm{g/cm^3}$ and the pycnometric density $d = 6.10 \pm 0.05\,\mathrm{g/cm^3}$.

Further investigations were aimed at establishing the phase equilibria over the whole components concentration range of the system $BiVO_4$–ZnO. Table 2 presents the composition of the samples prepared for research and the phases detected in individual samples after the last heating stage.

The research results prove that ZnO and $BiVO_4$ are not inert towards each other in the solid state. In the concentration range up to 33.33 mol% $BiVO_4$ the phases remaining at equilibrium are Zn_2BiVO_6 and ZnO, while at the content of $BiVO_4$ equal to 33.33 mol% the components of the system react with each other (according to the reaction 1) forming a new compound which formula is Zn_2BiVO_6; and in the concentration range of $BiVO_4$ above 33.33 mol% the phases remaining at equilibrium are Zn_2BiVO_6 and $BiVO_4$.

Fig. 3 presents the DTA curves of selected samples belonging to the investigated system and having attained an equilibrium state.

In the DTA curves of equilibrium samples containing in their initial mixtures up to 33.33 mol% $BiVO_4$ one endothermic effect was recorded, caused by melting Zn_2BiVO_6 at 1078 ± 5 K (Fig. 3a). The DTA curves of the samples with $BiVO_4$ concentration from 35.00 to 60.00 mol% contained two endothermic effects with their onset temperatures amounting to 1033 ± 5 and 1078 ± 5 K, respectively (Fig. 3b). The first of these effects, recorded also in DTA curves of samples containing in their initial mixtures 60.00 or more mol% $BiVO_4$, was assumed to be an effect associated with melting of the eutectic mixture of Zn_2BiVO_6 and $BiVO_4$. This effect occurred as the only one in the DTA curve of the sample containing 60.00 mol% $BiVO_4$ and its intensity was the biggest (Fig. 3c), hence the composition of the eutectic mixture was determined to be: ∼33 mol% Zn_2BiVO_4 and ∼67 mol% $BiVO_4$. The other effect recorded in the DTA curves of these samples is due to melting Zn_2BiVO_6. In DTA curves of samples containing in their initial mixtures above 60.00 mol% $BiVO_4$ two effects were also recorded (Fig. 3d), where the first one with its onset temperature equal to 1033 ± 5 K was considered to be due to melting of the eutectic mixture of Zn_2BiVO_6 and $BiVO_4$, while the other one with its temperatures varying from 1123 to 1183 K was assumed to be due to melting the mixture $BiVO_{4(s)}$ + liquid.

On the base of the data presented in Table 2, the DTA curves of equilibrium samples (Fig. 3) as well as the results of XRD analysis of samples heated additionally at temperatures above the solidus line and next "frozen", a diagram of phase equilibria has been worked out for the system ZnO–$BiVO_4$ over the whole components concentration range (Fig. 4). The solid lines were drawn on the base of DTA curves and XRD

Table 1
Results of indexing the powder diffraction pattern of $BiZn_2VO_6$

No.	d_{exp} (nm)	d_{cal} (nm)	*h k l*	I/I_0 (%)
1	0.6714	0.6719	0 0 1	6.6
2	0.5679	0.5569	0 1 0	3.2
3	0.5116	0.5115	$1\ 0\ \underline{0}$	83.4
4	0.4682	0.4681	$0\ \underline{1}\ \underline{1}$	32.6
5	0.4616	0.4614	$1\ 1\ \underline{1}$	57.0
6	0.4451	0.4451	$1\ 0\ \underline{2}$	30.0
7	0.4021	0.4022	1 1 1	32.8
8	0.3976	0.3976	$0\ 1\ \underline{1}$	47.5
9	0.3507	0.3506	$1\ \underline{1}\ \underline{2}$	7.1
10	0.3444	0.3448	1 1 2	4.1
11	0.3358	0.3356	$0\ 0\ \underline{2}$	100
		0.3359	2 0 2	
12	0.3186	0.3184	$1\ 0\ \underline{1}$	21.1
		0.3186	$2\ 0\ \underline{1}$	
13	0.3110	0.3110	$0\ \underline{1}\ 2$	76.3
14	0.3070	0.3070	$1\ \underline{1}\ \underline{1}$	92.5
		0.3072	$2\ 1\ \underline{2}$	
15	0.2851	0.2849	1 0 3	20.9
16	0.2785	0.2784	$0\ 2\ \underline{0}$	83.9
17	0.2714	0.2714	2 1 2	62.1
18	0.2686	0.2685	$0\ 1\ \underline{2}$	26.1
19	0.2624	0.2624	$1\ \underline{1}\ \underline{3}$	26.8
20	0.2589	0.2588	2 1 3	44.3
21	0.2558	0.2558	2 0 0	28.4

Table 2
Composition of samples prepared for research and phases detected in equilibrium samples

No.	Composition of initial mixtures in terms of the system components (mol%)		Composition of equilibrium samples
	ZnO	$BiVO_4$	
1	10.00	90.00	$BiZn_2VO_6$ + $BiVO_4$
2	20.00	80.00	
3	30.00	70.00	
4	40.00	60.00	
5	50.00	50.00	
6	60.00	40.00	
7	65.00	35.00	
7	66.67	33.33	$BiZn_2VO_6$
8	70.00	30.00	$BiZn_2VO_6$ + ZnO
9	75.00	25.00	
10	80.00	20.00	
11	85.00	15.00	
12	90.00	10.00	

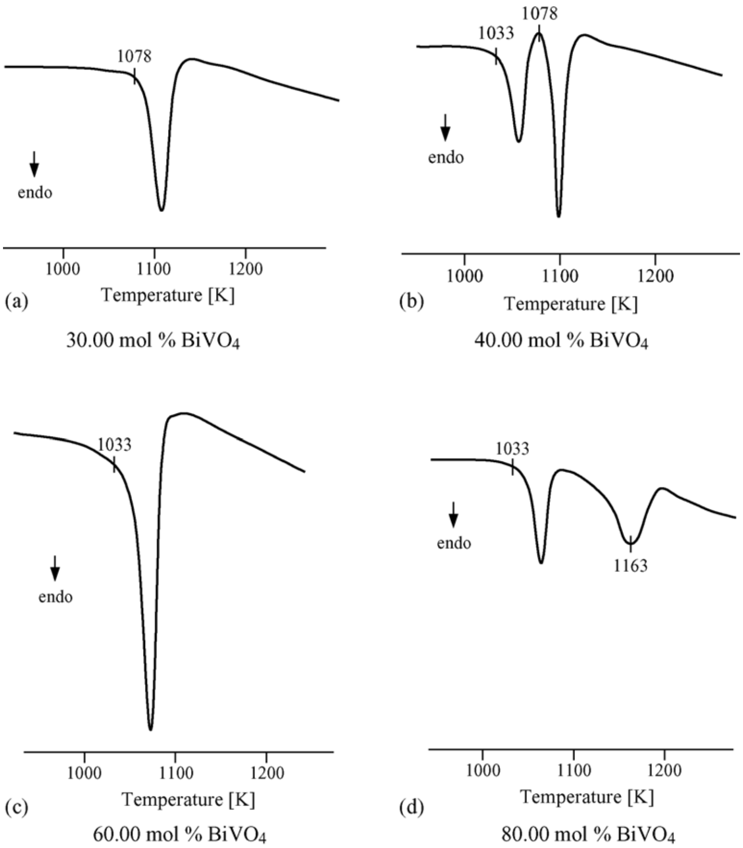

Fig. 3. DTA curves of selected samples of investigated system.

analysis of individual equilibrium samples, the dashed lines on the base only of XRD analysis of samples heated additionally and rapidly cooled to ambient temperature. The temperatures of the solidus line were determined on the base of the onset temperatures of first endothermic effects recorded in DTA curves of the investigated samples. The liquidus curves, on the other hand, were determined by reading the maxima of the effects recorded as the last ones in DTA curves.

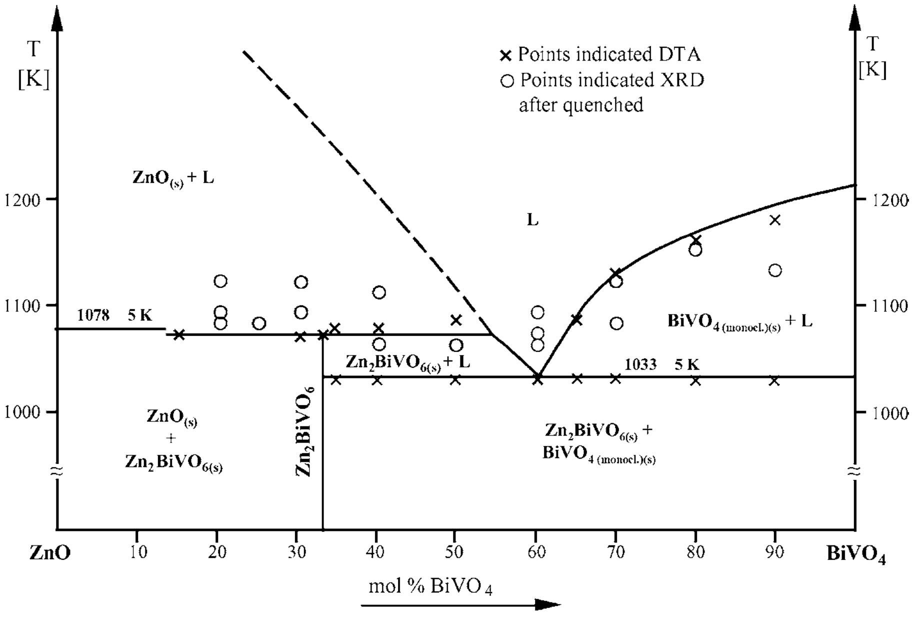

Fig. 4. Diagram of phase equilibria of the system ZnO–$BiVO_4$.

The diagram of phase equilibria presented in Fig. 4 implies that only one compound exists in the system ZnO–$BiVO_4$ with the formula Zn_2BiVO_6. This compound melts incongruently at 1078 ± 5 K with a deposition of ZnO crystals, which was corroborated by XRD analysis results of a preparation of Zn_2BiVO_6 heated additionally at 1123 K for 3 h and next rapidly cooled to ambient temperature. Bismuth(III) orthovanadate(V) forms with Zn_2BiVO_6 an eutectic melting at 1033 ± 5 K. Above the eutectic temperature, Zn_2BiVO_6 and $BiVO_4$ remain at equilibrium with liquid in the components concentration range above 33,33 mol% $BiVO_4$. Zn_2BiVO_6 and ZnO co-exist at equilibrium up to the temperature of the solidus line that is determined by the temperature of incongruent melting Zn_2BiVO_6, i.e. 1078 K. Above this temperature the phase remaining at equilibrium with liquid is zinc oxide.

4. Summary

1. The components of the investigated system mixed at a molar ratio of ZnO:$BiVO_4$ = 2:1 react with each other forming a new compound of $BiZn_2VO_6$. This compound was also obtained as a result of the reaction (2) occurring in the solid state, too.
2. $BiZn_2VO_6$ melts incongruently at 1078 ± 5 K with a deposition of ZnO crystals.
3. $BiZn_2VO_6$ crystallizes in the triclinic system ($a = 0.6879(5)$ nm, $b = 0.5725(3)$ nm, $c = 0.8903(3)$ nm, $\alpha = 91.0^\circ$, $\beta = 130.1^\circ$, $\gamma = 99.5^\circ$, $Z = 2$. Structural research of $BiZn_2VO_6$ is in progress.
4. A diagram of phase relations has been worked out for the system ZnO–$BiVO_4$ over the whole components concentration range up to 1273 K.

References

[1] T. Takahashi, H. Iwahara, Mater. Res. Bull. 13 (1978) 1447–1453.
[2] F. Abraham, M.F. Debreuille-Gresse, G. Mariesse, G. Nowogrocki, Solid State Ionics 28–30 (1988) 529–536.
[3] A.W. Sleight, Science 208 (1980) 895–900.
[4] I. Radosavljevic, J.S.O. Evans, A.W. Sleight, J. Solid State Chem. 137 (1998) 143–147.
[5] X. Xun, S. Uma, A. Yokochi, A.W. Sleight, J. Solid State Chem. 167 (2002) 245–248.
[6] I. Radosavljevic, J.S.O. Evans, A.W. Sleight, J. Alloys Compd. 284 (1999) 99–103.
[7] J. Huang, Q. Gu, A.W. Sleight, J. Solid State Chem. 105 (1993) 599–606.
[8] E. Ketatni, B. Mernari, F. Abraham, O. Mentre, J. Solid State Chem. 153 (2000) 48–54.
[9] J. Huang, A.W. Sleight, J. Solid State Chem. 100 (1992) 170–178.
[10] I. Radosavljevic, J.S.O. Evans, A.W. Sleight, J. Solid State Chem. 141 (1998) 149–154.
[11] I. Radosavljevic, A.W. Sleight, J. Solid State Chem. 149 (2000) 143–148.
[12] A. Mizrahi, J.P. Wignacourt, M. Drache, P. Conflant, J. Mater. Chem. 5 (1995) 901–904.
[13] I. Radosavljevic, J.A.K. Howard, R.L. Withers, J.S.O. Evans, Chem. Commun. (2001) 1984–1985.
[14] F. Abraham, M. Ketatni, G. Mairesse, B. Mernari, Eur. J. Solid State Inorg. Chem. 31 (1994) 313–321.
[15] A. Mizrahi, J.P. Wignacourt, H. Steinfink, J. Solid State Chem. 133 (1997) 516–521.
[16] J. McMurdie, Powder Diff. J. 1 (1986) 40–44.
[17] R.S. Roth, J.L. Waring, Am. Mineral 21 (1936) 809–816.
[18] J.D. Bierlein, A.W. Sleight, Solid State Commun. 21 (1975) 69–70.
[19] A.K. Bhattacharya, K.K. Mallick, A. Hartridge, Mater. Lett. 30 (1997) 7–13.
[20] J.B. Liu, H. Wang, S. Wang, H. Yan, Mater. Sci. Eng. B 104 (2003) 36–39.
[21] Powder Diffraction File, International Center for Diffraction Data, Swarthmore, USA, File Nos.: 14-688, 14-133, 14-699, 36-1451.
[22] D. Taupin, J. Appl. Crystallogr. 6 (1973) 380–385.
[23] Z. Kluz, I. Waclawska, Rocz. Chem. 49 (1975) 839–849.