

Journal of Alloys and Compounds 261 (1997) L1-L3

Journal of ALLOYS AND COMPOUNDS

Letter

Subsolidus phase relations in the system BaO-B₂O₃-P₂O₅

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Received 4 February 1997; revised 21 April 1997; accepted 29 April 1997

Abstract

The subsolidus phase relations in the system $BaO-B_2O_3-P_2O_5$ were determined. The system can be divided into 16 three-phase regions. There are nine binary compounds and three ternary compounds in this system. © 1997 Elsevier Science S.A.

Keywords: Ternary oxide system; Alkaline earth borophosphates; Crystal structure

1. Introduction

The structural complexity of borophosphate compounds is influenced by localized bonding arrangements of the principal components, B₂O₃ and P₂O₅. In the structure of the borate, the boron atoms can form planar or pyramidal BO₃ groups with 3-oxygen atoms via trigonal sp^2 bonding, or they can form tetrahedral BO₄ groups with 4-oxygen atoms via tetrahedral sp³ bonding [1]. Besides, the borates can contain not only the above two simple groups, but also many complex groups, such as the more elaborate symmetrical B_3O_6 boroxol ring [2], the infinite chain $(BO_2)_n$ containing only three-fold coordinated borons [3] and the group containing interconnected BO₃ and BO₄ [4]. In the structure of the phosphates there are mainly two kinds of groups: the relatively simple PO₄ tetrahedral group, and the complex $P_2O_7^{4-}$ group consisting of two distorted PO₄ tetrahedra with non-linear P-O-P bonds [5]. For the borophosphate Levesseur et al. [6] reported the existence of the "BPO₄ group" which is the basic constituent of a silica-like network where B and P are four-fold coordinated and all oxygens are bridging ones. In addition, the introduction of alkaline earth oxide may create new structural units. Therefore, the considerable variety in crystal structures of borophosphate compounds provides an interesting object for studies aiming at exploring new functional materials.

Although B_2O_3 , P_2O_5 and BaO are technologically important, ternary phase relations in this system have not been studied in detail, except for the report of Sedmale et al. [7] regarding the structural glass formation and chemical reactions. The purpose of this work is to establish the phase relationships in the system $BaO-B_2O_3-P_2O_5$ as a prelude to investigations of series alkaline earth borophosphates.

2. Experimental procedure

2.1. Preparation of samples

The specimens were prepared by standard solid-state reaction techniques by heating mixtures of BaCO₃ (99.0%), H₃BO₃ (99.5%) and NH₄H₂PO₄ (99.0%), which were used as starting materials. The specimens according to their stoichiometric compositions were weighed on an analytical balance to an accuracy of 0.05 mg, thoroughly mixed in an agate mortar, pressed at about 10⁸ Pa into the 1 cm diameter pellets, heated to 400 °C for 10 h in covered Pt crucibles (in order to avoid the unexpected chemical reaction caused by B_2O_3 and the oxide crucible) to eliminate volatilities (NH₃, CO₂ and H₂O), then reground and again pressed into pellets. Hereafter, a variety of heat treatments was carried out on the above prereacted samples according to different compositions: In the rare earth rich part of the system, specimens were calcined at 1150 to 1300 °C for about 48 h. In the middle part of the ternary phase diagram, specimens were sintered at 1000 °C for 48 h. In the vorate and phosphate rich, glass forming easily part, specimens were heated only to 750 °C for 30 min to avoid loss of P2O5 and B2O3, air-quenched, reground and fired at 650 °C by crystallization from glasses. Solid-state

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reactions were done in SiC Globar muffle furnaces. Temperatures were measured with a Pt-PtRh (10%) thermocouple.

2.2. X-Ray powder diffraction analysis

The phase identification of all specimens was examined at room temperature by X-ray diffraction (XRD) with a Guinier-de Wolff monochromatic-focusing transmission camera. Equilibrium was considered to have been reached when the X-ray pattern of the specimen showed no change with successive heat treatment or the X-ray powder data were consistent with results predicted from a previous set of experiments.

3. Results and discussion

The three binary systems which form the boundary of this ternary system have been investigated by several workers [8–10]. Nine binary compounds have been reported. In the ternary system $BaO-B_2O_3-P_2O_5$, three

compounds $BaBPO_5$, $Ba_3BP_3O_{12}$ and Ba_3BPO_7 were found. Fig. 1 is the phase diagram constructed from XRD data of 25 specimens (Table 1), which consists of 16 three-phase regions. Apparently the extent of two-phase regions and solid solution ranges is very small and beyond detection by XRD.

The ternary compound BaBPO₅ (noted as A in the phase) was first prepared by Bauer [11], who defined its chemical formula as 2BaO.B₂O₃.P₂O₅. In our previous work [12] we reported that this compound has a trigonal structure, space group P3₁21, with lattice constants a = 7.109 Å, c = 6.990 Å, V = 1576.39 Å³ and Z = 3.

During the investigation of thermal decomposition of BaBPO₅, another ternary compound Ba₃BP₃O₁₂ (noted as B) was found. When BaBPO₅ was heated at 1100 °C for 24 h, it decomposed into Ba₃BP₃O₁₂ because of the loss of B₂O₃, and if the latter compound was continuously sintered at 1150 °C for 48 h, the final product was Ba₂P₂O₇, where B₂O₃ totally volatilized. The crystal structure of Ba₃BP₃O₁₂ has been determined by single crystal XRD method [13]. The results are as follows: orthorhombic structure, space group Ibca, with lattice



Fig. 1. Subsolidus phase relations in the system $BaO-B_2O_3-P_2O_5$ (temperature range from 650 to 1300 °C), the star symbol denotes the 11th three-phase region, and the characters A, B and C represent compounds $BaBPO_5$, $Be_3BP_3O_{12}$ and Ba_3BPO_7 , respectively.

Table 1	l										
List of	phase	identification	for	various	composition	specimens	in tl	he system	BaO-B ₂	0,-	$-P_2O_5$

No.	BaO (at.%)	B ₂ O ₃ (at.%)	P ₂ O ₅ (at.%)	Phase identification
1	80	10	10	Ba ₃ BPO ₂ +BaO
2	75	12.5	12.5	Ba, BPO,
3	75	18	7	$Ba_{3}BPO_{7} + 3BaO.B_{2}O_{3}$
4	75	5	20	3BaO.P.O. + Ba, BPO,
5	72	14	14	$Ba_{3}BPO_{7} + 3BaO.P,O_{5} + BaO.B_{2}O_{7}$
6	70	20	10	Ba, BPO, +BaO.B, O,
7	66.7	16.7	16.6	$3BaO.P_2O_5 + BaO.B_2O_3$
8	60	20	20	$Ba_{3}BP_{3}O_{1}$, +3BaO.P,O, +BaO.B,O,
9	64	4	32	Ba ₃ BP ₃ O ₁ ,+2BaO.P,O ₅
10	60	10	30	Ba ₃ BP ₃ O ₁ ,
11	54	19	27	BaBPO, +Ba ₃ BP ₃ O ₁ ,
12	60	6	34	$Ba_{3}BP_{3}O_{12} + 3BaO.2P_{2}O_{3}$
13	57	7	36	3BaO.2P,O,+BaBPO,
14	50	17	33	BaBPO ₅ +3BaO.2P ₂ O ₅ +BPO ₄
15	50	25	25	BaBPO
16	50	8	42	$3BaO.2P,O_{4} + BPO_{4}$
17	33.5	16.5	50	BaO.P.O. + BPO.
18ª	30	10	60	BaO.P.O. + BPO.
19	57	21.5	21.5	$Ba_{1}BP_{1}O_{1}$, + $BaO.B.O.$
20	50	36	14	BaO.B.O. + Ba.BP.O. + BaO.2B.O.
21	46	35	19	$Ba_{1}BP_{1}O_{1}$ + $BaO.4B_{2}O_{3}$
22	44	36	20	BaBPO ₅ +BaO.4B ₂ O ₃
23ª	33.5	50	16.5	BaBPO ₅
24	33.4	33.3	33.3	$BaBPO_5 + BPO_4$
25°	30	40	30	BaBPO ₅ +BPO ₄

^a The diffraction patterns of B₂O₃ and P₂O₅ could not be observed because of their weak X-ray diffraction intensity.

constants a=7.0859(13) Å, b=14.2903(22) Å, c=22.1868(32) Å, V=2246.6(3) Å³ and Z=8.

The compound Ba_3BPO_7 (noted as C) is a novel compound which has not been reported before, except that it is similar to the compound Ba_3BPO_4 [14]. The hexagonal lattice constants of Ba_3BPO_7 were determined by using the TREOR program [15]: a=5.4903(4) Å and c=14.752(7)Å.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China.

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