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Phase diagram study of $BaO-Bi_2O_3-V_2O_5$ system

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ABSTRACT

The sub−solidus phase relations in Ba−Bi−V−O quaternary system were determined at 1123 K in air. To confirm the formation and stability of reported phases at this temperature, ternary and quaternary compounds in $BaO-Bi_2O_3$, $Bi_2O_3-V_2O_5$, $BaO-V_2O_5$ and $BaO-Bi_2O_3-V_2O_5$ systems were synthesized by solid state route. $BaCO_3$, Bi_2O_3 and NH_4VO_3 were reacted in desired molar proportions at 1123 K. A pseudo−ternary phase diagram of $BaO-Bi_2O_3-V_2O_5$ system was drawn on the basis of phase analysis of various phase mixtures and reported phases and phase fields were established by powder X−ray Diffraction (XRD). In the phase diagram, a single quaternary compound $Ba_2BiV_3O_{11}$ was identified. Thermal Expansion (TE) behavior and heat capacity (C_p) measurement of $Ba_2BiV_3O_{11}$ were carried out using High−Temperature X−Ray Diffraction (HTXRD) technique and Differential Scanning Calorimeter (DSC), respectively.

1. Introduction

Bismuth vanadates doped with aliovalent cations have attracted much attention in recent years as they have vast industrial applications in various fields. They have been mainly developed for potential visible light active photocatalysts, promising candidates as electrolyte for solid oxide fuel cells (SOFC), ferroelectric materials suitable for fabrication of various electronic devices, good conductors, used in fabrication of multilayered microwave devices, pigments in paint industry, etc. [1–6]. $\gamma-Bi_4V_2O_{11-x}$, a highly distorted high temperature phase of $Bi_4V_2O_{11-x}$, having an inherent oxygen deficiency with higher ionic conductivity can be stabilized at room temperature with the doping of divalent, trivalent or tetravalent metal cations at vanadium site [7,8]. Owing to such a wide scope of applications, a lot of interests have been shown in compounds containing both Bi^{3+} and alkaline−earth metal cations in bismuth vanadates. and several papers have been published in recent years in this direction [3,9–13].

Barium bismuth vanadate is one such important functional material having divalent alkaline earth metal and Bi^{3+} cations. In Ba−Bi−V−O system three quaternary compounds such as $Ba_2BiV_3O_{11}$, Ba_2BiVO_6 and $BaBi_8V_2O_{18}$ are reported in literature, which are having bismuth in +3 and vanadium in +5 oxidations states. A synthesis and crystal structural study of $Ba_2BiV_3O_{11}$ was first carried out by Huang et al. [14]. Synthesis of the same at lower temperature has been reported by Su et al. [15]. Recently, microstructural and microwave dielectric properties of $Ba_2BiV_3O_{11}$ have been investigated by Li et al. [1]. Studies on structural, microstructural and electrical properties of $Ba(Bi_{0.5}V_{0.5})O_3$ or Ba_2BiVO_6, a promising ferroelectric material, have been carried out by Sutar et al. [2]. Synthesis of another quaternary phase $BaBi_8V_2O_{18}$, a key material in modern communication technology having an important application in mobile phones, TV satellite dish, military radar etc. has been patented by Fang et al. [16]. Barium bismuth vanadates are also used to develop low−firing microwave dielectrics. Thermal analysis and structural characterization of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ ($0.02 \leq x \leq 0.50$) solid solutions, where V^{5+} is partially substituted by Ba^{2+} in $Bi_4V_2O_{11}$ has been studied by Malta and Medeiros [17]. From powder XRD study they have reported that a new phase $Bi_4Ba_{0.5}V_{1.5}O_8$ ($BaBi_8V_3O_{16}$) began to form above x = 0.14. However, no detail studies of the compound have been carried out by them. Recently, structural, thermal and conducting properties of barium doped $Bi_4V_2O_{11}$, and $Bi_4Ba_xV_{2-x}O_{11-\delta}$, ($0.0 \leq x \leq 0.20$) have been investigated by Gupta et al. [18].

The phase diagram study of $BaO-Bi_2O_3$, $BaO-V_2O_5$ and $Bi_2O_3-V_2O_5$ ternary systems have been carried out in detail. However, no phase diagram is available for $BaO-Bi_2O_3-V_2O_5$ pseudo ternary system. This stimulates us to establish the phase diagram of $BaO-Bi_2O_3-V_2O_5$ using powder X−ray diffraction as prime characterization technique. Here, attempts were made to synthesize the quaternary barium bismuth vanadate compounds by solid state route. Since limited data is available regarding their thermo−-physical properties, the thermal expansion behavior and heat

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capacity measurements of quaternary compounds were also carried out using HTXRD and DSC techniques, respectively and reported in this paper.

2. Experimental

2.1. Synthesis

All the ternary and quaternary phases reported in $BaO-Bi_2O_3$, $Bi_2O_3-V_2O_5$, $BaO-V_2O_5$ and $BaO-Bi_2O_3-V_2O_5$ systems were synthesized by solid state route. Ammonium hydrogen vanadate (NH_4VO_3), $BaCO_3$ '(both analar grade, Merck, 99.99% purity)' and Bi_2O_3 '(analar grade, Aldrich 99.9% purity)' were used as starting materials. BaO, Bi_2O_3 and V_2O_5 mixed in different molar proportions for making equilibrium phase mixtures are listed in Table 1.

All the mixtures were well ground in agate mortar and pestle using acetone as a binder. These mixtures were heated in a resistance heating furnace in an alumina boat initially at 673 K for 6 h and cooled to room temperature. The mixtures were reground and reheated in air at 1073 and 1123 K for 48 h. It is reported that decomposition of NH_4VO_3 starts at 473 K and completes at 723 K and reactions of $BaCO_3$ and other reactants starts at 890 K and completes at 1050 K. The well established ternary oxides in $BaO-Bi_2O_3$, $Bi_2O_3-V_2O_5$, $BaO-V_2O_5$ systems were synthesized by mixing respective reactants in desired molar proportions and heated at 1123 K for 48 h. All the heated products were air quenched to stabilize 1123 K heated product phases at room temperature.

2.2. Characterization

XRD was used as prime tool for identification of various phase mixtures synthesized at 1123 K. XRD data of the products was collected on 'Rigaku Miniflex-600 theta–theta diffractometer' with graphite monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) at the scanning rate of 2° (2θ) per minute. High temperature X-ray diffraction data (HTXRD) data for quaternary compound was collected on a 'STOE theta–theta high temperature X–ray diffractometer' using 'HDK–2.4 Buhler' high temperature attachment in 10^{-5} mbar vacuum from 298 to 1123 K. Instrumental details of HTXRD are discussed elsewhere [19]. Prior to the collection of HTXRD data, the diffractometer was calibrated at room temperature using silicon powder and thermocouple of HTXRD was calibrated using phase transitions in K_2SO_4 [20]. MgO was used as a standard for thermal expansion coefficient measurements and values obtained were within 5% of the reported values [21].

Table 1
Phases identified in the products of various reaction mixtures heated at 1123 K in the $BaO-Bi_2O_3-V_2O_5$ system.

Mix. No.	Mole fraction of the oxides			Phases identified by XRD		
	BaO	Bi_2O_3	V_2O_5			
B1	0.66	0.17	0.17	$Ba_3V_2O_8$	$Ba_2Bi_6O_{11}$	$Ba_9Bi_2O_{12}$
B 2	0.5	0.12	0.38	**$Ba_2BiV_3O_{11}$**	–	–
B 3	0.18	0.09	0.73	BaV_2O_6	$BiVO_4$	V_2O_5
B 4	0.6	0.1	0.3	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Bi_8V_2O_{17}$
B 5	0.5	0.17	0.33	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Bi_8V_2O_{17}$
B 6	0.17	0.5	0.33	$Ba_2BiV_3O_{11}$	$Bi_8V_2O_{17}$	$Bi_4V_2O_{11}$
B 7	0.5	0.25	0.25	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Bi_8V_2O_{17}$
B 8	0.67	0.08	0.25	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Bi_8V_2O_{17}$
B 9	0.33	0.33	0.34	$Ba_2BiV_3O_{11}$	$Bi_8V_2O_{17}$	$Bi_4V_2O_{11}$
B 10	0.125	0.625	0.25	$Ba_2BiV_3O_{11}$	$Bi_4V_2O_{11}$	$Bi_8V_2O_{17}$
B 11	0.57	0.07	0.36	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Ba_3V_4O_{13}$
B 12	0.6	0.2	0.2	$Ba_3V_2O_8$	$Bi_{11}VO_{19}$	$Ba_2Bi_6O_{11}$
B 13	0.275	0.45	0.275	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Bi_8V_2O_{17}$
B 14	0.1	0.5	0.4	$Ba_2BiV_3O_{11}$	$Bi_4V_2O_{11}$	$BiVO_4$
B 15	0.8	0.1	0.1	$Ba_3V_2O_8$	$Ba_2Bi_6O_{11}$	$Ba_9Bi_2O_{12}$
B 16	0.1	0.8	0.1	$Bi_{11}VO_{19}$	$Ba_3V_2O_8$	–
B 17	0.4	0.57	0.03	$Ba_2Bi_6O_{11}$	$Ba_3V_2O_8$	$Bi_{11}VO_{19}$
B 18	0.5	0.05	0.45	$Ba_2BiV_3O_{11}$	BaV_2O_6	$BiVO_4$
B 19	0.55	0.4	0.05	$Ba_2Bi_6O_{11}$	$Ba_9Bi_2O_{12}$	$Ba_3V_2O_8$
B 20	0.05	0.8	0.15	$Bi_{12}V_2O_{23}$	$Bi_8V_2O_{17}$	$Ba_3V_2O_8$
B 21	0.55	0.03	0.42	$Ba_2BiV_3O_{11}$	$Ba_3V_4O_{13}$	BaV_2O_6
B 22	0.9	0.04	0.06	$Ba_9Bi_2O_{12}$	$Ba_3V_2O_8$	BaO
B 23	0.3	0.6	0.1	$Ba_2Bi_6O_{11}$	$Ba_3V_2O_8$	$Bi_{11}VO_{19}$
B 24	0.06	0.9	0.04	$Bi_{11}VO_{19}$	$Ba_2Bi_6O_{11}$	–
B 25	0.167	0.667	0.166	$Bi_{12}V_2O_{23}$	$Ba_3V_2O_8$	–
B26	0.33	0.5	0.17	$Bi_{11}VO_{19}$	$Bi_{12}V_2O_{23}$	$Ba_3V_2O_8$
B27	0.25	0.28	0.47	$Ba_2BiV_3O_{11}$	BaV_2O_6	$BiVO_4$
B28	0.6	0.03	0.37	$Ba_2BiV_3O_{11}$	$Ba_3V_2O_8$	$Ba_3V_4O_{13}$

Bold denotes a single pure quaternary phase could established during present work.

Heat capacity measurements of quaternary compound was carried out using a 'heat flux–type differential scanning calorimeter (model number DSC 1/700 of M/s. Mettler Toledo GmbH, Switzerland)' in high purity argon atmosphere (supplied by INOX Air Product Ltd., India) from 303 to 768 K. The oxygen impurity in argon gas was detected by solid state oxygen sensors and was found to be less than 20 ppm. Temperature calibration of DSC was performed by determining the melting point of In, Zn and Pb. For measurement of heat capacity, classical three–step method was used for blank, sapphire and sample runs in a continuous heating mode with identical experimental conditions. The details of instrument and procedure adopted for C_p data collection are described as earlier [22]. The average of six specific heat data measurements was taken for quaternary compound.

3. Results and discussion

3.1. Phase diagram study

The pseudo ternary phase diagram of $BaO-Bi_2O_3-V_2O_5$ system was established at 1123 K. Various ternary compounds synthesized in $BaO-Bi_2O_3$, $Bi_2O_3-V_2O_5$ and $BaO-V_2O_5$ systems and a quaternary compound, $Ba_2BiV_3O_{11,}$ formed in $BaO-Bi_2O_3-V_2O_5$ system during the present work were used for drawing the phase diagram. The data available in literature for various phases in $BaO-Bi_2O_3$, $Bi_2O_3-V_2O_5$, $BaO-V_2O_5$ and $BaO-Bi_2O_3-V_2O_5$ systems are discussed below in detail.

3.2. $BaO-Bi_2O_3$ system

Barium bismuth oxides, interesting materials because of their ability to exhibit either superconducting property or anionic conductivity are extensively studied. However, phase diagram of $BaO-Bi_2O_3$ system is not well established. Hovhannisyan has mentioned that the $BaO-Bi_2O_3$ system is very complex and critical to experimental conditions such as type of atmospheres and pressure [23]. He has stated that in phase diagram study of $BaO-Bi_2O_3$ system in air or oxygen atmosphere, two low melted eutectic areas (1013–1063 K) have been observed in high bismuth content region, with BaO mole % 5–7 and 25–30. Well established oxides reported in $BaO-Bi_2O_3$ system are $BaBi_3O_{5.5}$, $BaBiO_{2.5}$ and $Ba_9Bi_2O_{12}$ with $BaO:Bi_2O_3$ ratios of 0.4:0.6, 0.67:0.33 and 0.9:0.1, respectively. Structures of $BaBi_3O_{5.5}$ ($Ba_2Bi_2O_{11}$) and $BaBiO_{2.5}$ ($Ba_2Bi_2O_5$) have been derived by Michel et al. [24] and Lightfoot et al. [25], respectively. Formation of $BaBi_3O_{5.5}$ was confirmed by Michel by heating $Ba(NO_3)_2$ and Bi_2O_3 in 2:3 M ratio at 1003 K in air. Lightfoot et al. have reported the synthesis of $BaBiO_{2.5}$ by slow cooling of $BaBiO_3$ compound in reduced atmosphere. $Ba_9Bi_2O_{12}$ has been prepared by reacting Bi_2O_3 and BaO at 1173 K for 5 h [26]. During the present work for the phase diagram study at 1123 K, we could confirm only two barium bismuth oxides in pure form, such