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Heat capacities of $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s)

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Abstract

Heat capacities of $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) were measured by differential scanning calorimetry in the temperature range 280–820 K and 280–660 K, respectively. $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) showed order–disorder transitions whose onset temperatures are 520 K and 700 K, respectively. The measured heat capacities of $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) as a function of temperature are expressed as:

$$C_p < PbBi_{12}O_{19} > (J\,K^{-1}\,mol^{-1}) = 791.68 + 112.18 \times 10^{-3}\,T - 13.58 \times 10^{6}\,T^{-2} \qquad (280 - 820\,K)$$

$$C_p < \phi\text{-}Pb_5Bi_8O_{17} > (J\,K^{-1}\,mol^{-1}) = 700.02 + 161.58 \times 10^{-3}\,T - 12.85 \times 10^{6}\,T^{-2} \qquad (280 - 660\,K)$$

Enthalpy increments, entropies and Gibbs energy functions were derived from the measured heat capacity data.

Keywords: Pb–Bi–O; Heat capacity; High temperature X-ray diffraction; Electrical conductivity; Order–disorder transition

1. Introduction

Liquid lead and lead–bismuth eutectic (LBE) alloy are currently being explored for service as spallation target and coolant in accelerator driven systems (ADS) [1,2]. Though these coolants are corrosive to structural steels, corrosion can be minimized by forming a protective oxide layer by control of oxygen concentration in the coolant [3]. Effective oxygen control requires understanding of the thermodynamics of the Pb–Bi–O system. The pseudo binary phase diagram of PbO–Bi_2O_3 system has been established and four ternary compounds are known, viz., $PbBi_{12}O_{19}$(s), $Pb_2Bi_6O_{11}$(s), $Pb_5Bi_8O_{17}$(s) and $Pb_3Bi_2O_6$(s) [4]. $Pb_2Bi_6O_{11}$(s) and $Pb_3Bi_2O_6$(s) are stable only in narrow temperature ranges viz., 848–882 K and 853–876 K, respectively. The compounds $PbBi_{12}O_{19}$(s) and $Pb_5Bi_8O_{17}$(s) are stable from room temperature up to ∼988 K and ∼868 K, respectively. $PbBi_{12}O_{19}$(s) exists in cubic form (bcc) [5–7]. $Pb_5Bi_8O_{17}$(s) has at least three polymorphs of which β_2-$Pb_5Bi_8O_{17}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) are low temperature phases [8–10]. β-$Pb_5Bi_8O_{17}$(s) is a high temperature phase [8–10], which exhibits high oxygen ion conductivity [11] thus making it suitable for use as an oxygen selective membrane [12]. β_2-$Pb_5Bi_8O_{17}$(s), a meta stable phase with tetragonal structure, is formed when quenched from 883 K either in air or nitrogen while ϕ-phase is formed on slow cooling [10,13]. The structure of ϕ-$Pb_5Bi_8O_{17}$(s) has been reported to be triclinic [8,9,14–16]. Although data on structural characteristics of these compounds have been reported, their thermodynamic properties have not yet been investigated.

In the present work, heat capacities of $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) have been measured as a function of temperature by differential scanning calorimetry. Enthalpy increments, entropies and Gibbs energy functions of these compounds have been derived from the heat capacity data.

2. Experimental

2.1. Sample preparation

Ternary compounds $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) were prepared by solid-state reaction between high purity PbO

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Table 1
Thermodynamic functions of $PbBi_{12}O_{19}$(s)

Temperature (K)	C_p (J K^{-1} mol^{-1})		$(H_T^0 - H_{298}^0)$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
280	649	650	–	–	–
298.15	–	672	0	901	901
300	677	674	1246	905	901
400	753	752	73023	1111	929
500	791	793	150450	1284	983
600	819	821	231261	1431	1046
700	836	842	314487	1559	1110
800	861	860	399644	1673	1173

(99.999 mass%, M/s. Aldrich, USA) and Bi_2O_3 (99.99 mass%, M/s. Nuclear Fuel Complex, India) powders taken in stoichiometric mole ratios. The oxide powders were mixed thoroughly, ground with a mortar and pestle and compacted into discs. The discs in an alumina crucible were placed inside a quartz tube which was evacuated and filled with argon gas two to three times and sealed under vacuum. $PbBi_{12}O_{19}$(s) was prepared by heating the compacted oxide mixture at 908 K for 200 h while ϕ-$Pb_5Bi_8O_{17}$(s) was prepared by heating at 823 K for 200 h with an additional intermediate step of grinding, mixing, pelletising and vacuum sealing. The compounds were cooled slowly (∼5 K min^{-1}) after the heat treatment. The products obtained were characterised by X-ray diffraction. The XRD patterns of $PbBi_{12}O_{19}$(s) and $Pb_5Bi_8O_{17}$(s) matched the patterns reported in JCPDS file 24–1184 for the cubic phase and 52–1497 for the triclinic phase [17].

2.2. Calorimetric measurements

A heat flux differential scanning calorimeter, model number DSC821e/700 of M/s. Mettler Toledo GmbH, Switzerland was used in this study. The samples for DSC measurements were pelletised and hermetically sealed in 40 μl Al-pans. High purity argon gas at a flow rate of 50 ml min^{-1} was used as the purge gas. DSC measurements were done from 280 K to 820 K at a heating rate of 10 K min^{-1}. Additionally, measurements with heating rates of 5 K min^{-1} and 20 K min^{-1} were also carried out. A disc of sapphire was used as the standard for heat rate calibration. The heat capacity data of sapphire given by National Institute of Standards and Technology (NIST), USA was used for computing the heat capacities of the samples [18]. A three-segment temperature program was used. The first segment lasting for 5 min was isothermal at the initial temperature, the second was with a heating rate of 10 K min^{-1} and the third, lasting for 5 min was again isothermal at the final temperature. The samples were characterized by XRD before and after the calorimetric runs. The data at each temperature is derived as the mean of 10 measurements and the associated relative standard deviations is <3%.

2.3. High temperature X-ray diffraction studies

High temperature X-ray diffraction studies were done with a Philips-X'pert® system with Cu Kα radiation. The sample was loaded as a thin layer over a thin, resistance-heated, platinum foil in the high temperature attachment of the X-ray diffractometer. Temperature was controlled within ±1 K. A heating rate of 30 K min^{-1} and a holding time of 10 min at each temperature of measurement were adopted. Data was recorded under a vacuum of ∼10^{-5} Torr as well as in static air.

2.4. Electrical conductivity measurements

Pellets of $PbBi_{12}O_{19}$(s) and $Pb_5Bi_8O_{17}$(s) (10 mm diameter and 2–3 mm thickness) were prepared by compacting the powders under 20 MPa pressure and sintering at 923 K and 823 K, respectively, for 20 h under argon. A sample pellet was mounted between two spring-loaded platinum foils of identical dimensions and placed inside a quartz chamber, which in turn was heated by a furnace. The conductivity of the pellet was measured under flowing argon (∼30 ml min^{-1}) with a frequency response analyser (model SI 1255 of Solartron, M/s. Schlumberger, UK) coupled to an electrochemical interface (model 1286 of Solartron, M/s. Schlumberger, UK) in the frequency range of 1 Hz–1 MHz. The data were analysed by a deconvolution technique using Boukamp analysis program [19]. The conductivity values were reproducible during heating, cooling and random cycles. The samples were characterized by XRD before and after the electrical conductivity measurements.

3. Results and discussion

The heat capacity of $PbBi_{12}O_{19}$(s) is shown in Table 1 and Fig. 1. It can be seen from Fig. 1 that there is a small but distinct peak at 540 K with an onset temperature of 520 K in the heat capacity data, indicating the presence of a phase transition. To confirm the existence and to delineate the nature of the phase transition, high temperature X-ray diffraction studies were carried out at 480 K, 540 K, 600 K and 773 K. The XRD pattern does not exhibit any change with increase in temperature. Since the atomic scattering factors for lead and bismuth are very close, an order–disorder type transition is not expected to change the XRD pattern [20] except for a small shift due to lattice expansion. Murray et al. [5] has also indicated that it is difficult to obtain definite information about the distribution of Pb^{2+} over the lattice sites because of similar

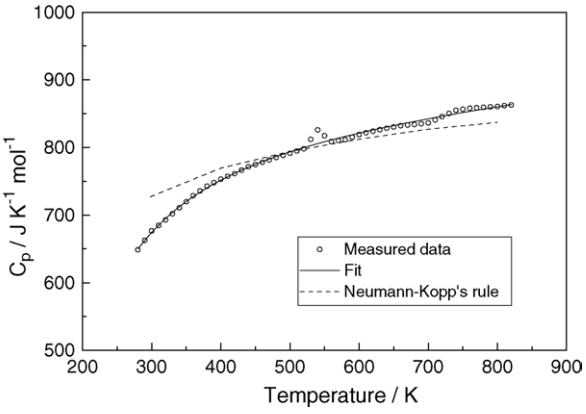

Fig. 1. Heat capacity data of $PbBi_{12}O_{19}$(s).

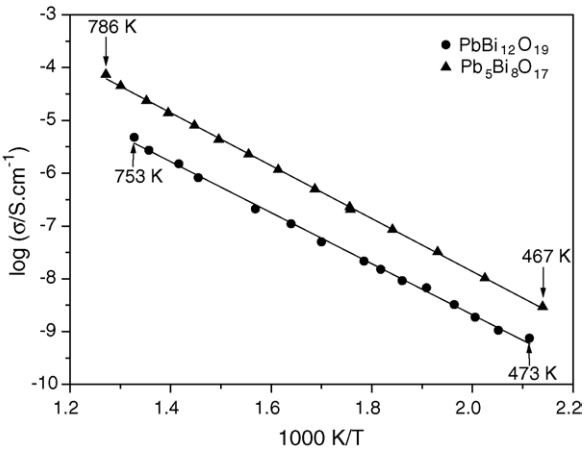

Fig. 2. Arrhenius plot for electrical conductivity of $PbBi_{12}O_{19}$(s) and ϕ-$Pb_5Bi_8O_{17}$(s) in argon atmosphere.

scattering lengths of Pb^{2+} and Bi^{3+}. Hence, it is concluded that the transition is an order–disorder one. Results of the additional DSC measurements at heating rates of 5 K min^{-1}and 20 K min^{-1} have shown that the onset temperatures were within ±1 K and the variation of the peak area was ±10%. These results indicate that the transition observed is fast and hence the heat capacity of the compound is independent of the scan rate.

Electrical conductivity measurements were carried out in the range 473–753 K to unravel the nature of phase transition. Since the scatter in the impedance data was higher at lower temperatures due to the high resistivity of the sample, the conductivity measurements were not done below 473 K. Fig. 2 shows the electrical conductivity of $PbBi_{12}O_{19}$(s) in argon as a function of temperature. The observed variation of conductivity with temperature can be represented as $\log \sigma = A - E/kT$, where A is the Arrhenius constant, E the activation energy for the conduction process, k the Boltzmann constant and T is the Kelvin temperature. The activation energy was calculated to be 0.42 ± 0.02 eV. Although the number of data points below 540 K are limited, there is no significant change in the temperature dependence of electrical conductivity indicating that the order–disorder transition in $PbBi_{12}O_{19}$(s) does not involve any significant change in electrical conductivity.

Since the order–disorder transition does not affect the C_p values except in the temperature range of 520–560 K, heat capacity values of $PbBi_{12}O_{19}$(s) measured at other temperatures were fitted to the following expression by the least squares method:

$$C_p\langle PbBi_{12}O_{19}\rangle(J\,K^{-1}\,mol^{-1}) = 791.68 + 112.18 \times 10^{-3}T - 13.58 \times 10^{6}T^{-2}, \quad (280–820\,K) \qquad (1)$$

The standard error of the fit is ±4.21 J K^{-1} mol^{-1}. These fitted values are shown in Table 1 along with the measured values. These data on heat capacity of $PbBi_{12}O_{19}$(s) are the first to be reported.

The heat capacity of $PbBi_{12}O_{19}$(s) was computed by Neumann–Kopp's rule using heat capacity data for PbO(s) and Bi_2O_3(s) [21], and is compared with the measured values in Fig. 1. The experimental $C_{p,298K}$ is 7.5% lower than the estimated value. Assuming S^0_{298} of $PbBi_{12}O_{19}$(s) to also be 7.5% lower than the value derived from Neumann-Kopp's rule, it was deduced to be 901 J K^{-1} mol^{-1} from S^0_{298} values of PbO(s) and Bi_2O_3(s), viz., 65.480 J K^{-1} mol^{-1} and 151.461 J K^{-1} mol^{-1}, respectively [21]. To examine the validity of this assumption underlying this correction, the reported thermochemical data of ternary oxides in [21] were considered. The difference between the Gibbs free energies of formation per oxygen atom of PbO and Bi_2O_3 at 298.15 K is ∼25 kJ. Ternary oxide systems were chosen such that the difference between the Gibbs free energies of formation per oxygen atom of the constituent binary oxides is less than or equal to ∼35 kJ. The differences between

Table 2
Thermodynamic functions of ϕ-$Pb_5Bi_8O_{17}$(s)

Temperature (K)	C_p (J K^{-1} mol^{-1})		$(H^0_T - H^0_{298})$ (J mol^{-1})	S^0_T (J K^{-1} mol^{-1})	$-(G^0_T - H^0_{298})/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
280	582	581	–	–	–
298.15	–	604	0	826	826
300	606	606	1119	830	826
400	685	684	66068	1016	851
500	726	729	136916	1174	900
600	760	761	211521	1310	957
700	771	–	–	–	–
800	861	–	–	–	–

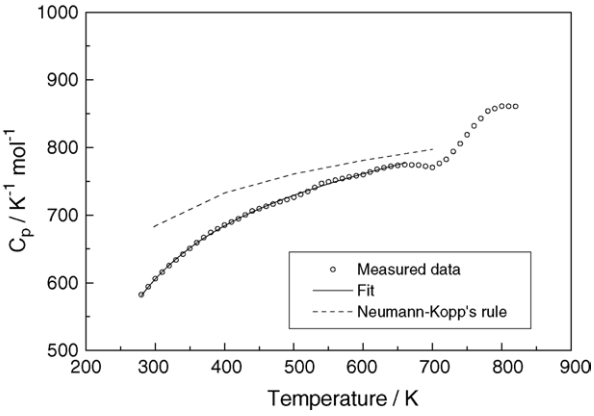

Fig. 3. Heat capacity data of ϕ-$Pb_5Bi_8O_{17}$(s).

the reported heat capacity values [21] and those estimated using Neumann–Kopp's rule ($\Delta C_{p,298K}$) for these ternary oxides were calculated. The corresponding values for $\Delta S^0_{298\,K}$ were also computed from the entropy data listed in [21]. For ∼67% of these systems, $\Delta C_{p,298K}$ and $\Delta S^0_{298\,K}$ have the same sign though the magnitudes differ. Hence, the above correction procedure for estimating S^0_{298} was adopted in this work. Similar approach has been adopted for the estimation of the S^0_{298} of $BaThO_3$ described elsewhere [22]. Using the value for S^0_{298} thus estimated and expression (1) for heat capacity, the enthalpy increments, entropies and Gibbs energy functions of $PbBi_{12}O_{19}$(s) were computed as shown in Table 1.

The experimental heat capacity of ϕ-$Pb_5Bi_8O_{17}$(s) as a function of temperature is shown in Table 2 and Fig. 3. Fig. 3 shows an abnormal increase of C_p with increase in temperature from 700 K and attained the normal pattern only above 800 K. This observation indicates that ϕ-$Pb_5Bi_8O_{17}$(s) undergoes a second order transition whose onset temperature is 700 K.

High temperature X-ray diffraction studies and electrical conductivity measurements were also carried out for this compound to characterise the phase transition. XRD patterns obtained at 623 K, 673 K, 723 K, 773 K and 823 K showed no phase transition. We propose that an order–disorder type transition also takes place with this compound at 700 K. Fig. 2 shows the electrical conductivity of ϕ-$Pb_5Bi_8O_{17}$(s) in argon as a function of temperature. The observed variation of conductivity with temperature in the temperature range of measurement (467–786 K) can be represented as $\log\sigma = A - E/kT$. The activation energy was calculated to be 0.43 ± 0.01 eV. The electrical conductivity also does not vary significantly during the order–disorder transition.

Because of the large monotonous increase in C_p between 700 K and 800 K, preceded by a small dip in the temperature range of 660–700 K, the measured heat capacity values of ϕ-$Pb_5Bi_8O_{17}$(s) from 280 K to 660 K were fitted to the following expression by using the least squares method.

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = 700.02 + 161.58 \times 10^{-3}T - 12.85 \times 10^{6}T^{-2}, \quad (280\text{–}660\,\mathrm{K}) \qquad (2)$$

The standard error of the fit is $\pm 1.60\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The heat capacity values computed from Eq. (2) are shown in Table 2 along with measured values. S^0_{298} values of ϕ-$Pb_5Bi_8O_{17}$(s) were also estimated as in the case of $PbBi_{12}O_{19}$(s). The experimental $C_{p,298}$ is 11.5% lower than the value estimated by invoking Neumann–Kopp's rule. Assuming that the S^0_{298} value of ϕ-$Pb_5Bi_8O_{17}$(s) will also be 11.5% lower than the value computed using Neumann–Kopp's rule, the S^0_{298} value of ϕ-$Pb_5Bi_8O_{17}$(s) was computed to be $826\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Using this value and expression (2) for heat capacity, the enthalpy increments, entropies and Gibbs energy functions of the compound in the temperature range of 280–660 K were computed and are shown in Table 2. For ϕ-$Pb_5Bi_8O_{17}$(s) also, the present C_p data are the first to be reported.

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