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Thermodynamic investigations on barium indate

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ABSTRACT

Barium indate ($Ba_2In_2O_5$) is an interesting compound with potential applications as oxide-ion conductor, oxygen sensor, separation membrane and electrochemical device material. Information on thermodynamic stability of barium indate is essential for long term use of this compound under reactive chemical environments. The present paper deals with the detailed thermodynamic investigations on barium indate, $Ba_2In_2O_5$. Standard molar enthalpy of formation of $Ba_2In_2O_5$(s) at $T = 298$ K ($\Delta_f H^0_{298}$) has been determined employing an isoperibol solution calorimeter. The standard molar heat capacity (Cp^0) of barium indate was derived from enthalpy increment data measured employing a high temperature calorimeter and the thermodynamic functions such as $H^0_T - H^0_{298}$, Cp^0_m, S^0_T, H^0_T, G^0_T, $-(G^0_T - H^0_{298})/T$, $\Delta_f H^0_T$ and $\Delta_f G^0_T$ have been generated.

1. Introduction

Barium indate ($Ba_2In_2O_5$) has been at the focus of attention due to its potential applications, viz., as fast oxide-ion conductor, as oxygen sensor, as separation membrane and in other electrochemical devices [1–6]. Investigations by various techniques reveals [7,8] two crystallographic phases of this compound those are directly related to its conductivity behavior [9]. Above the transition temperature, $T_t \sim 1198$ K, (from orthorhombic to tetragonal) it shows a dramatic increase in electrical conductivity and is attributed to partial ordering of trapped oxygen vacancies [9]. This has generated high interest on the compound for its possible use as fast ion conductor. On the other hand, on further heating (~1313 K), the order of vacancies is completely lost and the structure reverts back to a highly defective cubic perovskite phase of a pure oxide ion conductor [10]. Apart from these, due to its low activation energy for proton conduction (40 to 60 kJ · mol^{-1}), $Ba_2In_2O_5$ can also find uses as proton conducting oxide (electrolyte) in intermediate temperature (873 to 1073) K solid oxide fuel cell ITSOFC. However, the main challenge involving $Ba_2In_2O_5$ is its thermodynamic stability and its compatibility issues with other materials under reactive chemical environments. In this work we present, the thermodynamic properties of $Ba_2In_2O_5$ such as standard molar enthalpy of formation, standard molar heat capacity and Gibbs free energy of formation, derived from calorimetric measurements. To the best of our knowledge, this is the first thermodynamic study of this compound.

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2. Experimental

2.1. Preparation and characterization

$Ba_2In_2O_5$ was prepared by the solid state reaction of barium carbonate (Alfa Aesar 99.95%) and Indium oxide (Alfa Aesar 99.9). Starting powders were mixed in stoichiometric proportions and thoroughly ground in an agate mortar to make a homogeneous mixture. The mixture was initially heated at $T = 873$ K for 10 h. Heated powder was again ground into fine powder, made into pellet and re-heated at $T = 1373$ K for 12 h. The compound formed was characterized by X-ray diffraction technique using a Philips X-ray diffractrometer (PW-1729) with CuK_α radiation in the 2θ range of (10 to 70)°. The composition of the single phase compound was established from the chemical analysis of the samples using atomic Emission Spectroscopy (AES) (ICP-AES 600, Thermo Fisher). Table 1 gives details of chemical source, purity and analysis method used for chemical analysis of $Ba_2In_2O_5$ and other starting materials. Thermal stability of barium indate was studied using Thermogravimetry–Differential Thermal Analysis (TG-DTA) instrument (SETARAM SETSYS Evolution) under flowing argon atmosphere at a scan rate of 10 K · min^{-1}.

2.2. Solution calorimetric measurements

The standard molar enthalpy of formation of $Ba_2In_2O_5$ at $T = 298$ K was determined from the values of enthalpies of dissolution of $BaCO_3$(s,), $InCl_3$(s), H_2O(l, distilled water) and $Ba_2In_2O_5$(s) in 1:1 (v/v) mixture of HCl and H_2O (11.98 M) solution measured employing an isoperibol solution calorimeter. The construction

TABLE 1
Sample chemical Table.

Chemical compound	Formulas CAS No	Supplier	Purity	Mass fraction	Analytical Method
$BaCO_3$	513-77-9	Alfa Aesar	99.95% metal basis	0.9995	ICP-AES
In_2O_3	1312-43-2	Alfa Aesar	99.9%	0.999	ICP-AES
$InCl_3$	1002582-8	Aldrich	99.9%	0.999	ICP-AES
$Ba_2In_2O_5$		Prepared in Laboratory	99.6% ± 0.6	0.996	ICP-AES

and operation of the calorimeter is similar to the instrument reported earlier [11,12]. Calorimetric measurement was carried out in 0.150 dm^3 of 1:1 (v/v) mixture of HCl (11.98 M) and H_2O solution corresponding to 0.1774 mol fraction of HCl solution equilibrated at T = 298 K. The energy equivalent of the calorimeter was determined by electrical calibration using standard resistance, before and after each of the experiment. The enthalpy change for dissolution of the reactants was determined from the plot of electrical signal (mV) versus time plot recorded during the dissolution process. The amplitude of the mV signal due to temperature change (ΔT) during the reaction was corrected for heat loss processes by the method of Kubaschewski and Alcock [13]. The performance of the calorimeter was tested using KCl standard. For each measurement an accurately weighed sample was introduced into a glass bulb, which was then thermally equilibrated in the calorimetric solvent medium. The glass bulb was broken to introduce the sample into the solvent when a steady state thermal signal was obtained on the mV versus time plot (real time analysis). Using these experimental values and other auxiliary data from literature the enthalpy of formation of $Ba_2In_2O_5$(s) was determined. A correction in enthalpy of dissolution of $BaCO_3$ was applied for evaporation of solvent, where 1 mol of CO_2 was evolved per mole of the solute. The necessary data were obtained from reference [14] for computing this value.

2.3. Heat capacity measurements

The pellets of $Ba_2In_2O_5$(s) were annealed in air at T = 1000 K for 50 h and stored in a desiccator for $H_T^0 - H_{298}^0$ measurements. For the measurements of enthalpy increments of the compound, a high temperature Calvet calorimeter (Model HT-1000) was used. The calorimeter has an isothermal alumina block which contains two identical one end closed alumina cells surrounded by a series of thermopiles. The sample, in the form of a pellet, maintained at T = 298 K in the sample holder, was dropped into the sample cell maintained at a preset experimental temperature. The $H_T^0 - H_{298}^0$ values for $Ba_2In_2O_5$(s) were measured in the temperature range (325 to 973) K. The temperature of the isothermal block was measured using a Pt–Pt10% Rh thermocouple (±0.1 K). The heat flow between the isothermal block and either of the cells was recorded in the form of a millivolt signal of thermo-emf. The details of the experimental measurements have been described elsewhere [15]. The heat calibration was carried out using a synthetic sapphire [NIST SRM-720].

3. Results and discussion

Figure 1 gives the XRD pattern of barium indate prepared by solid state route. The observed pattern is found to be in good agreement with the reported orthorhombic phase of $Ba_2In_2O_5$ (JCPDS No. 30-0068) [16]. No XRD peaks due to the starting components BaO, $BaCO_3$ and In_2O_3 and any other impurity phases were found. The XRD pattern for $Ba_2In_2O_5$(s) could be indexed with orthorhombic structure having cell parameters, a = 16.71(4)°A, b = 6.095(6)°A, c = 5.95(1)°A, against the reported values of a = 16.79°A, b = 6.08°A, c = 5.89°A. The results of thermogravimetric analysis of $Ba_2In_2O_5$ performed under flowing argon atmosphere in the temperature range (298 to 1473) K indicates that there is no observable mass loss due decomposition of the sample and the

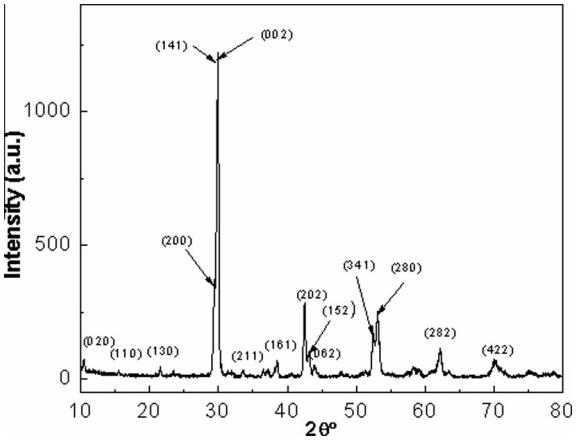

FIGURE 1. XRD pattern of $Ba_2In_2O_5$.

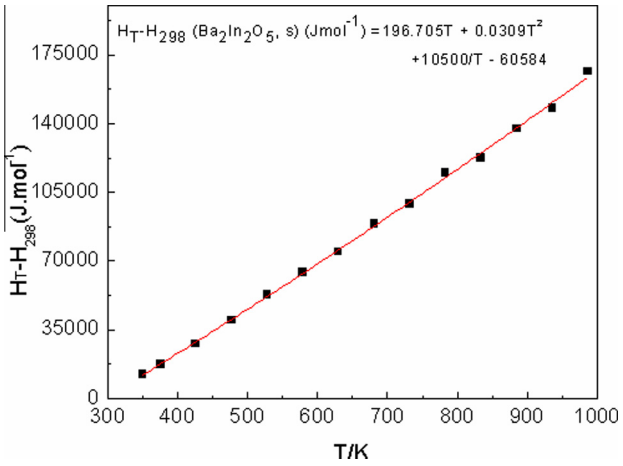

FIGURE 2. Plot of $H_T - H_{298}$ for $Ba_2In_2O_5$(s) as a function of temperature.

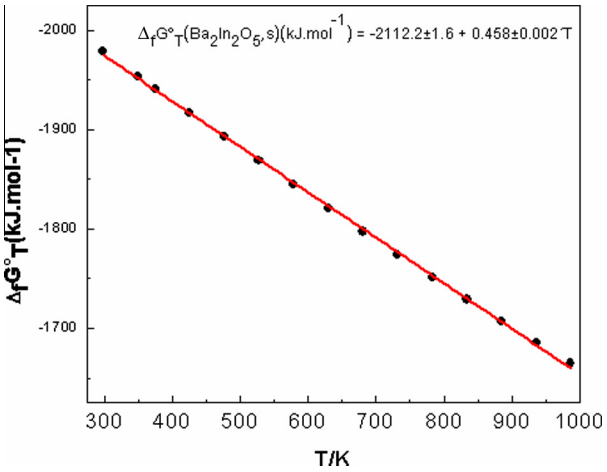

FIGURE 3. Plot free energy of formation of $Ba_2In_2O_5$ as a function of temperature.