

## Thermodynamic Studies on Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub> Employing Calorimeter

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### Abstract

In this study, Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) was synthesized using conventional solid-state reaction route, characterized by powder XRD and SEM-EDAX. The standard molar enthalpy of formation of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) was determined measuring enthalpies of solution of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) in {PbO + B<sub>2</sub>O<sub>3</sub>} solvent (in 2:1 molar ratio) at  $T = 966$  K using an oxide melt solution high temperature calorimeter. The enthalpy increment of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) was measured with same calorimeter. The heat capacity of the Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) was also measured employing DSC. Based on the smoothed values of heat capacity, a table of thermodynamic data from 298 to 1000 K for Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) was also constructed.

**Keywords:** Heat capacity; dsc; high temperature calorimeter; enthalpy of formation; niobates.

### 1. Introduction

During the fission of Mixed OXide (MOX) fuel e.g. (U<sub>x</sub>Pu<sub>1-x</sub>)O<sub>2</sub>; Ba, Sr and Nb are produced among other fission products. They can form ternary or higher order oxides in an operating nuclear reactor with oxide fuels under certain oxygen potential. Evaluations of thermodynamic functions of these oxides are therefore, important for assessment of fission product interactions and modeling of fuel. Furthermore, thermodynamic data of these oxides are also of relevance because of computation of phase diagram and phase stability of pseudo-ternary system BaO-SrO-Nb<sub>2</sub>O<sub>5</sub> and BaO-SrO-Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> etc. in which some of the compounds are potential candidate materials for microwave ceramics with high dielectric constant, electro-optic, pyroelectric and piezoelectric devices [1-10]. Strontium barium niobate (SBN) are also promising candidate as a ferroelectric glass ceramic material. Carruthers and Grasso [11] experimentally investigated the phase equilibria relation in BaO-SrO-Nb<sub>2</sub>O<sub>5</sub> system. In this system, compounds having composition (Ba<sub>5-x</sub>Sr<sub>x</sub>)Nb<sub>4</sub>O<sub>15</sub>, possesses high permittivity and low loss in the microwave frequency region [12]. More recently, a structure refinement of Ba<sub>3</sub>SrM<sub>2</sub>O<sub>9</sub> (M = Nb, Ta) has been reported [13]. It has modified hexagonal BaTiO<sub>3</sub> type structure, where the entire octahedral are skewed around their threefold axis and Nb(V) ions occupy the face-sharing octahedral [13]. However, thermodynamic data of this compound is not available in the literature. As a part of programme to study the thermodynamic properties of fission product compounds, we have report thermodynamic data of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) compound.

In present research, the enthalpy of formation of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) compound was determined using high temperature solution calorimeter. The enthalpy increment and high temperature heat capacity values of the Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) compound were also measured using high temperature calorimeter and differential scanning calorimeter, respectively.

### 2. Experimental procedure

#### 2.1. Synthesis of compounds and characterization

The starting materials used for preparation of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) powders using solid state reaction route for the present study were BaCO<sub>3</sub> (Alfa Aesar, mass fraction 0.9995), SrCO<sub>3</sub> (Alfa Aesar, mass fraction 0.9995) and Nb<sub>2</sub>O<sub>5</sub> (Alfa Aesar, mass fraction 0.999). BaCO<sub>3</sub> and SrCO<sub>3</sub> were first dried in Ar at 200°C for 8 h prior mixing. Stoichiometric amount of carbonates and Nb<sub>2</sub>O<sub>5</sub> were properly mixed using an agate mortar and made into pellets. The pellet was taken in a platinum boat and it was then heated at 900 K inside a muffle furnace, for a period of 120 h. Finally, the above-mentioned pellets were powdered and pressed into pellets, and then the samples were sintered at 1300 K for 48 h. Phase formation and lattice parameters of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) were determined by powder X-ray diffraction technique using the Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) to ascertain the phase purity of the compound. For this, a Miniflex 600 X-ray diffractometer (Model: Rigaku, Japan) using graphite monochromatized Cu K $\alpha_1$  radiation ( $\lambda = 0.15406$  nm) was used. The diffraction data  $g$  was scanned in the range  $10^\circ < 2\theta < 60^\circ$  with a step of  $0.01^\circ$  and 0.3 s dwell time.

The surface morphology of the Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) ceramic powders was investigated by Scanning Electron Microscopy (SEM, JEOL Ltd., JSM-5910LV) equipped with EDS after gold coating.

#### 2.2 High temperature solution calorimetry

The determination of the standard molar enthalpy of formation of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) involved two kinds of calorimetric measurements. The standard molar enthalpy of formation of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub> compound was determined by measuring the enthalpy change for the dissolution of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub> and its starting materials such as BaCO<sub>3</sub>(s), SrCO<sub>3</sub>(s) and Nb<sub>2</sub>O<sub>5</sub>(s) in liquid {PbO + B<sub>2</sub>O<sub>3</sub>} solvent (in 2:1 molar ratio) at 966 K using Alexsys high temperature

calorimeter (Setaram, France). For the sake of better understanding, schematic of calorimeter has been represented in Figure 1.

~7g of {PbO + B<sub>2</sub>O<sub>3</sub>} solvent (in 2:1 molar ratio) was taken in platinum crucible during each experiment. The heat flow signal in microvolt as a function of time was measured. The change in enthalpy per unit mass of solute indicates the infinite dilute condition and composition independency during the experiment. Three sets of solubility experiments for each solute were carried out to check consistency of the experimental data. The calibration of the calorimeter was carried out by adding small pieces of synthetic sapphire [NIST SRM-720] from ambient temperature into reaction platinum crucible, maintained at 966 K [15]. The weight of the sample and synthetic sapphire [NIST SRM-720] was in the range 20-30 and 30-50 mg, respectively. The accuracy of the instrument obtained by using enthalpy increment values of high purity molybdenum (99.997% purity) and NBS standard synthetic sapphire (SRM 720) was better than ±2 %.

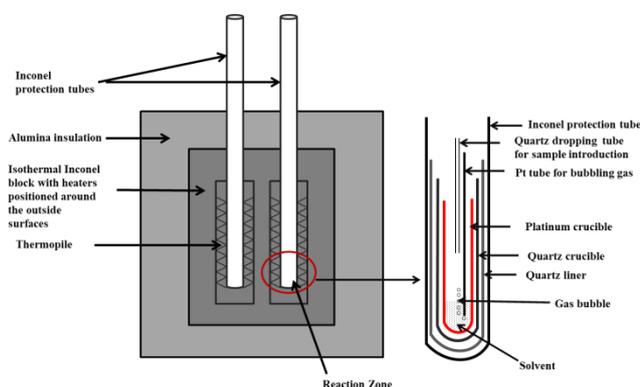


Figure 1. Schematic of high-temperature Calvet-type solution calorimeter (Alexsys-1000, make SETARAM, France).

### 2.3 Measurement of heat capacity using differential scanning calorimeter

A standard three step method i) blank-blank, ii) blank-reference and iii) blank-sample was followed for the determination of the heat flow rate signal of base line, reference vs. signal and sample vs. signal, respectively. Heat capacity measurements of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) were carried out in a platinum crucible with lids using Labsys Evo1600 simultaneous thermal analyzer system (Setaram Instrumentation, France) in C<sub>p</sub> mode. The flow rate of 30 mL·min<sup>-1</sup> of dry argon (purity, 99.9999%) and heating rate of furnace at 5 K·min<sup>-1</sup> with continuous scanning mode was maintained during all measurements. The phase transition temperature of standard reference materials In, Sn, Pb, Al and Ag under the scanning rate of 2, 5 and 10 K·min<sup>-1</sup> was measured for the temperature calibration of the DSC. A temperature correction factor as a function of heating rate was plotted and the value corresponding to zero heating rate was obtained. The corrected temperature was used for the heat capacity measurement of the compound. 400.0 (±0.1) mg of 800 K sintered sample of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) powder was taken into the platinum crucible for measurement. NIST synthetic sapphire (SRM-720, mass fraction purity 0.9999) sample was used as reference material with known heat capacity values taken from the literature [15, 16]. The values of heat capacity of Zirconia (Alfa Aesar, USA, mass

fraction 0.99978) were measured in the same temperature range to check the accuracy of the calorimeter which was found to be within ±2% compared to the literature values [16].

### 2.4 High temperature enthalpy increment

High temperature enthalpy increment measurements of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) were carried out using same high-temperature calorimeter without solvent as given in Figure 1. Each measurement involved at least three consecutive drops of the pellets of the sample and the pieces of the synthetic sapphire α-Al<sub>2</sub>O<sub>3</sub> (SRM-720) in a constant flow of argon gas (purity, 99.9995%). The calibration of the calorimeter was found by comparing the peak area of α-Al<sub>2</sub>O<sub>3</sub> with literature values of enthalpy increment data for α-Al<sub>2</sub>O<sub>3</sub> [15]. At each isotherm, the enthalpy increment values were calculated by taking mean of the values of at least three individual sample drops.

## 3. Result and Discussion

### 3.1 Characterization

The purity of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) powder was ascertained by using X-ray diffraction (XRD) analysis. The XRD pattern of the sample is shown in Figure 2. The XRD pattern of the sample is in well agreement with that of diffraction line of compound given in the reference (JCPDS XRD file No. 35-1157) [17]. The compound crystallizes in the orthorhombic type structure, space group *Pbca* (No. 61) with the cell parameters a = b = 6.0649(2) Å and c = 15.3705(5) Å and were found to be in well agreement with that of reported cell parameters such as a = b = 6.0648(1) Å and c = 15.3703(3) Å [17]. Presence of starting material phases and other unwanted phases were not observed in XRD pattern of the compound.

In SEM analysis, the single phase of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) compound was observed without any impurity phase. The SEM picture of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) is shown in Figure 3a. Elemental analysis of synthesized sample was carried out using EDS technique which is already connected to SEM instrument (Figure 3b). The Ba, Sr and Nd atomic ratio obtained from EDS analysis was found to be the same as the formulae ratio of these metals present in the Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s). The accuracy of EDS analysis is equal to ±2%.

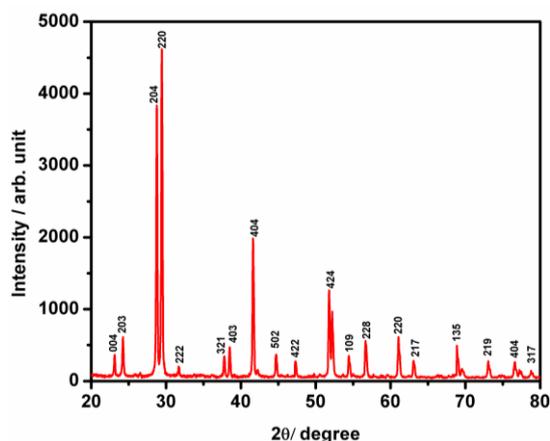


Figure 2. Powder XRD pattern of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s).

The phase purity of Ba<sub>3</sub>SrNb<sub>2</sub>O<sub>9</sub>(s) is confirmed from results of all characterization techniques. The percentage of elemental composition of Ba, Sr and Nd metals are given in Table 1.

Table 1. Elemental composition of Ba, Sr and Nb from EDS spectrum.

Element	EDS (At%)	Theor.(At%)
Ba	50.2	48.9
Sr	16.5	15.5
Nb	33.3	35.6
Total	100	100

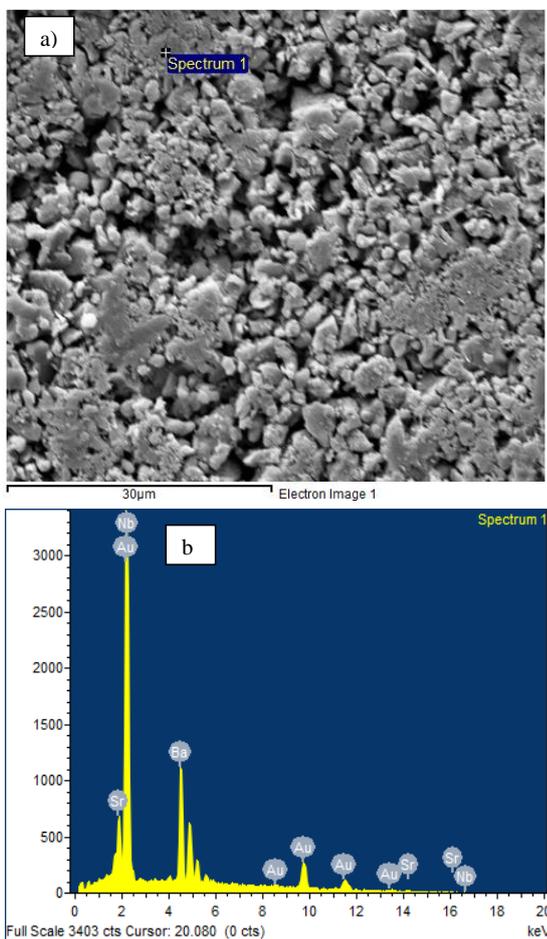


Figure 3. SEM-EDS analyses of  $Ba_3SrNb_2O_9$  a) SEM micrograph at  $\times 5000$  magnification, b) EDS spectrum.

### 3.2 High-temperature enthalpy increment

The mean of enthalpy increment data of the compound from three set of experiments at each temperature is given in Table 2, along with corresponding measurement errors. The relative deviation (RD%) between experimental and calculated enthalpy increments was found to better than 2%. The least square fitting of experimental values of enthalpy increment as function of temperature is given in Eq. (1).

$$H(T)-H(298) \text{ (J}\cdot\text{mol}^{-1}) (\pm 2\%) = -118256 + 340.77 \times T + 0.03728 \times T^2 + 3991943.6/T \quad (1)$$

The two boundary conditions were used during fitting (i) enthalpy increment value is zero at 298.15 K and (ii) heat capacity of the compound is  $319.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , at 298.15 K. The heat capacity at 298.15 K for the compound was taken from the calculated heat capacity using Neuman-Kopp's additivity method [16]. The enthalpy increment values from experimental and fitted values are plotted in Figure 4.

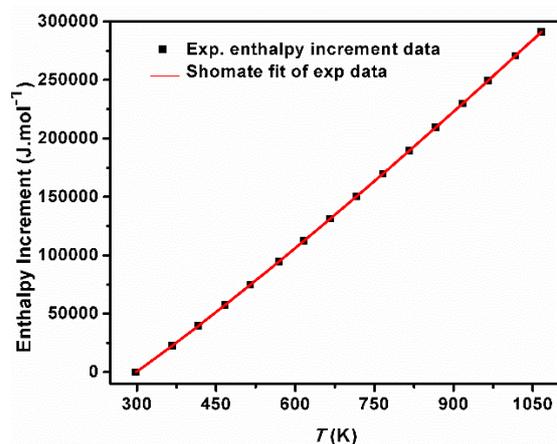


Figure 4. Enthalpy increment of  $Ba_3SrNb_2O_9$  compound.

Table 2. Comparison of experimental and calculated enthalpy increment data of  $Ba_3SrNb_2O_9$ .

T (K)	H(T)-H(298) (exp) (J.mol <sup>-1</sup> )	H(T)-H(298) (Calc) (J.mol <sup>-1</sup> )	RD%
298	-	0	-
367	22817.5	22705.0	0.5
416	39450.9	39551.9	0.3
467	57393.8	57562.0	0.3
515	74500.9	74879.5	0.5
569	94775.6	94727.7	0.1
616	112275.5	112284.9	0.0
666	131372.5	131226.5	0.1
716	149350.6	150422.5	0.7
766	169135.5	169859.5	0.4
816	190959.9	189527.5	0.8
866	208773.5	209418.8	0.3
917	230078.1	229931.7	0.1
965	248578.2	249439.8	0.3
1017	268280.9	270790.6	0.9
1066	289646.3	291113.0	0.5

### 3.3 Measurement of heat capacity

The molar heat capacity of  $Ba_3SrNb_2O_9$  (s) was measured in the temperature range from 350 K – 900 K. Change of heat capacities values of the  $Ba_3SrNb_2O_9$  was plotted as a function of temperature and shown in Figure 5. Best of our knowledge the heat capacity values of  $Ba_3SrNb_2O_9$  (s) is not available in literature. Least square fitting of individual values of heat capacities in the temperature interval 350 K – 900 K, is represented as

$$C_{p,m}^o \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = (340.7 \pm 0.6) + (0.075 \pm 0.001) \times (T/K) - (3991943.6 \pm 53751.1) / (T/K)^2 \quad (350 \leq T/K \leq 900) \quad (2)$$

The heat capacity of  $Ba_3SrNb_2O_9$  (s) at 298 K is estimated using Neuman-Kopp's additivity method [16] and the value is found to be  $319.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  which is in good agreement with the extrapolated values calculated from fitted heat capacity values in Eq. (2). The experimental heat capacity values and estimated Neumann-Kopp's values of heat capacity of the compound are shown in the Figure 5. It can be seen that the heat capacity values obtained directly from DSC is slightly higher than the values calculated using Neumann-Kopp's rule of additivity.

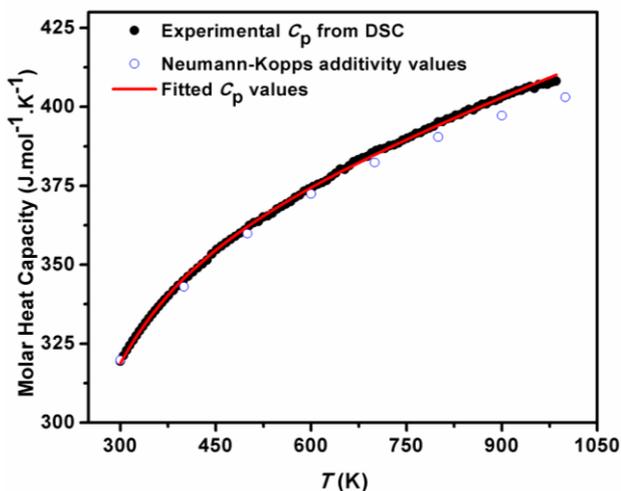


Figure 5. Heat Capacity of  $Ba_3SrNb_2O_9$  compound.

### 3.4. Enthalpy of formation using high temperature oxide melt solution calorimetry

Standard molar enthalpy of formation of  $Ba_3SrNb_2O_9$  (s) sample was derived from the enthalpy of dissolution data of the compound and its component oxides viz.,  $BaO$ (s),  $SrO$ (s) and  $Nb_2O_5$ (s) in molten  $PbO+B_2O_3$  (2:1 molar ratio) solvent maintained at 966 K. Since alkaline earth oxide MO (where M= Ba/Sr) is highly hygroscopic and reactive material, the value of molar enthalpy of dissolution of MO(s) was therefore, obtained indirectly using a separate thermo chemical cycle employing enthalpy of dissolution of their carbonates  $MCO_3$ (s). The details of the experimental measurements have been described elsewhere [14]. Table 3 gives the thermo-chemical cycle for derivation of standard molar enthalpies of dissolution of MO (s, 298K). The enthalpies of decomposition of alkaline earth carbonate,  $\Delta_{decom}H(MCO_3)$ , for  $BaCO_3$  and  $SrCO_3$  are  $-269.2$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $-234.3$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. The value of enthalpy increment of  $CO_2$  (g) was taken from literature and is equal to  $32$   $\text{kJ}\cdot\text{mol}^{-1}$  [16]. Enthalpy increments for carbonates are measured at the same experimental temperature and are used for the calculation. The enthalpy of solution of  $BaO$  and  $SrO$ , when added from 298.15 K,  $\Delta_{ds}H(MO)$ , also known as enthalpy of drop solution, is calculated to be  $-93.3$  and  $-59.5$   $\text{kJ}\cdot\text{mol}^{-1}$ . The enthalpy of solution of the  $Nb_2O_5$ (s) in liquid  $PbO + B_2O_3$  (2:1) solvent at 966 K at infinite dilution was measured for few successive additions and presented in Table 4.

Table 3. Standard molar enthalpies of dissolution of MO(s, 298K) (where M=Ba/Sr); sol= molten  $PbO + B_2O_3$  (2:1) solvent at 966 K;  $\Delta_{ds}H_{298}^o(MO) = \Delta H_1 + \Delta H_2 + \Delta H_3$ .

Reactions	$\Delta H_i$	Ref.
$MCO_3(s, 298 K) + \text{sol}(T K) = (MO)\text{sol}(T K) + CO_2(g, T)$	$\Delta H_1$	This Work
$MO(s, 298 K) + CO_2(g, 298 K) = MCO_3(s, 298 K)$	$\Delta H_2$	Ref. [16]
$CO_2(g, T K) = CO_2(s, 298 K)$	$\Delta H_3$	Ref. [16]
$MO(s, 298 K) + \text{sol}(T K) = (MO)\text{sol}(T K)$	$\Delta_{ds}H_{298}^o$	This Work

The calculated values of enthalpy of drop solution of  $BaO$  and  $SrO$ , obtained from present experiment using lead borate solvent and other literature data using lead borate solvent and sodium molybdate solvent are given in Table 5.

The enthalpy of solution of  $Nb_2O_5$  in lead borate solvent is not available in literature to the best of our knowledge. The values of enthalpy of drop-solution of  $Nb_2O_5$  in lead borate solvent and in sodium molybdate solvent are compared in Table 5. It indicates that enthalpy of drop-solution of  $Nb_2O_5$  in lead borate solvent is more exothermic than that in the sodium molybdate solvent. However, the dissolution of  $Nb_2O_5$  in both the solvent is slow.

Table 4. The molar enthalpy of dissolution of  $Ba_3SrNb_2O_9(s)$  and  $Nb_2O_5(s)$  in molten  $PbO+B_2O_3$  (2:1 molar ratio) solvent maintained at  $966.1 \pm 0.1$  K and  $P = 0.1$  MPa;  $\Delta_{ds}H_m$  = molar enthalpy of drop solution.

Solute	Mass /mg	$\Delta_{ds}H$ / $\text{kJ}\cdot\text{mol}^{-1}$
$Ba_3SrNb_2O_9$ (s)	11.2	341.5
Mol. Mass	11.1	343.2
=829.41 $\text{g}\cdot\text{mol}^{-1}$	11.1	343.9
	11.3	344.0
	11.3	343.9
	11.4	344.1
		Mean: $344.5 \pm 3.5$
$Nb_2O_5$ (s)	10.4	68.1
Mol. Mass	11.8	65.0
= 265.81 $\text{g}\cdot\text{mol}^{-1}$	11.4	66.5
	10.6	66.6
	10.3	66.3
	11.6	65.6
		Mean: $66.6 \pm 1.9$

In present experiments, enthalpy of drop solution of the  $Ba_3SrNb_2O_9$ (s) compound in liquid  $PbO + B_2O_3$  (2:1) solvent at  $T = 966$  K at infinite dilution was and given in Table 4.

The values of enthalpies of solution of the compound are composition independent and random in nature. This indicates that there is no significant dilution effect and the infinite dilution condition is maintained during each experiment.

Table 5. Comparison of enthalpy of drop-solution ( $\Delta_{ds}H$ ) of  $BaO$ ,  $SrO$  and  $Nb_2O_5$  in different solvent. The error is twice the standard deviation of the mean.

Compo	$\Delta_{ds}H/\text{kJ}\cdot\text{mol}^{-1}$ in und (2PbO+B <sub>2</sub> O <sub>3</sub> ) solvent	$\Delta_{ds}H/\text{kJ}\cdot\text{mol}^{-1}$ in (3Na <sub>2</sub> O+4MoO <sub>3</sub> ) solvent
BaO	$-94.2 \pm 1.7$ at 966 K [This study]	-
	$-90.8 \pm 2.2$ at 975 K [18]	
SrO	$-59.5 \pm 1.69$ at 966 K [This study]	$-134.47$ at 973 K [20]
	$-60.5 \pm 2.0$ at 975 K [19]	$-135.82 \pm 2.5$ at 975 K [21]
		$-131.42 \pm 1.9$ at 975 K [22]
		$-129.25$ at 1073 K [23]
$Nb_2O_5$	$66.6 \pm 1.9$ at 975 K [This study]	$141.8 \pm 6.0$ at 1073 K [20]
		$91.97 \pm 0.78$ at 973 K [24]

Thermodynamic cycles were constructed to calculate the enthalpy of formation of  $Ba_3SrNb_2O_9$  from the elements and are presented in Table 6. The  $\Delta_f H_m^o(298.15$  K) of the compound from the elements is  $-4772.2 \pm 5.1$   $\text{kJ}\cdot\text{mol}^{-1}$ . Enthalpy of formation of the component oxides,  $BaO$ (s),  $SrO$ (s) and  $Nb_2O_5$ (s) are taken from ref. [16].

The standard molar entropy of compound at 298 K,  $S_{298}^0$  ( $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$ ), has been estimated by adding the standard molar entropies ( $S_{298}^0$ ) of component oxides, viz.  $\text{BaO}(\text{s})$ ,  $\text{SrO}(\text{s})$ ,  $\text{Nb}_2\text{O}_5(\text{s})$  in their molar ratio, from the literature [16]. The entropy ( $S_{298}^0$ ) value at 298 K estimated in this study is  $404.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , the enthalpy of formation of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  from its constituent elements ( $-4772.2 \text{ kJ}\cdot\text{mol}^{-1}$ ) [This Study], and the entropies of Ba ( $62.42 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) [16], Sr ( $55.69 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) [16], Nb ( $36.40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) [16] and  $\text{O}_2$  ( $205.04 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) [16] were used to calculate the standard Gibbs energy of formation of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$ :

$$\Delta_f G_{298}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})) = \Delta_f H_{298}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})) - 298 \times 0.001 \times [S_{298}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})) - 3 \times S_{298}^0(\text{Ba}(\text{s})) - S_{298}^0(\text{Sr}(\text{s})) - 2 \times S_{298}^0(\text{Nb}(\text{s})) - 4.5 \times S_{298}^0(\text{O}_2(\text{g}))]$$

$$= -4523.4 \text{ kJ}\cdot\text{mol}^{-1}$$

The standard molar enthalpy of formation of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  with respect to the constituent oxides (i.e.,  $\text{BaO}$ ,  $\text{SrO}$  and  $\text{Nb}_2\text{O}_5$ ) at 298 K is found to  $-620.2 \text{ kJ}\cdot\text{mol}^{-1}$ . This indicates that  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  is relatively more stable compared to its binary oxides.

#### 4. Thermal function of the $\text{Ba}_3\text{SrNb}_2\text{O}_9$ compound

The standard molar enthalpy of formation of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  determined by high-temperature calorimetric technique is listed in Table 7. The smoothed values of measured heat capacity at regular interval of temperature were used to estimate the standard molar

entropy and enthalpy for  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$ . The standard molar entropy and enthalpy for  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  are related to heat capacity as per the relation (3) and (4) respectively.

$$S_{TK}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9) - S_{298\text{K}}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9) = \int_{298\text{K}}^{TK} (C_p^0(\text{Ba}_3\text{SrNb}_2\text{O}_9)/T) dT \quad (3)$$

$$\Delta H_{TK}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9) - \Delta H_{298\text{K}}^0(\text{Ba}_3\text{SrNb}_2\text{O}_9) = \int_{298\text{K}}^{TK} C_p^0(\text{Ba}_3\text{SrNb}_2\text{O}_9) dT \quad (4)$$

The calculated values of these thermodynamic functions have been presented in Table 7, and have an uncertainty of within  $\pm 2-3\%$ . It is evident that the entropy and enthalpy changes gradually increase with temperature and thus mimic the signature of the non-magnetic compounds. The standard molar entropy of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  was estimated by adding the standard molar entropies of component oxides in their respective molar ratio from the literature [16].

Free energy function (FEF) for compound can be derived using the following "Eq. (5)":

$$\text{FEF} = -(H_T^0 - H_{298}^0) / T + S_T^0 \quad (5)$$

The Free energy function (FEF) of the compound also listed in Table 7 as a function of temperature. Uncertainties for thermodynamic functions were calculated as twice the standard deviation ( $\pm 2\sigma$ ) of the experimental values.

Table 6. Thermodynamic cycles for the standard molar enthalpy of formation ( $\Delta_f H_m^0$  at 298 K) of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  from elements.

Reactions	Enthalpy per mole
$\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s}, 298 \text{ K}) \rightarrow 3\text{BaO}(\text{dis}, 966 \text{ K}) + \text{SrO}(\text{dis}, 966 \text{ K}) + \text{Nb}_2\text{O}_5(\text{dis}, 966 \text{ K})$	$\Delta H_1$
$3\text{BaO}(\text{s}, 298 \text{ K}) \rightarrow 3\text{BaO}(\text{dis}, 966 \text{ K})$	$\Delta H_2$
$\text{SrO}(\text{s}, 298 \text{ K}) \rightarrow \text{SrO}(\text{dis}, 966 \text{ K})$	$\Delta H_3$
$\text{Nb}_2\text{O}_5(\text{s}, 298 \text{ K}) \rightarrow \text{Nb}_2\text{O}_5(\text{dis}, 966 \text{ K})$	$\Delta H_4$
$\text{Ba}(\text{s}, 298 \text{ K}) + 0.5\text{O}_2(\text{g}, 298 \text{ K}) \rightarrow \text{BaO}(\text{s}, 298 \text{ K})$	$\Delta H_5$
$\text{Sr}(\text{s}, 298 \text{ K}) + 0.5\text{O}_2(\text{g}, 298 \text{ K}) \rightarrow \text{SrO}(\text{s}, 298 \text{ K})$	$\Delta H_6$
$2\text{Nb}(\text{s}, 298 \text{ K}) + 2.5\text{O}_2(\text{g}, 298 \text{ K}) \rightarrow \text{Nb}_2\text{O}_5(\text{s}, 298 \text{ K})$	$\Delta H_7$
$3\text{Ba}(\text{s}, 298 \text{ K}) + \text{Sr}(\text{s}, 298 \text{ K}) + 2\text{Nb}(\text{s}, 298 \text{ K}) + 4.5\text{O}_2(\text{s}, 298 \text{ K}) \rightarrow \text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s}, 298 \text{ K})$	$\Delta H_8$
Hence, $\Delta_f H_m^0$ at 298 K of $\text{Ba}_3\text{SrNb}_2\text{O}_9 = \Delta H_8 = -\Delta H_1 + 3 \times \Delta H_2 + \Delta H_3 + \Delta H_4 + 3 \times \Delta H_5 + \Delta H_6 + \Delta H_7$	

Table 7. Thermodynamic functions for the compound  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$ .

$T / \text{K}$	Fitted $C_p$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	NK $C_p$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$(S_T^0 - S_{298.15}^0)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$(H_T^0 - H_{298.15}^0)$ / $\text{kJ}\cdot\text{mol}^{-1}$	fef/ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
298	318.1	319.3	0	0	404.1
300	318.8	319.8	2.1	0.64	404.1
400	345.6	343.1	97.9	33.99	417.0
500	362.1	359.9	176.9	69.43	442.2
600	374.4	372.5	244.1	106.28	471.0
700	384.8	382.4	302.6	144.25	500.6
800	394.2	390.5	354.6	183.21	529.7
900	402.9	397.3	401.6	223.07	557.8
1000	411.3	403.1	444.4	263.79	584.7

## 5. Conclusions

Standard enthalpy of formation of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  is determined employing oxide melt solution calorimeter for the first time and is found to be  $-4772.2 \pm 5.1 \text{ kJ}\cdot\text{mol}^{-1}$ . The molar heat capacity and enthalpy increment of the  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  is measured using DSC and high temperature isothermal calorimeter, respectively. The standard molar heat capacity of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  derived from the measured ( $H_T - H_{298}$ ) values and data obtained from DSC experiment are in good agreement with each other and given in the Table 7. Smoothed heat capacities values are used for the calculation of the thermodynamic table. The values of standard thermodynamic functions for  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  at  $T = 298 \text{ K}$  are:  $C_{p,m}^\circ(298 \text{ K}) = 318.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ;

$\Delta_f H_m^\circ(298 \text{ K}) = -4772.2 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta_f G_m^\circ(298 \text{ K}) = -4523.4 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $f_{ef}(298 \text{ K}) = 404.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . These data, therefore, are important for assessment of fission product interactions and for modeling of fuel thermodynamics which plays an important role in predicting long term stability of these materials under different reactive conditions. Enthalpy of formation and Gibbs energy formation data for this compound would be useful for predicting the stability of the compound in different physico-chemical conditions. The standard entropy of  $\text{Ba}_3\text{SrNb}_2\text{O}_9(\text{s})$  derived in this study can be obtained more accurately from the low temperature heat capacity measurement.

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