



## Thermodynamic stability of SrThF<sub>6</sub>(cr) and BaThF<sub>6</sub>(cr)

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### ABSTRACT

In the present paper we report the standard molar Gibbs energy of formation of SrThF<sub>6</sub> and BaThF<sub>6</sub> measured by gas equilibration method employing transpiration technique. The chemical equilibrium between MThF<sub>6</sub>(cr) (M = Sr, Ba) and moisture:  $MThF_6(cr) + 2H_2O(g) = MF_2(cr) + ThO_2(cr) + 4HF(g)$  has been employed to determine thermodynamic stability of these compounds. The equilibrium constant 'K<sub>p</sub>' at different temperatures was calculated using partial pressure of HF(g) measured at a fixed vapour pressure of water p(H<sub>2</sub>O). The Gibbs energy of formation for SrThF<sub>6</sub>(cr) and BaThF<sub>6</sub>(cr) could be expressed as:  $\Delta_f G_m^\circ(\text{SrThF}_6, \text{cr})(\pm 8 \text{ kJ mol}^{-1}) = -3288 + 0.3776 T$  and  $\Delta_f G_m^\circ(\text{BaThF}_6, \text{cr})(\pm 7 \text{ kJ mol}^{-1}) = -3292 + 0.378 T$ . The isobaric heat capacity of these compounds was measured employing differential scanning calorimetric technique. Based on the experimental results thermodynamic functions for SrThF<sub>6</sub> and BaThF<sub>6</sub> have been generated.

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## 1. Introduction

Molten Salt Breeder Reactor (MSBR) is a class of generation IV nuclear reactor, where the proposed fuel in the form of molten salt (8.6 wt % UF<sub>4</sub> + 68.9 wt % ThF<sub>4</sub> + 22.5 wt % LiF) will be circulated through the heat exchangers [1–3]. These reactors have several advantages such as online reprocessing of spent fuel, potentiality to achieve self sustainable <sup>233</sup>U/Th cycle, reliability and proliferation resistance etc. MSBR is an inherently safe reactor as in the case of loss of coolant scenario (LOCA) the fuel can be drained out of the core safely [4]. Since the molten salt is continuously circulated through the heat exchanger, interaction of the corrosive molten salt with the structural material is of primary concern. Thermodynamic analysis of molten salt systems is therefore very important for the long term containment of molten fuel salt. Data on the thermodynamic properties of the molten salt systems including the compounds that could be formed due to possible interactions between fuel, fission products and the constituents of the clad are necessary to predict performance of MSBR system. Among others 'Sr' and 'Ba' are the two major fission products formed in significant amount during fission (~10% yield). Formation of Sr and Ba bearing compounds with higher melting points in the fuel salt mixture may affect thermo-physical properties of the molten salt nuclear fuel

system. Information on the thermodynamic stability of these compounds is therefore important to predict formation of these compounds in the molten fuel salt. In addition thermodynamic data are useful for the assessment of MF<sub>2</sub>-ThF<sub>4</sub> phase diagram. MThF<sub>6</sub> is the only compound in pseudo binary MF<sub>2</sub>-ThF<sub>4</sub> (M = Sr and Ba) system. Zachariasen [5] and Salzer et al. [6] have reported crystal structure of SrThF<sub>6</sub>. D'Eye et al. [7] have studied high temperature solubility and phase diagram of SrF<sub>2</sub>-ThF<sub>4</sub> system. Crystal structure of BaThF<sub>6</sub> has been studied by many investigators viz. Friese et al. [8], Keller et al. [9], Salzer et al. [6] and Zachariasen et al. [5]. P. Mesnard et al. [10] have reported the luminescent properties of 'Ce' doped in BaThF<sub>6</sub>. Differential thermal analysis of BaThF<sub>6</sub> carried out by Maxwell et al. [11] shows that the compound melts incongruently above 1423 K. In the present work we have determined the thermodynamic stabilities of SrThF<sub>6</sub> and BaThF<sub>6</sub> by gas equilibration method employing dynamic transpiration technique and the heat capacity by differential scanning calorimetry. To the best of our knowledge, thermodynamic properties of SrThF<sub>6</sub> and BaThF<sub>6</sub> have not been reported in the literature.

## 2. Experimental

### 2.1. Materials

High purity SrF<sub>2</sub> and BaF<sub>2</sub> (>99.9%, M/s Alfa Aesar, USA) and ThF<sub>4</sub> (Nuclear Grade, BARC) were used in the sample preparation. Since ThF<sub>4</sub> shows an additional tendency to oxidize and form

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oxyfluorides, it was purified by heating it with fluorinating agent  $\text{NH}_4\text{HF}_2$  as described in literature [12].  $\text{SrF}_2$  and  $\text{BaF}_2$  were also subjected to pre-heat treatments at 673 K under inert argon flow to remove any residual moisture. Furthermore, the purity of the starting compounds was confirmed by X-ray analysis, which indicated pure phase with no contaminants. All the materials after purification were stored inside an argon glove box having very low level of oxygen and water (typically below 5 ppm).

## 2.2. Synthesis and characterization

The ternary fluorides viz.,  $\text{MThF}_6$  ( $M = \text{Sr}, \text{Ba}$ ) were prepared by conventional solid state reaction route by heating equimolar amounts of  $\text{MF}_2$  and  $\text{ThF}_4$ .  $\text{MF}_2$  and  $\text{ThF}_4$  were intimately mixed by an agate mortar and pressed into cylindrical pellets in a glove box. These green pellets were subsequently heated under dynamic vacuum of  $10^{-6}$  mbar at 1100 K and 1273 K for 10 h in a platinum crucible for  $\text{SrThF}_6$  and  $\text{BaThF}_6$  respectively. In order to avoid any interference due to oxygen, zirconium sponge was used as a getter. The mass of the pellets were measured before and after the reaction to monitor any change in the composition during heating cycle. The purity of these compounds was ascertained by powder X-ray diffraction (XRD) technique. The Powder XRD measurements of the samples were carried out on a Pan Analytical X-pert Pro diffractometer using  $\text{CuK}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation and Ni filter. The operating conditions were 30 kV and 20 mA, in the  $2\theta$  range  $10\text{--}70^\circ$ .

## 2.3. Heat capacity measurements

Heat capacity  $Cp_m^o(T)$  of  $\text{SrThF}_6$  and  $\text{BaThF}_6$  compounds was measured employing a Mettler Toledo differential scanning calorimeter (DSC-1). The temperature and heat flow calibration of the DSC were performed by melting high purity 'In' and 'Zn' standards. Heat capacity measurements were carried out in the temperature range of 300–700 K. High pure argon gas was passed at a flow rate of  $0.02 \text{ dm}^3 \text{ min}^{-1}$  over the sample. For measurement of  $Cp_m^o(T)$ , blank, sapphire and sample were heated in a continuous mode at a heating rate of 7.5 K/min. The heat flow signal for the blank was subtracted from that of sample and sapphire. The heat capacity of the sample was determined from the subtracted heat flow signals of sample and sapphire using STARe Software provided by M/s Mettler. For each measurement about 120–130 mg of sample was pelletized and loaded in a sealed 40  $\mu\text{l}$  aluminium pan.

## 2.4. Vapour pressure measurement by transpiration technique

Fig. 1 gives the sketch diagram of transpiration apparatus used in the present experiment. Details of this transpiration equipment have been described elsewhere [13]. The novel dynamic vertical transpiration system consisting of a micro thermo balance (SETARAM, Model B-24) had mass sensitivity of  $\pm 0.1 \mu\text{g}$ . One 'S' type thermocouple (Pt-10%Rh, Pt) located very close to the sample ( $\sim 5 \text{ mm}$ ) was used for measuring the sample temperature. The sample and the thermocouple were placed well within the uniform heating zone of the reaction tube. The temperature calibration was carried out at melting points of pure metals viz., Sn, Al and Ag following the drop method [14]. The calibration was found to conform to ITS-90 scale [15]. A two tier Pt holder served as sample container during all the experiments. High purity (HP) argon saturated with moisture was used as carrier gas during all vaporization experiments involving  $\text{MThF}_6$  ( $M = \text{Sr}, \text{Ba}$ ). In order to measure the vapour pressure of the compounds, it is necessary to establish the equilibrium condition for the vaporization reaction

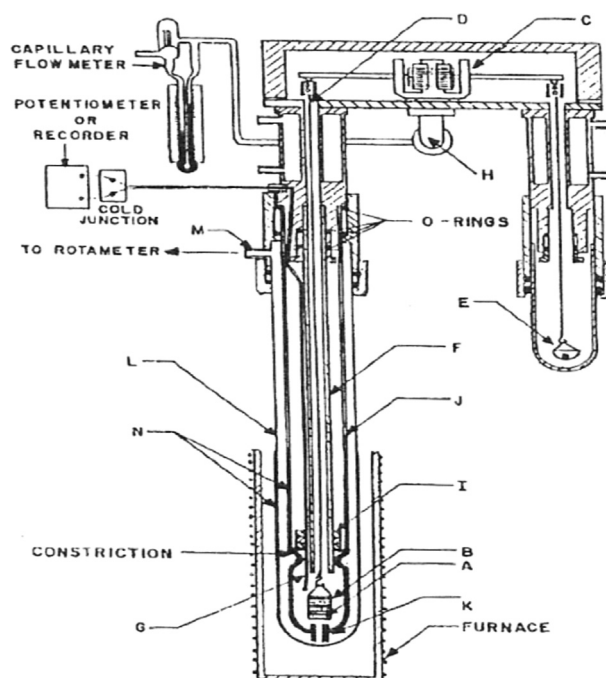


Fig. 1. Sketch diagram of micro thermo-balance assembly used as transpiration apparatus. A: Sample, B: Sample holder, C: Balance, D: Platinum suspension wire, E: Counter Balance, F: Inner tube, G: Thermocouple, H: Balance rest, I: Constrictions, J: Reaction tube, K: Capillary, L: Outer tube, M: Flow meter, N: Platinum coating, O: O-rings.

and co-existing phases in equilibrium with the vaporizing compound over the temperature range of measurement. The equilibrium condition for the measurement of vapour pressure was established by measuring apparent vapour pressure as a function of carrier gas (argon) flow rate swept over the samples at the mean temperature of vaporization reaction. The region where the apparent vapour pressure of vapour species is independent of flow rate (plateau region) of the carrier gas was assigned to the equilibrium condition between solid and vapour phases. The measurement of vapour pressure at different temperatures was carried out using the constant flow rate of the carrier gas in the plateau region. The instrument was calibrated by measuring the vapour pressure of standard  $\text{CdI}_2$  sample. Details of the calibration are given in the [supplementary information](#).

## 3. Results and discussion

No observable mass change of the sample pellets was found after heating cycle indicating that the composition of the samples has remained unchanged during synthesis. Figs. 2 and 3 show the XRD patterns of  $\text{SrThF}_6$  and  $\text{BaThF}_6$  samples respectively. No other XRD peak due to impurity phases including starting materials viz.,  $\text{MF}_2$  and  $\text{ThF}_4$  or oxy-fluoride compounds could be observed.  $\text{SrThF}_6$  and  $\text{BaThF}_6$  compounds were found to crystallize in hexagonal crystal lattice with space group  $P-31c$  (163) and  $P6_3/mmc$  (194), respectively. The observed cell parameters for  $\text{SrThF}_6$  are found to be  $a = 4.133(4) \text{ \AA}$  and  $c = 7.374(7) \text{ \AA}$  against the reported values of  $a = 4.133 \text{ \AA}$  and  $c = 7.342 \text{ \AA}$  [5]. The corresponding values for  $\text{BaThF}_6$  are found to be  $a = 4.277(4) \text{ \AA}$  and  $c = 7.541(6) \text{ \AA}$  against the reported values of  $a = 4.296 \text{ \AA}$  and  $c = 7.571 \text{ \AA}$  [8].

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