Indian Molten Salt Breeder Reactor

Thermophysical Properties of Frozen Coolant Salt

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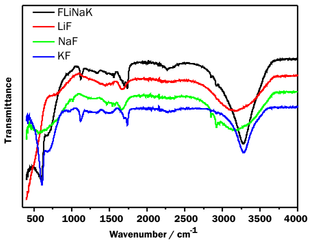

IR spectrum of
FLiNaK, LiF, NaF and KF

ABSTRACT

This report summarises experimental data on thermo physical properties of frozen coolant salt for high temperature Molten Salt Breeder Reactor (MSBR). Based on superior physical, nuclear and chemical properties, eutectic mixture containing 46.5 mol. % LiF, 11.5 mol. % NaF and 42.0 mol. % KF (FLiNaK) has been proposed as coolant salt for MSBR. In this report, thermo-physical data of frozen coolant salt such as melting point, latent heat of fusion, thermal conductivity, density, heat capacity, coefficient of thermal expansion etc. are presented which are required to calculate its heat transport properties. This data is necessary for the accurate design of freeze valve which is a key component of MSRs passive safety system.

KEYWORDS: Molten salt reactor, Coolant salt, FLiNaK, Freeze valve, Passive safety, Thermo-physical properties.

Introduction

Molten salt breeder reactor (MSBR) is one among the six innovative reactor concepts proposed by Generation IV international forum (GIF) to establish enhanced sustainability, feasibility, safety, high thermal efficiency and proliferation resistance[1-5]. At ORNL, from 1958 to 1976, molten salt reactor program was operated with the objective of development of fluid fuelled nuclear reactor[6]. In these reactors, fuel (fissile or fertile material dissolved in suitable carrier salt) is circulated through heat exchangers, hence these fluids act as both fuel (producing heat) and coolant (transferring the heat). As a part of three stage Indian nuclear power programme, for effective utilization of its large thorium reserves, MSRs are considered as long term sustainable solution for energy demand. For Indian molten salt breeder reactor (IMSBR) the proposed fuel (also primary coolant) is mixture of LiF-CaF$_2$-ThF$_4$-UF$_4$ (70:8:20.6:1.4 mol.%) and coolant (secondary) is eutectic mixture of LiF-NaF-KF (46.5:11.5:42 mol.%) i.e. FLiNaK. For enhanced safety in these Gen IV reactors, passive shut down system is key component. In MSRs, instead of relying only on traditional nuclear safety approach of inserting control rods to make nuclear reactor subcritical, self-draining (transfer) of molten salt into passively cooled subcritical tanks due to gravity in case of any power outage scenario, is efficient safe shut down mechanism. After draining, molten salt solidifies in drain tanks and hence trapping dangerous radioactive fission products. A critical component of the molten salt (fuel as well as coolant) circuit and the associated salt conditioning system is the freeze valve[7-10], where the flow of molten salt is prevented by freezing a section of the pipe (solid plug) during reactor normal operation. In the accidental scenario, when the reactor overheats due to failure of other active control systems, the plug will melt. During any accidental scenario, failure of this freeze valve to thaw the molten salt poses a major safety concern regarding integrity of the fuel salt system. It could lead to release of hazardous material in the environment[11]. Hence the accuracy in the design of the freeze valve becomes very important in order to ensure more efficient passive shutdown system. In order to optimise its design, the freeze and thaw phenomena of the molten salt (fuel and coolant) needs to be modelled, for which the thermo-physical data of both fuel and coolant salt is required[10,12-16]. In the present study, data on thermo-physical parameters of frozen coolant salt are reported. These data are required to estimate the melting time for the frozen salt in the coolant salt drain tank when salt needs to be put back in reactor system after any necessary repairs (maintenance) / trouble – shooting event.

Salt Preparation and Characterization

The sample was prepared by thoroughly mixing perfectly dried constituent fluoride salts i.e. LiF, NaF and KF of desired molar ratio in an agate mortar. As this salt mixture is highly hygroscopic, it was first heated at 473 K under dynamic vacuum (10^{-3} mbar) for 48 hours to remove the moisture. The sample was then melted at 823 K and homogenized for 10 hours at the same temperature under dynamic vacuum. The phase purity of thus prepared salt was ascertained using powder X-ray diffraction (XRD) technique. X-ray diffraction pattern of FLiNaK was recorded employing Cu $K\alpha$ radiation of PANalytical X-pert Pro diffractometer. Since FLiNaK is highly hygroscopic so perfectly dried FLiNaK was covered with kapton tape for recording its XRD pattern. Analysis of XRD pattern for phase identification was aided by the ICDD-PDF-2 database.

The observed reflections in the powder XRD data of FLiNaK are found to be in good agreement with reported XRD pattern[17]. XRD pattern of frozen FLiNaK shows peaks of starting compounds i.e. LiF(s), NaF(s) and KF(s). No peak due

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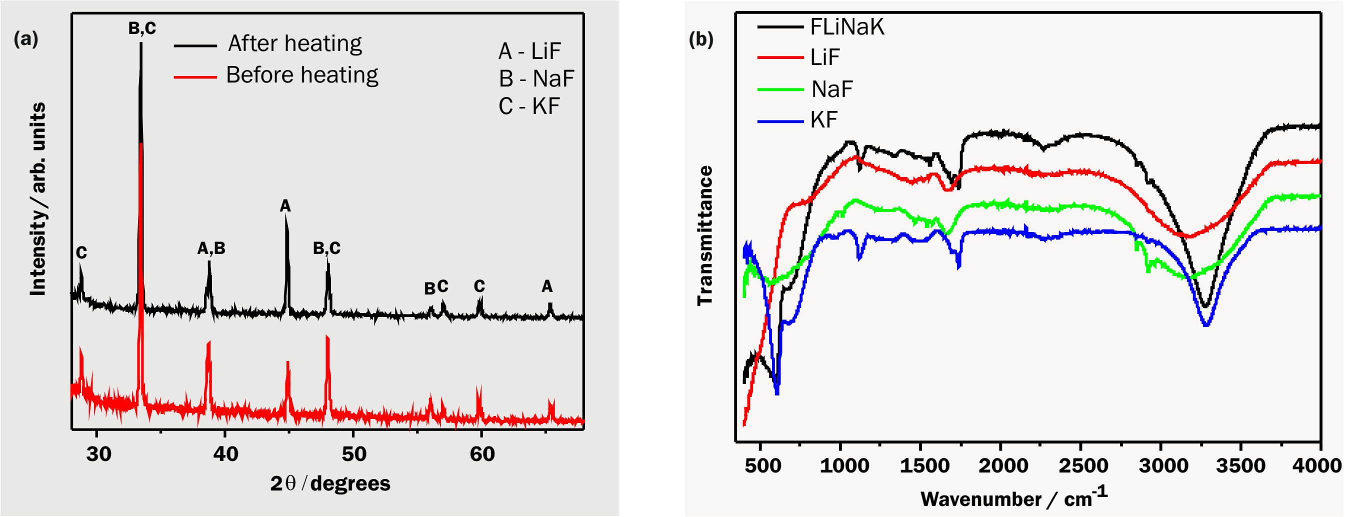

Fig.1: (a) XRD pattern of solidified FLiNaK, (b) IR spectrum of FLiNaK, LiF, NaF and KF.

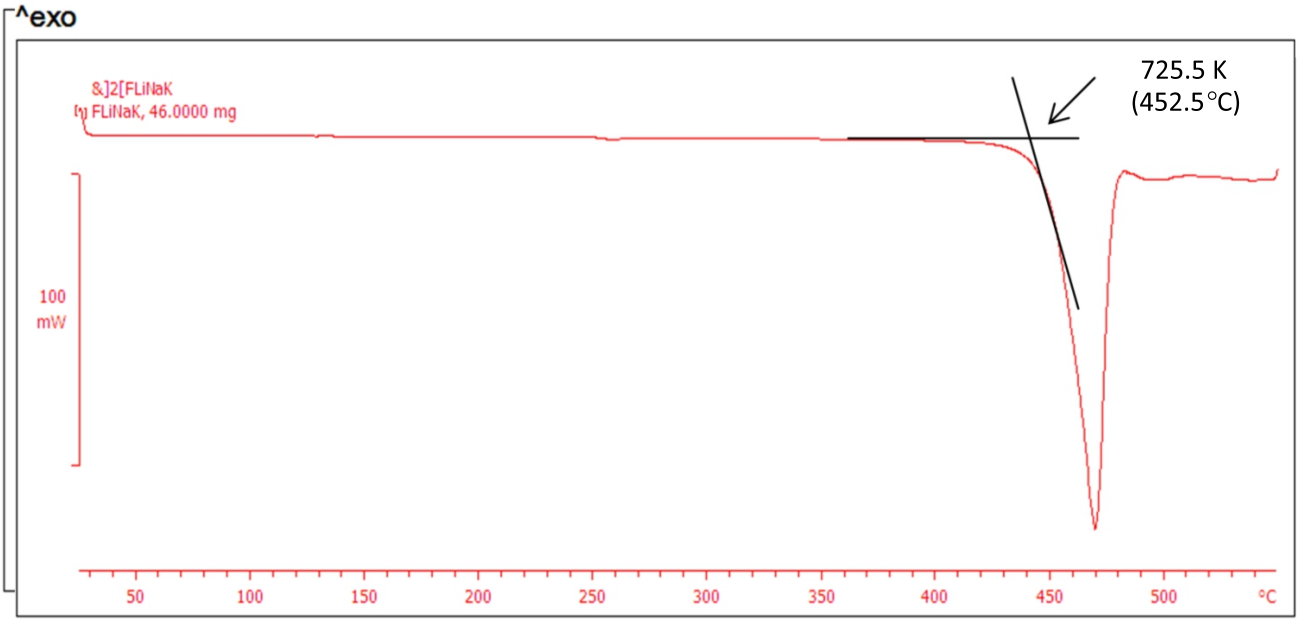

Fig.2: DSC plot for FLiNaK.

to any oxy-fluoride compounds was observed. The comparison of XRD peaks before and after heating of FLiNaK is shown in Fig. 1(a). The absence of any oxy-fluoride compound in FLiNaK was also confirmed using infrared spectroscopy. The FTIR spectra has been recorded using Alpha-II spectrophotometer (Bruker make) in attenuated total reflection (ATR) mode within the wavenumber region 400 to 4000 cm^{-1}. The infrared frequencies corresponding to molecular vibrations of sample get absorbed when infrared light interacts with sample. The IR spectrum of FLiNaK is shown in Fig. 1(b). All the peaks observed in FLiNaK were identified to be due to LiF, NaF and KF only.

Thermo-physical properties of frozen FLiNaK

After salt characterization, the following properties of frozen FLiNaK were measured and compared with literature.

- Melting point
- Density
- Heat capacity
- Thermal diffusivity
- Thermal expansion coefficient

Melting point

Melting point of coolant salt was determined employing a MettlerToledo DSC instrument (DSC1 Star^{e} system). This instrument was calibrated for temperature measurement using In, Sn, Zn as standards. In the present study, salt was sealed in aluminum crucible and the DSC run was recorded (Fig. 2) in the temperature range 298 to 823 K at a heating rate of 5K/min under high pure argon flow. The heat flux was recorded as function of temperature. The melting point was found to be 725.5 K against the reported value of 727 K [18,19].

Density

The density of the frozen FLiNaK at room temperature was determined using liquid immersion technique employing Archimedes Principle. Perfectly dried toluene was used as liquid in which FLiNaK pellet was immersed. As FLiNaK is highly hygroscopic so any liquid containing even trace amount of water cannot be used as it will lead to inaccuracy in weight measurement. In this procedure, the apparent weight loss suffered by the sample when immersed in liquid was measured using a sensitive single pan electronic balance. A density measurement accessory supplied along with this balance was used for this purpose. This accessory consisted of a cradle for immersing the pellet into the liquid and a table for supporting a beaker containing the pellet. The density value reported is the arithmetic mean of the values measured with as many as five pellets. Before measuring the density of FLiNaK, equipment was first calibrated by measuring density of few standards e.g. gold, aluminium.

Equation for density measurement:

Vol. of the displaced liq. = *mass of displaced liq./density of liq.* = *mass of displaced liq.*/0.87

(Density of toluene is 0.87 g/ml at 298K)

Mass of displaced liq. = *mass of FLiNaK in air – mass of FLiNaK in liq*.

Therefore,

$$\rho(FLiNaK) = \left[\frac{\text{weight of FLiNaK in air}}{\text{volume of displaced liq.}}\right] \qquad (1)$$

The density of FLiNaK at 298 K was found to be 2.552±0.01 g/ml. The reported value of density of solid FLiNaK at 293 K is 2.56 g/ml[20].

Heat Capacity

Heat capacity $C^{o}_{p,m}(T)$ of solid FLiNaK was measured in the temperature range of 300-650 K with a heating rate of 5K min^{-1} using a pre-calibrated Mettler Toledo Differential Scanning Calorimeter (DSC I) under the flow of high purity argon gas. Classical three-step method *viz.*, blank, sapphire and sample runs in a step heating mode was employed for measuring the heat capacity. About 50 mg FLiNaK was taken in a sealed 40µl Al pan for the heat capacity measurement. The heat capacity of FLiNaK as a function of temperature could be expressed as:

$$C^{o}_{p,m} / J\,mol^{-1}K^{-1} = 25.1 + 0.037*T + 703840/T^{2} \qquad (2)$$

Fig.3 gives comparison of measured heat capacity of solid FLiNaK as a function of temperature with literature value[21]. The measured heat capacity values as a function of temperature were used for calculating thermal conductivity values of FLiNaK.

Coefficient of Thermal Expansion

Coefficient of thermal expansion of a material is a very important parameter in order to estimate extent of its swelling at a specified temperature. In the present study, thermal expansion coefficient of frozen FLiNaK was measured employing Linseis Dilatometer in the temperature range 523 - 623 K. Sintered FLiNaK pellet (6mm dia) was loaded in the instrument and heated to 523 K under dynamic vacuum of 10^{-6} mbar to remove any adsorbed moisture. Then the change in length of pellet (ΔL) was measured under high pure argon gas at a heating rate of 6 K/min. The change in length per unit length (ΔL/L) of FLiNaK sample can be expressed as

$$\Delta L/L = -0.01206 + 3.94\text{x}10^{-5}\,T/K \qquad (3)$$

The coefficient of average linear thermal expansion can be calculated as

$$\alpha_L = \frac{1}{L_0}\left(\frac{\Delta L}{\Delta T}\right) \qquad (4)$$

Coefficient of thermal expansion of FLiNaK was found to be 3.84×10^{-5} / K. The plot of change in length per unit length *(ΔL/L)* vs temperature is given in Fig. 4.

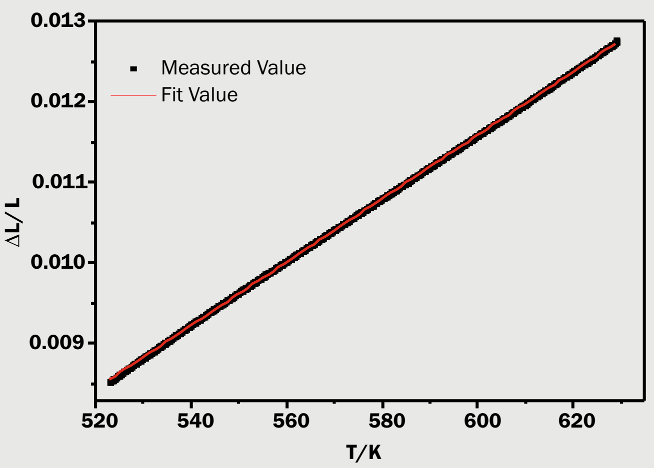

Fig.4: Thermal expansion of FLiNaK as a function of temperature.

The data on thermal expansion of FLiNaK will be useful during optimization of the design parameters of freeze valve in order to avoid any mechanical interaction between salt and constituent material of freeze valve.

Thermal Conductivity

Determination of thermal conductivity of FLiNaK as a function of temperature is of great importance in order to predict its heat transport properties. Thermal diffusivity of frozen FLiNaK was measured employing laser flash technique

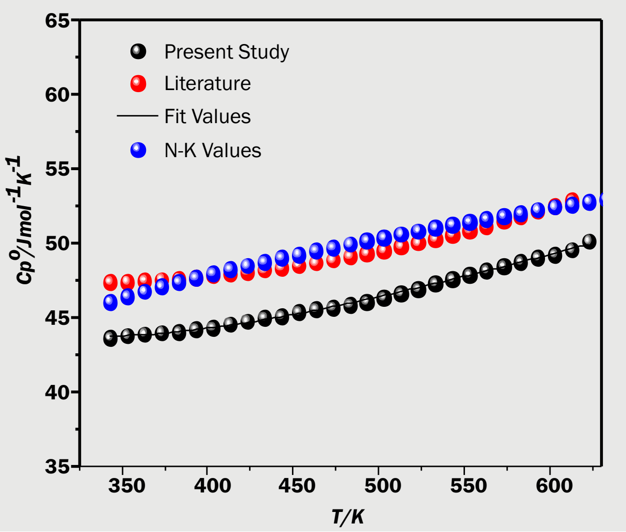

Fig.3: Heat capacity of solid FLiNaK as a function of temperature.

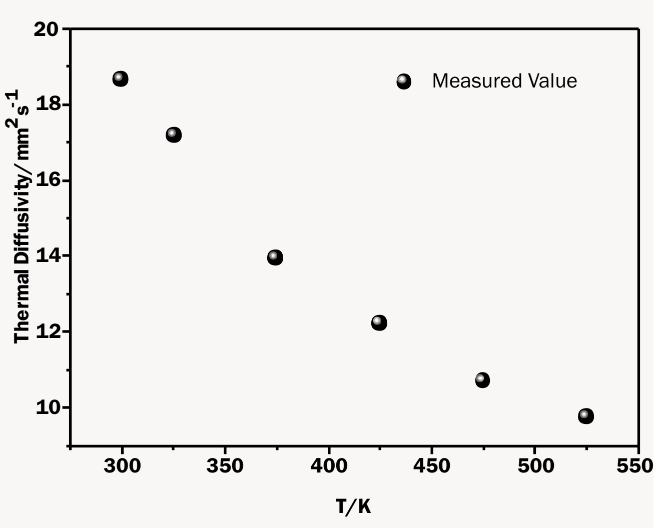

Fig.5: Thermal diffusivity of FLiNaK as a function of temperature.

(LFA 427, M/s. NetzschGmBH, Germany) using Nd-YAG Pulsed laser of duration 0.4 ms. The sample in the form of pellet (diameter 10 mm and thickness ~1 mm) was equilibrated at 298, 323, 373, 423, 473, 523 K under dynamic vacuum of 10^{-6} mbar. The temperature dependence of thermal diffusivity of FLiNaK is shown in Fig. 5. Thermal diffusivity of FLiNaK decreases with temperature and follow inverse temperature dependence behaviour. The temperature dependence of thermal diffusivity of FLiNaK can be expressed as following equation:

$$\frac{1}{\textit{thermal diffusivity (FLiNaK)} / mm^{2}s^{-1}} = -0.01213 + 2.20074x10^{-4}\ T/K \quad (5)$$

Thermal conductivity (K) of the FLiNaK at above mentioned temperatures was calculated from the measured values of thermal diffusivity, heat capacity and density using the following relation.

$$K(T) = \text{Thermal diffusivity}(T) \times Cp(T) \times \rho(T) \quad (6)$$

Thermal diffusivity value taken for thermal conductivity calculation at each temperature is the arithmetic mean of three different measurements. The values of heat capacity as a function of temperature was calculated using equation 2 and temperature dependence of density was calculated using linear thermal expansion data measured using dilatometer. The values of thermal conductivity of FLiNaK as a function of temperature can be expressed in the form of following equation:

$$\frac{1}{K\ (FLiNaK) / Wm^{-1}K^{-1}} = -0.02322 + 8.2107x10^{-4}T/K \quad (7)$$

The values of K as a function of temperature are given in Fig.6.

Summary

Coolant salt proposed for IMSBR i.e. FLiNaK was prepared and characterized. The thermo-physical properties of frozen FLiNaK were measured. These properties are required for modelling freezing and thaw phenomenon and hence for designing of freeze valve which is a key component of passive safety system of MSRs.

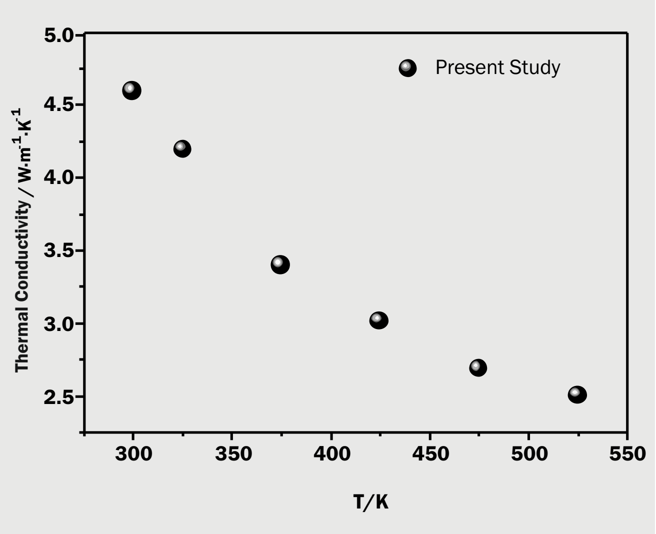

Fig.6: Temperature dependence of thermal conductivity of solid FLiNaK.

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