A Device for Measuring the Density and Liquidus Temperature of Molten Fluorides for Heat Transfer and Storage

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An experimental device is constructed for measuring the density and liquidus temperature of molten fluorides by using the Archimedean and cooling curve methods respectively. Its operation is tested by measuring the density and liquidus temperature of NaCl salt. The accuracy of the liquidus temperature measurement is about ±1 K. The density of NaCl measured is in good agreement with the widely recognized data and the deviation is less than 0.2%. The liquidus temperature and density of a typical heat transfer fluoride LiF-NaF-KF (46.5-11.5-42mol%) are investigated.

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Molten salts were known as ideal media of high-temperature heat transfer and storage, for their low viscosity and vapor pressure, large specific capacity, high thermal conductivity and wide temperature range.[1−6] In a molten salt reactor (MSR), molten fluoride salts have been used as the fuel carrier and coolants in 1960s.[4,6−8] Recently, molten salt heat-transport systems are also being considered to move heat from the advanced high-temperature reactor (AHTR)[3,6,9−12] or solar power systems to thermochemical hydrogen plants. Thermophysical properties of molten salt such as density (thermal expansion), liquidus temperature, viscosity, thermal conductivity have important influences on the performance of heat transfer and storage for the heat-transport systems.[2,12] The liquidus temperature is definitely the most important parameters for the media in the heat-transport systems, because temperature drops, and subsequent partial freezing, can adversely affect heat transport properties in a heat transfer loop, operating at high temperatures. The density is closely associated with temperature reactivity in MSR physics and the basic parameters for thermal hydraulic design. Thus accurate and precise data of the density and liquidus temperature for heat transfer and storage salts are very important for heat-transport systems. On the basis of the past decades of experience, LiF-NaF-KF (46.5-11.5-42mol%) (FLiNaK) is a good heat transfer and storage medium, and has been studied by many researchers.[3−4,13−22] However, the data of thermophysical properties obtained exist considerable discrepancies[3,16−23] as the density measured by different researchers shown in Fig. 4(a).

In this work, an experimental device for measuring the density and liquidus temperature of the molten salts is constructed. To validate the accuracy of measurement of the device, the density and liquidus temperature of NaCl are measured. After that, the density and liquidus temperature of FLiNaK are investigated, and the precise density of FLiNaK and uncertainty of the measurement are obtained.

The traditional Archimedean method is used to measure the densities of molten salts. The schematic diagram of the measuring device is shown in Fig. 1. The one-end-closed corundum furnace tube is heated by 4 SiC heating elements, and sealed by a brass lid which is tightened with a brass O-ring holder by 6 fastening bolts, with an O ring made of fluoroelastomer rubber between them. The brass lid is continuously cooled by a copper cooling piper flowing 298 K cooling water. The temperature of salts is measured by a calibrated S-type or K-type thermocouple. A platinum cylinder, 14 mm in diameter and 16 mm high, suspended on a platinum wire 0.2 mm in diameter and attached to an electronic balance which is placed on a moveable stage. The salt was contained in a cylindrical BN or graphite crucible, 63 mm in inner diameter and 124 mm in height. Dry argon was admitted through the corundum pipe and maintained during the whole experiment.

Before experiments, the volume of the platinum cylinder must be calibrated by measuring the density of distilled water at room temperature, according to the equation

$$V_0 = \frac{m_0 - m_1}{\rho_w} + \frac{\pi D \sigma_w}{\rho_w g}. \tag{1}$$

The density of the salt, ρ in units of g/cm^3, was cal-

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culated by

$$\rho = \frac{m_0 - m_2 + \pi D\sigma/g}{V_0[1+\alpha(T-298)]^3}, \quad (2)$$

where m_0 and V_0 are the weight and volume of the platinum cylinder in air, m_1 and m_2 are the weights of the platinum cylinder in pure water and molten salts, respectively, ρ_w is the density of distilled water at 298 K and can be obtained from density table on the ITS-90, D is the diameter of platinum wire ($D = 0.2$ mm or 0.3 mm), σ_w and σ (mN/m) are the surface tension of pure water and molten salts, g is the gravitational constant, T is the temperature of molten salts in Kelvin, α is the linear expansion coefficient of Pt ($\alpha = 0.000009\,\mathrm{K}^{-1}$).

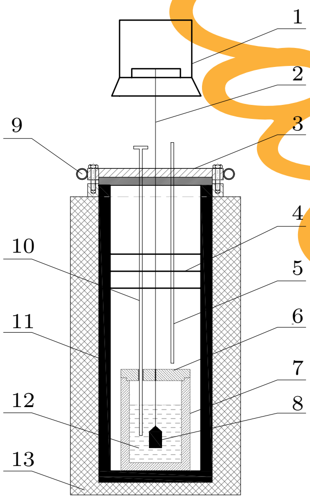

Fig. 1. Schematic diagram of the density measuring device: (1) electronic balance, (2) platinum wire, (3) brass lid, (4) heat insulation plate, (5) corundum inlet pipe for Ar gas, (6) crucible lid, (7) BN or graphite crucible, (8) platinum cylinder, (9) copper cooling pipe, (10) thermocouple, (11) corundum furnace tube, (12) molten salts, (13) thermal insulator.

The density measuring procedure is as follows: First the sample powder or ingots are transferred to a BN or graphite crucible covered by a lid with a 20-mm hole in the center to allow the platinum cylinder to go through. Then, the crucible is placed in the furnace to be heated up under the argon atmosphere. After the salt melted completely, the platinum cylinder was placed into the melt by lower down the moveable stage. When the reading of the balance is steady, the cooling procedure with a cooling rate less than 1 K/min is performed and the reading of the balance will be recorded.

The liquidus temperature of molten salts can be measured by the cooling curve method with this device as well. The furnace and the cooling system are the same as those used to measure the density, and the BN or graphite crucible is also the same as the crucible mentioned above except holes in the lid. The electronic balance and platinum cylinder are replaced by a graphite stirrer attached to a stainless rod which is driven rotationally by an electric motor. A computer is used to collect and record the temperature of the molten salts.

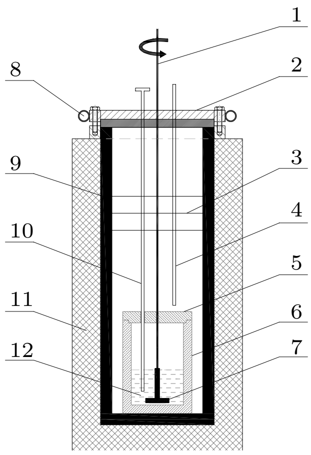

Fig. 2. Schematic diagram of the cooling curves measuring device: (1) stainless steel connecting rod, (2) brass lid, (3) heat insulation plate, (4) corundum inlet pipe for Ar gas, (5) BN crucible lid, (6) BN or graphite crucible, (7) graphite stirrer, (8) copper cooling pipe, (9) corundum furnace tube, (10) thermocouple, (11) thermal insulator, (12) molten salts.

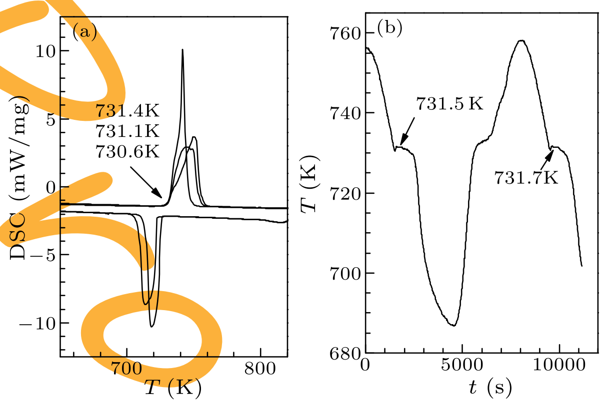

Fig. 3. DSC profiles of FLiNaK eutectic salt (a) and the measured cooling curves of FLiNaK (b).

The operation of the device was tested in experiments involving the measurement of the density and liquidus temperature of NaCl salts. The density and liquidus temperature of FLiNaK salt was also investigated again to verify the repeatability and corrosion resistance of the device. NaCl from Sinopharm Chemical Reagent Co. Ltd, with initial mass fraction purity 99.5%, was purified by melting in a graphite crucible under an argon atmosphere. FLiNaK from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, was analyzed by ICP-OES, and the result indicates that the impuritis greater than 10 ppm are Fe, 13.89; Ni, 13.62; Al, 10.56; Ca, 22.11; Mg, 18.59. Analysis shows 400 ppm for oxygen. Because most salts are hygroscopic, to minimize adsorption of moisture, all the samples were weighed in dry glove box, and transferred to the crucible as soon as possible.

The measured liquidus temperature of NaCl is 1074.7 K and in agreement well with the values 1074 K or 1075 K in available literature.[16,24]

The cooling curves of FLiNaK measured are shown in Fig. 3(b). The results are almost the same as those obtained by the differential scanning calorimetry (DSC), also in accord with the data of 727 K generally reported.[3,5]

The density data of NaCl measured are listed in Table 1. The results coincide well with the widely recognized data reported in the literature[25] and deviation is less than 0.2%.

Table 1. Density of molten NaCl.

T (K)	Density (g/cm^3) Our work	Density (g/cm^3) Ref. [25]	Deviation (%)
1133	1.522	1.522	0
1123	1.525	1.527	0.13
1113	1.530	1.531	0.06
1103	1.536	1.536	0
1093	1.541	1.541	0

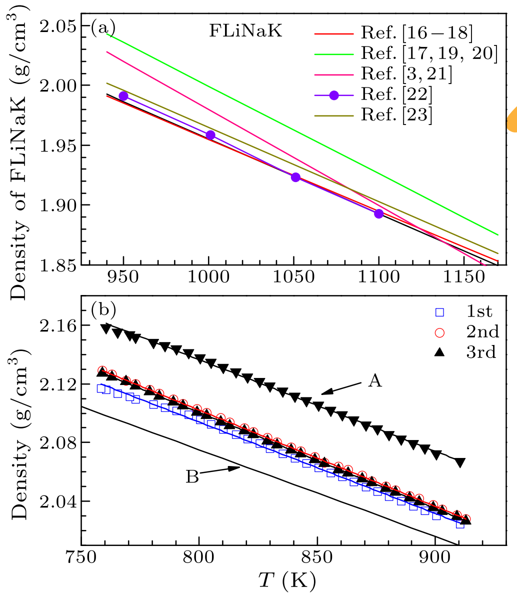

Fig. 4. (a) Density of FLiNaK measured by different researchers.[4,16–23] (b) Temperature dependence of FLiNaK density measured. The 1st, 2nd, 3rd are the three separate runs of measurements. Curve A is the density by averaging the results of three runs taking into account of the surface tension, and curve B is the density calculated by additive principle.

The density measurement of FLiNaK was carried out in the temperature range 753–973 K. Figure 4(b) shows three runs of the measured temperature dependence of FLiNaK densities. For the 1st run, 0.3 mm wire was used, 0.2 mm for 2nd and 3rd. The results in Fig. 4(b) indicate that the effect of the surface tension on the experimental data is obvious. However, the deviations of the three results are very slight after taking the surface tension into account as shown by curve A in Fig. 4(b).

These data obtained experimentally are approximated to the linear equation. The surface tension of FLiNaK used in Eq. (2) is taken from Ref. [24] and it satisfies

$$\sigma = 217.24 - 0.1014T, \tag{3}$$

where σ and T are in units of mN/m and K, respectively.

By averaging the three results, the density of FLiNaK, ρ in units of g/cm^3, can be expressed as

$$\rho = 2.6133 - 0.6431 \times 10^{-3}T. \tag{4}$$

Compared to the density without considering the surface tension effect, the contribution of surface tension to the density of FLiNaK is about 0.5%.

The density of molten mixtures can be derived from the density of the pure components. The idealized mixture exhibits a molar volume that is the mole fraction weighted sum of individual constituents,[26] so the density of the ideal mixtures can be calculated by

$$\rho_{mix} = \frac{\sum_{i=1}^{n} N_i M_i}{\sum_{i=1}^{n} N_i V_i(T)}, \tag{5}$$

where N_i and M_i are the molar fraction and molar weight of component i, respectively. Figure 4(b) also contains density calculated by this additive principle, the molar volumes of pure components are taken from Ref. [27]. The result indicates a positive deviation in the FLiNaK mixture. The maximum deviation between the value calculated and the value measured is about 5%.

$$U = ku = k\sqrt{\sum \left(\frac{\partial \rho}{\partial x_i} u_{x_i}\right)^2}, \tag{6}$$

where u_{x_i} is the uncertainty component caused by x_i which refers to the variable in Eq. (2), k is the confidence factor.

The major sources of experimental errors on each determination of density are accuracy of volume measurements of platinum cylinder ($<2\times10^{-4}$ cm^3), accuracy of the balance (0.1 mg), and determination of temperature (±1 K). Equation (2) is used to determine the uncertainty u in Eq. (6) of the measured density of FLiNaK, and the total uncertainty U is estimated to be less than 0.25% (0.0039 g/cm^3) with confidence probability 0.95.

In summary, the device constructed for measuring the density and liquidus temperature of molten salts by using the Archimedean and cooling curve methods has been tested by measuring the density and liquidus temperature of NaCl salt. The accuracy of the liquidus temperature measurement is about ±1 K. The density of NaCl measured is in good agreement with the data widely recognized, and the deviation is less than 0.2%.

The liquidus temperature and density of FLiNaK have been investigated. The results show that the melting point of FLiNaK is $727 \pm 1\,\mathrm{K}$; and the density obtained can be expressed as ρ (g/cm^3) $= 2.6133 - 0.6431 \times 10^{-3}T$ with T in units of K, with the uncertainty within $\pm 0.25\%$, and temperature range from 753 K to 973 K. The contribution of the surface tension to the density measured is about 0.5%. Compared to the results obtained by additive principle, FLiNaK salt reveals a positive deviation, and the maximum deviation is less than 5%.

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