X-ray diffraction study of the NaF – LiF – LnF_3 (Ln=La,Nd) eutectic composition in the liquid and solid states

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The ternary eutectic alloy with the composition 33 mol % NaF+53 mol % LiF+14 mol % NdF_3 has been studied in the liquid and solid states using differential thermal analysis and X-ray diffraction at room and high temperatures. The obtained results demonstrate that the eutectic alloy undergoes no phase transformations at temperatures from 298 K to melting point. Analysis of RMC models of the melt indicates that there is no dense non-crystalline packing of the fluorine anions in contrast to the eutectic NaF—LiF—LaF_3 melt.

Introduction

Systems of alkali and rare-earth fluorides are used as a basis for formulating more complex mixtures and also for understanding the physicochemical processes underlying the regeneration of spent nuclear fuel [1-3]. The composition of the fuel solvent in such processes is dictated by the requirement that it have a relatively low melting point. It is also known that the key components of fuel mixtures for next-generation nuclear reactors are fluorides of metals with a small capture cross section for thermal neutrons [3-4]. The NaF—LiF—LnF_3 (Ln = La, Nd) eutectics corresponds to all these requirements. The report [5] has presented an X-ray diffraction (XRD) study of the eutectic alloy 44 mol % NaF + 42 mol % LiF + 14 mol % LaF_3. In this paper, we report results of an XRD study of the ternary eutectic alloy of NaF -LiF -LnF_3 (Ln = La, Nd) systems in the liquid and solid states.

Analysis of total and partial structural characteristics obtained by XRD and neutron diffraction techniques and the short-range order (SRO) of some molten salts were presented in [6-7]. Particular attention was paid to salt systems whose structure factor (SF) curves had a small peak at small scattering angles, referred to as prepeak in the literature. The origin of the prepeak on the SF of halide melts is the subject of serious controversy [5], and rather many hypotheses have been proposed to interpret it. In general, the presence of the prepeak corresponds to the formation of structural units whose spatial arrangement is correlated on a length scale greater than the nearest neighbor distance. The

arrangement of the atoms (or ions) in the structural units determines the local atomic order in the melt and the position of the first (main) SF peak. By analogy, the position of the prepeak characterizes the size of the structural units, and its full width at half maximum provides information about the size of the correlation region or clusters consisting of several structural units. Such groups, exceeding the length scale of the local atomic order, are the subject of detailed studies because they have a significant effect on the physicochemical properties of the melt and crystallization and glass formation processes.

Experimental part

Appropriate amounts of the sodium and lithium fluorides (reagent grade) and neodymium (III) fluoride (pure grade) were thoroughly ground in an agate mortar, weighed, mixed, and reground. The mixture was then transferred to a platinum crucible and melted at 750°C for 60—70 min in an electric furnace under an argon atmosphere. The melt was poured into a cold platinum holder in an amount that ensured a flat melt surface for subsequent XRD examination.

Differential thermal analysis (DTA) was carried out with a Q-1500 thermoanalytical system in an argon atmosphere. The heating rate was 5—10°C/min. Room temperature (RT) XRD measurements were made on a DRON-3 diffractometer (CuK_a-radiation). The X-ray diffraction measurements of the solid and liquid samples at higher temperatures in the atmosphere of the cleared helium were carried out using high-temperature θ-θ (MoK_a-radiation) [5]. The XRD examination at 350, 450, and 550°C showed that the phases present in the solid sample were in the crystalline state. At 600, 700, and 800°C, the sample was in the liquid state. XRD results were analyzed using PowderCell and Mercury license programs and the Retrieve, Match, and PCPDFWIN XRD databases. The SRO in the melts were interpreted using measured scattering intensity (SI) and SF curves, radial distribution functions (RDFs), pair correlation functions $G(R)$. The structure models of the melts at different temperatures were reconstructed by means the Reverse Monte Carlo (RMC) simulations.

Results and discussion

The phase diagrams of the binary systems NaF— NdF_3 and LiF—NdF_3 have been studied in detail [8-10]. According to the Match database, $NaNdF_4$ exists as a high-temperature, cubic phase (*Fm3m*) and a low-temperature, hexagonal phase *(P6*). $NaNdF_4$ has only hexagonal cells. Neodymium (III) fluoride has a hexagonal structure with space group $P6_322$, $P3c1$, $P6_3cm$, or $P6_3/mcm$. NaF and LiF have the cubic close-packed lattice (*Fm3m*).

We investigated the phase diagram of the NaF—LiF—NdF_3 [11]. The peak between 580 and 590°C in the heating (cooling) curves of our samples had the largest area and corresponded to eutectic.

Using the Tammann method and calculating the enthalpy of melting ($\Delta_m H$), we have found the composition and melting point of the ternary eutectic. The highest value of $\Delta_m H$ (63.6 kJ/mol) corresponds to the eutectic composition NaF(33)-LiF(53)-NdF_3(14). The eutectic temperature is 580 ± 2°C [11]. For ternary system with La, the mixture NaF(44)-LiF(42)-LaF_3(14) corresponds to the eutectic composition with melting point ~580-590 °C.

High-temperature XRD results confirmed that the sample melted at 590°C. The XRD patterns obtained at RT, 350, 450, and 550°C indicated the presence of hexagonal phase with the composition $NaNdF_4$ (major phase) and the cubic phases LiF and NaF. No neodymium (III) fluoride phase was detected. The weak peaks of NaF observed at RT disappeared at higher temperatures. The XRD pattern has no significant changes with increasing temperature. The diffraction peaks are shifted to smaller angles due to increasing of the lattice parameters. The unit-cell parameters of NaF and $NaLnF_4$ (Ln=La,Nd) are linear functions of temperature.

The SF curves of the melts contain a well-defined, complex-shaped prepeak in the range 10-25 nm^{-1}. With increasing temperature, the height of the major SF peaks and prepeak decreases slightly that points to disordering of the SRO. The SF curves of the investigated melt correlate with ones of the NaF(44)-LiF(42)-LaF_3(14) melt [1], but in the latter case the prepeak is somewhat stronger

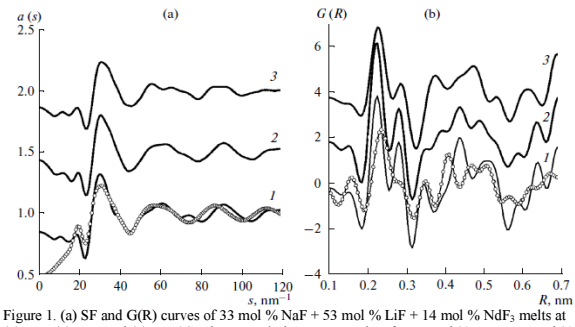

Figure 1. (a) SF and G(R) curves of 33 mol % NaF + 53 mol % LiF + 14 mol % NdF_3 melts at (1) 650, (2) 700, and (3) 800 °C. The open circles represent data for 44 mol % NaF + 42 mol % LiF + 14 mol %

and has a simpler shape. It should be noted that the pair correlation function of eutectic melts containing LaF_3 and NdF_3 has similar shape. The principal distinctions between their *G(R)* curves are the absence of a peak at 0.27 nm in case of melt with LaF_3.

Using the Shannon—Prewitt ionic radii, the first peak in the atomic distribution curves, located in the range 0.20-0.26 nm, was shown to be contributed by the Na-F, Li-F, Nd-F, Li-Li, and, to some extent, F-F pairs. The second peak, in the range 0.265-0.310 nm, is contributed by the cation-cation (Na-Na, Nd-Nd, Na-Li, La-Li, and Nd-Na) pairs and the F-F pairs in the nearest neighbor environment of the large sodium cations. It should be emphasized that the first two peaks are almost impossible to decompose into the contributions of these pairs.

The SRO of the eutectic melt was analyzed by means RMC simulation. The simulated SF curves agreed with the experimental ones to within experimental uncertainty. The the strong first peak below 20 nm^{-1} in both the $S_{NdNd}(Q)$ and $S_{LaLa}(Q)$ curves correlates with prepeak position in the measured SFs of the melts. The prepeaks in the $S_{NdNd}(Q)$ and $S_{LaLa}(Q)$ curves of the NdF_3 containing melt are similar in shape, which indicates that the Nd-

Nd pair plays a central role in determining its origin. The other peaks in the partial curves differ in position from the prepeak in the measured SF curve. It follows from the partial pair distribution functions $G_{ij}(R)$ thus obtained and the coordination numbers (CN) Z_{ij} (the number of atoms of type *j* around an atom of type *i)* that, in the temperature range 650- 800°C, the correlation between the cation positions in all of the pairs except Na-F, Li-F, and Nd-F, is limited to the nearest neighbor environment. At the same time, the oscillations in the $G_{ij}(R)$ partial curves of the NaF(44)-LiF(42)-LaF_3(14) melt are better defined, which points to a high degree of ion order in comparison with the NdF_3 containing melt. The nearest neighbor environment of the cations in the NaF(44)-LiF(42)-LaF_3(14) melt consists of six fluorine anions for Li^+, a slightly smaller number of anions (five or six) for Na^+, and six or seven for La^{3+}. In the NaF(33)-LiF(53)-NdF_3(14) melt, the coordination number of all cations is also almost six, with slight variations near this value with temperature. The F-F pair has a maximum at 0.275 nm, with $Z_{F(F)}$ = 7 or 8. This value of $Z_{F(F)}$ differs from the $Z_{F(F)}$ = 10—11 in the LaF_3-containing melt, which can be explained by the difference in melt concentration. It is worth noting that the $G_{Na-Nd}(R)$ and $G_{Nd-Nd}(R)$ curves are very similar in shape throughout the temperature range studied.

The peak positions in the $G_{NdNd}(R)$ and $G_{NaNa}(R)$ curves differ very little due to the small difference in ionic radius between Na^+ (0.116 nm) and Nd^{3+} (0.112 nm). According to PowderCell the R_{NdNd} and R_{NaNa} distances in hexagonal $NaNdF_4$ are 0.373 ± 0.004, 0.428, and 0.610 nm. The first two values correlate with the positions of the first two peaks in the $G_{NaNa}(R)$.

To estimate the minimum length of the correlation responsible for the prepeak (R_p), we used the Ehrenfest equation

$$R_p \cdot S_p = 1,23 \cdot 2\pi \qquad (2)$$

From the prepeak position of the measured SF (18—19 nm^{-1}), the minimum correlation length was determined to be 0.41-0.43 nm that agrees with the peak position in *G(R)*. The prepeak on the $S_{NdNd}(Q)$ curve (1.85 nm^{-1}) gives R_p = 0.42 nm that also correlates with the peak position in the $G_{NdNd}(R)$ curve. The first peak in the $G_{LaLa}(R)$ curve [5] is strong and narrow, and oscillations are well seen at distances of up to 1.60 nm, determining the size of the regions of ordered La^{3+} arrangement. At the same time, the first peak in the $G_{NdNd}(R)$ curve has a complex shape, and oscillations at larger distances are weak, being indiscernible at *R* = 1.10 nm.

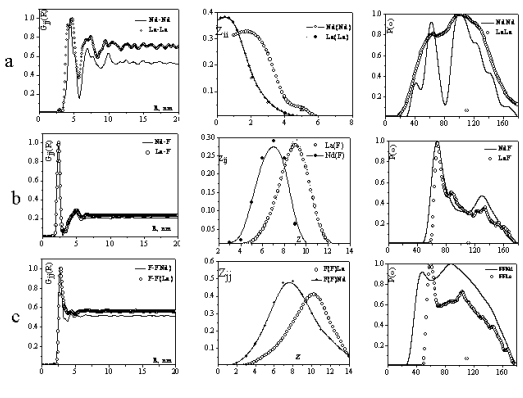

Figure 2. (1) Partial distribution function $G_{ij}(R)$, (2) CN distribution, and (3) bond angle distribution for the Ln-Ln (Ln = La, Nd), (b) Ln-F, and (c) F-F coordination where dots are lanthanum-containing melt and solid lines are neodymium-containing melt.

The first peak in the $G_{NdF}(R)$ curve is strong and narrow, like that in $G_{LaF}(R)$ [5], and corresponds to nearest neighbor distance of $R_{NdF} = 0.231$ nm, Nd^{3+} coordination polyhedron in the melt, in contrast to the nearest neighbor environment of the La^{3+} ion in the NaF(44)-LiF(42)-LaF_3(14) melt. This result is surprising because the Nd^{3+} ion is very similar in charge and ionic radius to the La^{3+} ion. The obtained CN is equal six that leads us to assume that the Li^+ and Na^+ ions are in octahedral coordination, but the rather broad and weak first peak in the $G_{LiF}(R)$ and $G_{NaF}(R)$ curves suggests that their coordination polyhedron in the melt is considerably distorted.

In the NaF(44)-LiF(42)-LaF_3(14) melt, $Z_{F(F)}$ = 10-11 that points to rather dense packing of the fluorine anions. In LaF_3 crystals, each F^- ion is surrounded by six F^- ions at 0.274 nm and six F^- ions at 0.336 nm. In $NaLaF_4$ crystals, $Z_{F(F)}$ is six at distances of 0.288 nm or shorter and increases to nine at distances of 0.326 nm. As shown earlier [5], the coordination polyhedron of the lanthanum atoms in the melt is a distorted trigonal prism capped on all of its faces. In the neodymium trifluoride-containing melt, $Z_{F(F)}$ = 7 or 8. NdF_3 crystals have six F-F distances in the range 0.246-0.266 nm and another six in the range 0.361-0.389 nm. $NaNdF_4$ crystals have five R_{F-F} distances no more than 0.282 nm and another two no more than 0.371 nm. The fluorine coordination of the Nd atoms in the melt is difficult to identify because the structural parameters of the melt have not been determined with sufficient accuracy.

The present data on the coordination of the anions in the fluorides correlate with those for crystalline $NaNdF_4$ and NdF_3, in drastic contrast to results obtained for the LaF_3-containing melt. At the same time, the complex shape of the first peaks in the $G_{NdNd}(R)$ and $G_{NaNa}(R)$ curves of the melt is inconsistent with formation of microgroups similar to the structural components of $NaNdF_4$ or NdF_3.

The present data lead us to assume that the fluorine anions do not form close-packed microgroups because the melt is not structurally uniform but consists of a mixture of microgroups that differ quantitatively in cation composition. In this respect, the neodymium trifluoride-containing melt differs significantly from the lanthanum trifluoride-containing melt, where the lanthanum cations form locally ordered centers with attached fluoride polyhedron having sodium or lithium atoms in their center.

Conclusions

The obtained results demonstrate that no changes in structure or phase composition of NaF(33)-LiF(53)-NdF_3(14) eutectic alloy undergoe at temperatures below the melting point. The lattice parameters of the coexisting phases NaF, LiF, and $NaNdF_4$ increase linearly with increasing temperature. The alloy melts at ~590°C, and further increase in temperature has significant effect on the SRO of the melt.

In contrast to those in the lanthanum (III) fluoride- containing melt, the fluorine anions in NaF(33)-LiF(53)-NdF_3(14) melt do not form close-packed microgroups. The melt is not structurally uniform but consists of a mixture of microgroups that differ quantitatively in cation composition. The Nd^{3+} do not form any locally ordered centers with attached fluoride polyhedra having sodium or lithium atoms in their center.

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