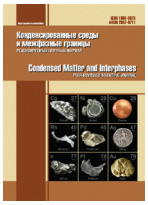

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Solubility of calcium and strontium fluorides in a sodium nitrate melt and choosing a crucible material for working with their solution melts

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Abstract

Sodium nitrate is a promising medium for the preparation of nanoparticles of some inorganic fluorides and for studying low-temperature phase equilibria in fluoride systems. In our study, we investigated the possibilities of carrying out long-term (hundreds of hours) experiments with MF_2–$NaNO_3$ (M = Ca, Sr).

We performed an experimental evaluation of the solubility of calcium (CaF_2) and strontium SrF_2 fluorides in a melt of sodium nitrate $NaNO_3$ in the temperature range of 320–500 °C. The article demonstrates that for both fluorides it is low, but the solubility of SrF_2 is almost an order of magnitude higher than the solubility of CaF_2 and is about 1 g/100 g of $NaNO_3$ at 500 °C. The absence of perceptible oxidative processes and the low solubility of CaF_2 and SrF_2 fluorides in sodium nitrate make it possible to synthesize solid solutions based on them in this medium. The article also considers the possibility of using crucibles made of glazed ceramics, glass-carbon, and aluminium for working with MF_2–$NaNO_3$ (M = Ca, Sr) melt solutions. It is shown that glass-carbon and aluminium react with the $NaNO_3$–SrF_2 melt solution to form strontium carbonate and several oxide phases, respectively.

It is recommended to use glazed ceramics as a crucible material for long-term solution-melt processes. The aluminium crucible showed high resistance to the $NaNO_3$ melt without dissolved fluorides.

Keywords: Calcium fluoride, Strontium fluoride, Sodium nitrate, Solubility, Solution melt, Powder X-ray diffraction analysis

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1. Introduction

Sodium nitrate melt is a promising medium for the preparation of nanoparticles of certain inorganic fluorides by means of molten salt synthesis (MSS) [1–4], as well as for studying low-temperature phase equilibria in fluoride systems [4, 5]. The MSS method for the production of nanofluorides has a large number of advantages over the deposition from aqueous solutions method. They include a fast reaction speed, the possibility to conduct synthesis in the air, and the possibility to use available equipment. Nitrates of alkali metals have been used in a number of studies as melt media for the preparation of inorganic fluorides.

In [6], ScF_3 (the most refractory one of the simple inorganic fluorides) was synthesised from precursors of $Sc(NO_3)_3$ and NH_4HF_2 in a $NaNO_3$–KNO_3 reaction medium for 0.5 hours at 310 °C. Micro- and nanocrystals of $NaBiF_4$:Er^{3+}/Yb^{3+} were synthesised from low-temperature salt melts in NH_4NO_3 [7], and CaF_2 was synthesised in a mixture of 53 wt% KNO_3, 7 wt% $NaNO_3$, and 40 wt% $NaNO_2$ [8]. Upconversion luminophores $NaYF_4$ and $LiYF_4$ were synthesised using eutectic melts $NaNO_3$–KNO_3, $NaNO_3$–$LiNO_3$, KNO_3–$LiNO_3$, and $NaNO_3$–KNO_3–$LiNO_3$ for 2 hours at 400 °C. The best result was obtained in a $NaNO_3$–KNO_3 eutectic melt. When salt media containing $LiNO_3$ were used, a tetragonal $LiYF_4$ was produced mixed with a rhombic $Y_6O_5F_8$ [9]. The MSS method was also used to synthesise CeF_3 and CeF_3:Tb^{3+} particles at a low temperature in $NaNO_3$ and KNO_3 melts [10].

The above given data demonstrates that a sodium nitrate melt is an effective reaction medium since it is water-soluble and non-toxic, has high stability, and does not contaminate synthesised fluorides with oxygen.

The choice of the crucible material for the experiments, however, is problematic. It should be resistant to both NO_3^- and F^- ions. This problem has not been discussed in the existing literature. Researchers often provide detailed descriptions of their experiments, but do not mention the material of the crucible (for instance, [6, 7], although it is of great importance. [4, 5] used glazed porcelain crucibles, and [8, 10] used alumina crucibles (Al_2O_3).

There is also literature data on the effective growth if $NaNO_3$ single crystals from a melt in aluminium crucibles [11]. The best material for working with the melts of inorganic fluorides is graphite, which does not interact with the melt and is not wetted by it. However, the crystallisation of fluorides from the melt is performed in vacuum or in inert and fluorinating environment, i.e. graphite crucible does not interact with oxygen. At low temperatures (up to 400 °C) graphite is hardly oxidized in the air. At higher temperatures, the oxidation process depends on a large number of factors, including the composition of the atmosphere, porosity, and the crystalline quality. The processes occurring in the C–$NaNO_3$ system (taken in a molar ratio from 5:1 to 1:4) were studied using a derivatograph in [12]. The study demonstrated that the components interacted at temperatures significantly higher than the melting point of $NaNO_3$. Depending on the ratio of the components, derivatograms demonstrated the beginning of a noticeable reaction at 380–420 °C. The approximate range for the salt melt synthesis of fluorides is the interval of stability of $NaNO_3$ from the melting point to the decomposition temperature (~310–500 °C). When using carbon crucibles, a temperature of ~380 °C is acceptable. [13] demonstrated the stability of SrF_2 and CaF_2 fluorides in the $NaNO_3$ melt in a glass-carbon crucible at 330 °C for 1 hour.

The purpose of our study was to analyse the suitability of three materials (glass-carbon, aluminium, and glazed porcelain) for long-term experiments with MF_2–$NaNO_3$ (M = Ca, Sr) solution melts. We assumed that the stability of the crucible material would depend on the amount of dissolved fluorides (the number of F^- ions in the melt). Therefore, we first had to use available methods to evaluate the solubility of SrF_2 and CaF_2 in the $NaNO_3$ melt.

2. Experimental

The initial materials were CaF_2 in the form of fragments of optical crystal produced by Vavilov State Optical Institute and SrF_2 in the form of crystalline boules preliminary melted from a 99.995 wt% (Sigma-Aldrich) reagent in a CF_4, $NaNO_3$ fluorinating environment (analytical reagent grade).

The solubility of fluorides in a sodium nitrate melt was assessed using two methods. 1) A MF_2 single crystal of a particular mass was put into

a crucible with a certain amount of the sodium nitrate melt and thermostated until the solution melt became saturated. During this stage, glazed porcelain and glass-carbon crucibles were used. The experiments demonstrated that the solution melt became saturated in 2 hours. Then the crystal was removed from the melt, the remaining nitrate was washed off with bidistilled water, and the crystal was weighed. The change in the mass of the crystal corresponded to the amount of fluoride dissolved in the melt at the set temperature. It was used to calculate the solubility. 2) MF_2 crystals were thermostated in the $NaNO_3$ melt. A sample of the melt was then taken with a scoop made from the same material as that of the crucible. The sample was cooled to room temperature and dissolved in bidistilled water. It was then washed three times until sodium nitrate was completely removed. The precipitate was filtered, dried, and weighed.

The initial reagents and the reaction products were controlled with the X-ray diffraction (XRD) method. The XRD was performed using a MiniFlex 600 powder X-ray diffractometer (Rigaku, Japan) using CuK_α (40 kV, 15 mA, Ni–K_β-filter) radiation in the angular range 2θ from 10° to 100° at 0.02° intervals and a scanning rate of 2°/min. The phases were identified using a PXDRL software (Rigaku, Japan) based on the ICDD PDF-2 database (2017 edition).

The morphology of the interaction products was studied using a POLAM L-213M optical microscope and scanning energy-dispersive microscopy (SEM) performed on a Scios scanning electron microscope (FEI, USA). The images were registered in a backscattered electrons mode using a T1 in-lens solid state detector (FEI, USA).

When conducting long-term experiments in a $NaNO_3$ melt, it is of utmost importance that there is no interaction with the material of the crucible [5]. To study the resistivity of various materials to the solution melt, we performed the following experiment. Samples with a molar ratio MF_2:$NaNO_3$ = 1:5 (M = Ca, Sr) were put into glass-graphite and glazed porcelain crucibles; $Ca_{0.5}Sr_{0.5}F_2$:$NaNO_3$ = 1:5. The samples were put into two crucibles made from 0.22μm aluminium foil together with pure $NaNO_3$ used as a reference. The samples were previously ground in a jasper mortar. All the crucibles were put in a muffle furnace and held in the air at a temperature of 410±5 °C for ~760 hours. After the annealing the content of the crucibles was washed with bidistilled water to remove $NaNO_3$.

3. Results and discussion

3.1. Solubility of CaF_2 and SrF_2 in the $NaNO_3$ melt

The obtained measurements of the solubility of fluorides in sodium nitrate were very low. The generalised results are experiments presented in Table 1. We should note that the solubility of SrF_2 in the studied temperature range is almost an order of magnitude higher than that of CaF_2. The solubility of CaF_2 was determined using only the first method based on the change in the mass of the crystal. It was not possible to filter the precipitate of CaF_2 due to its insignificantly small amount. Due to the evaluative nature of the analysis of solubility, without specialised equipment the obtained data varied greatly. However, the results obtained using two methods in both porcelain and glass-graphite crucibles are in satisfactory agreement with each other.

Table 1. Results of the experiments conducted to measure the solubility of CaF_2 and SrF_2 in a $NaNO_3$ melt

MF_2 T, °C	Solubility, g/100 g $NaNO_3$	
	CaF_2	SrF_2
350±10	–	0.35±0.14
450±20	~0.04	0.84±0.37
500±20	~0.14	1.03±0.19

*The solubility of CaF_2 below 450 °C could not be reliably recorded

When a glass-carbon crucible was used, the precipitate was visible even after 10 hours of thermostating of the melt with the SrF_2 crystal at temperatures of about 400 °C. SEM and XRD analysis demonstrated that besides strontium fluoride it contained a considerable amount of strontium carbonate increasing with a longer time of annealing and at higher temperatures. The results are shown in Fig.1a-c. Micrographs 1b and 1c demonstrate crystals of various morphology: small cubic crystals (probably SrF_2) and larger needle crystals (probably $SrCO_3$).

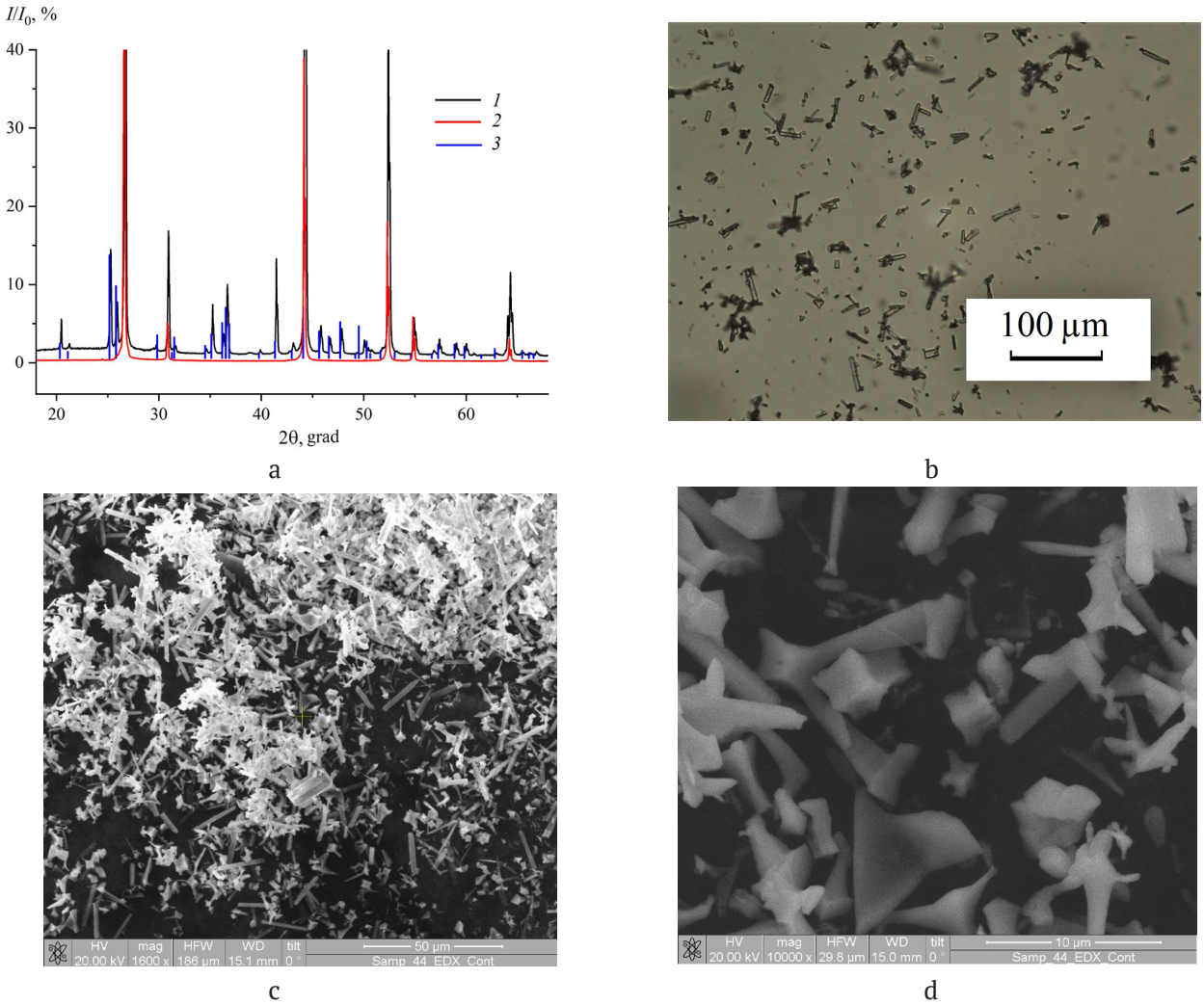

Fig. 1. Analysis of the precipitate after experiments with SrF_2–$NaNO_3$ composition in a glass-graphite crucible. XRD results: *1* – diffraction pattern of the sample, *2* – diffraction pattern of the initial reagent SrF_2, *3* – $SrCO_3$ (PDF No. 00-005-0418) (a). Photograph of the precipitate in an optical (b) microscope and electron (c, d) microscopes at different magnifications

3.2. Assessment of the crucible materials

As a result of annealing of melt solutions in a muffle furnace in the air at a temperature of 410±5 °C for ~760 hours, a $SrCO_3$ precipitate, as expected, formed in the near bottom part of the ingot from the glass-graphite crucible with c SrF_2–$NaNO_3$. When dissolving the CaF_2–$NaNO_3$ ingot from the glass-graphite crucible we also observed a very fine powder which could not be centrifuged and filtered due to its small amount. It might have been calcium carbonate.

CaF_2–$NaNO_3$ and SrF_2–$NaNO_3$ systems did not demonstrate any other phases besides the initial components in glazed porcelain crucibles.

Al foil crucibles proved to be ineffective. They transformed into a fragile substance grey at the top and pink at the bottom where it interacted directly with the melt solution. The diffraction patterns of the grey and the pink parts did not differ significantly. The XRD demonstrated that there was no metallic Al and cubic CaF_2 and SrF_2 based fluoride phases in the product. It also registered a large amount of $NaNO_3$ and probably $Na_{0.67}Al_6O_{9.33}$ oxides (card PDF No. 01-070-7114), and a Al_2O_3 modification (card PDF No. 00-012-0539). Fig. 2 demonstrates the diffraction pattern of the sample after washing with bidistilled water. $Na_{0.67}Al_6O_{9.33}$ and iota-Al_2O_3 spectra are imposed on the diffraction pattern. There are also unidentified peaks.

The reference Al foil crucible with pure $NaNO_3$ did not change visibly. The foil remained shiny

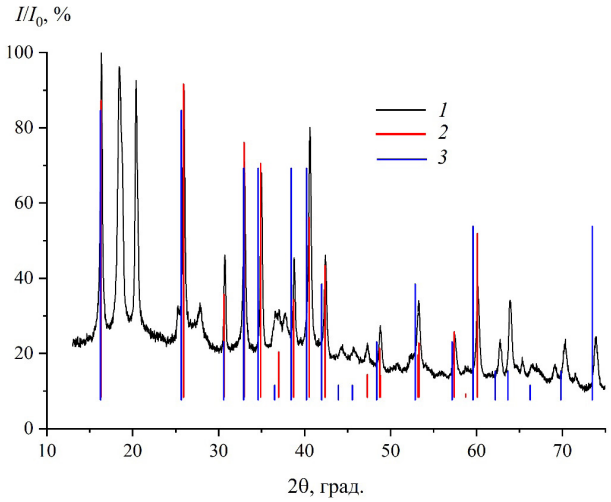

Fig. 2. *1* – X-ray diffraction pattern of reaction products of Al foil with $Ca_{0.5}Sr_{0.5}F_2$–$NaNO_3$ melt solution in the air; *2* – $Na_{0.67}Al_6O_{9.33}$ (PDF No. 01-070-7114); *3* – iota-Al_2O_3 (PDF No. 00-012-0539)

without any oxidation traces. The sodium nitrate ingot was colourless and transparent.

4. Conclusions

Calcium fluoride demonstrates significant solubility in a sodium nitrate melt, which is up to 0.14 g/100 g $NaNO_3$ at a temperature of ~500 °C. The solubility of strontium fluoride is an order of magnitude higher and reaches 1.03±0.19 g/100 g $NaNO_3$. The difference in the behaviour of the two fluorides might be the cause of a large difference in the morphology of crystals of both pure phases and solid solutions based on them and obtained in nitrate salt melts [14]. The absence of a visible oxidation process and low solubility of CaF_2 and SrF_2 fluorides in sodium nitrate make the latter a very promising medium for synthesising inorganic fluorides by means of the MSS method.

Glazed porcelain crucibles are preferable for working with MF_2–$NaNO_3$ (*M* = Ca, Sr) melt solutions. Carbonate impurities are observed in glass-graphite crucibles, and Al crucibles are destroyed as a result of oxidation.

Aluminium demonstrates high resistance to the sodium nitrate melt and is a good material for crucibles used with the melt.

Author contributions

Buchinskaya I. I. – problem statement, scientific supervision of research, X-ray phase analysis, text writing, discussion, conclusions. Ivchenko V. A. – carrying out the experiment, analysis of the results, text writing, conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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