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Article

Solubility of Al_2O_3 in Some Chloride–Fluoride Melts

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Alumina solubility in chloride–fluoride melts of KCl–NaCl–NaF mixtures with ratios of 0.425:0.425:0.15 (I), 0.38:0.38:0.24 (II), and 0.35:0.35:0.30 (III) (molar fractions) was investigated in the 973–1123 K temperature range using the isothermal saturation method. Al_2O_3 solubility in the ionic melts studied was shown to be on the order of 0.06 g kg^{-1} for system I, 0.12 g kg^{-1} for system II, and 0.14 g kg^{-1} for system III at 1073 K. All the "Al_2O_3 + melt" systems were found to demonstrate negative deviations from the ideal solutions. The solubility of Al_2O_3 in all the melts increases with the temperature increase; however, the dependences of $-\log N_{Al_2O_3}$ versus T^{-1} were characterized by the slopes $(2.6 \pm 0.4) \times 10^3$ K (I and II) and $(2.4 \pm 0.6) \times 10^3$ K (III), which were considerably less than the slope predicted by the Shreder–Le Chatelier equation ($\sim 5.8 \times 10^3$).

Introduction

Al_2O_3 single crystals (leuco-sapphire) possess many properties which make them available for some industrial applications, such as high optical transparence for UV, IR irradiation, and visible light, high hardness, and stability at high temperatures up to 2300 K. In addition, they are characterized by high electric resistance, heat conductivity and radiation, and chemical stability. Because of these properties leuco-sapphire is widely used for various optical, electronic, chemical, and medical applications.

The possibility of wide use of leuco-sapphire for these purposes arose in the seventies of the last century when this material was grown by the Czochralsky and Kiropoulos methods and horizontal-directed crystallization. This set of growth methods allowed crystals differing in shape, size, and composition to be obtained. However, the growth methods require high temperatures on the order of 2300 K (near the melting point of Al_2O_3); this is connected with the necessity of using complex equipment and with the high consumption of energy.

Therefore, considerable attention of investigators is now paid to routines providing the growth of alumina from solutions in molten salts that allows the growth temperature to be decreased to 1300 K. When the permanently increased demand for sapphire is taken into account, similar methods may result in appreciable economic effect. The problem of choice of flux solvent for Al_2O_3 is now far from being solved. Literature data contain some information concerning alumina solubility in fluoride melts (e.g., Na_3AlF_6),[1] serving as background electrolytes for electrochemically obtaining aluminum, and some calculated phase diagrams of an Al_2O_3–AlF_3–NaF system.[2–6]

An obvious advantage of mixed chloride–fluoride systems is the lower melting points (the melting points of NaF and Na_3AlF_6 are 1068 and 1279 K respectively, whereas the 0.425:0.425:0.15 KCl–NaCl–NaF mixture solidifies at 875 K). Second, chloride–fluoride mixtures themselves, as a rule, are soluble in water (whereas the Na_3AlF_6 solubility is very low); this facilitates separation of single crystals from the melt components.

The purpose of this work is to determine the solubility of Al_2O_3 in chloride–fluoride melts of KCl–NaCl–NaF mixtures of 0.425:0.425:0.15, 0.38:0.38:0.24, and 0.35:0.35:0.30 compositions and trace the thermal dependence of the solubility for these compositions.

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Experimental Section

Reagents. The potassium and sodium chlorides were “extra pure 23-3” grade (23-3 means that 23 impurities are controlled and that their content is less than 10^{-3} mass %), and the sodium fluoride was of reagent grade. The Al_2O_3 powder was obtained by reducing leuco-sapphire single crystals, which were kindly presented by Prof. L. A. Litvinov (Institute for Single Crystals of National Academy of Sciences of Ukraine), to smaller fragments.

The choice of the solvent compositions for the investigations was made with the following considerations. First, a solvent should be soluble in water; therefore it should consists of KCl, NaCl, and NaF (Li^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} cations are undesirable because the corresponding fluorides are insoluble in water), and its composition should belong to the KCl−NaCl (1:1)−NaF cross-section. Second, the melt should be relatively low melting with a wide enough temperature region of liquid state under 1273 K (at this temperature intensive evaporation of chlorides takes place) (i.e., it should fuse at temperatures near 973 K). Third, the melt should contain an appreciable concentration of the fluoride ion. The data necessary for the choice may be taken from the phase diagram constructed by Kovalev et al.[7] Namely, the range of concentration should be from 15 mol % of NaF (near eutectic, melting point = 875 K) to 38 mol % of NaF (melting point = 973 K). We chose to the study the melts with NaF concentrations of 15, 24, and 30 mol % of NaF using these data.

Method of Investigation. Determination of Al_2O_3 solubility was performed by the isothermal saturation method. The samples of Al_2O_3-saturated solutions were prepared as follows. The mixture of salts, in the proportion required to obtain 100 g of KCl−NaCl−NaF solvent of 0.425:0.425:0.15 (I), 0.38:0.38:0.24 (II), and 0.35:0.35:0.30 (III) compositions, was placed into an alundum crucible together with excessive amount of Al_2O_3 (usually within 2−3 g); the mixture was placed into the experimental cell and heated to the temperature of the experiment (973, 1023, 1073, and 1123 K) in argon flow: usually 2−3 h was required for temperature stabilization. Then, the solid phase was kept in contact with the melt for 30 min, after which a sample of the solution was extracted from the cell using the specially made alundum spoon. The next samples were obtained within a 30−40 min range, one after another. This method allows us to obtain the set of data for statistical treatment and to trace the process in the time.

The analysis of the Al_2O_3 concentration in the samples was performed by the atomic-emission spectral method,[8] which consisted of complete evaporation of the sample in the AC electric arc using an IBC-28 excitation source and a DFS-8 photoregistering device. Photoregistration of the sample spectra was performed at their evaporation from craters in the graphite electrodes into the arc at a current strength of 16 A and a voltage of 220 V; the duration was 60 s. The spectral range of 250−350 nm was used for the calculations. The lowest limit of aluminum detection was about 5×10^{-4} mass % with a determination error of 0.16.

The treatment of the experimental data consisted of recalculation of the aluminum concentration in the sample (mass %) with respect to the molar fraction of Al_2O_3 in the saturated melt with subsequent statistical treatment;[9,10] the latter was made after removal of obviously erroneous results from the data sets obtained. Statistical treatment was performed with the assumption of a normal distribution of the magnitudes.

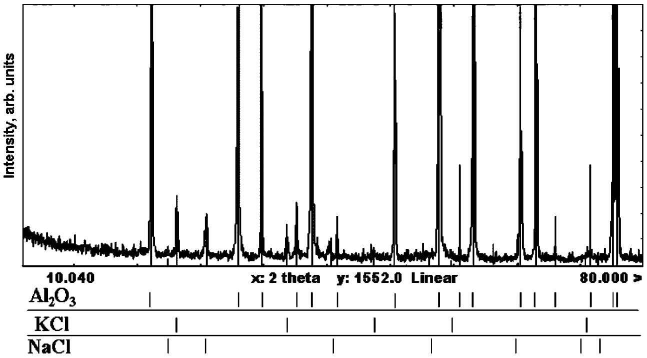

Figure 1. X-ray diffractogram of the Al_2O_3 sample used to obtain solubility data in the KCl−NaCl−NaF (0.35:0.35:0.30) melt. The diffractogram and the bar diagrams for pure phases are obtained at room temperature.

Since the destruction of Al_2O_3 by fluoride melts at high temperatures is possible and results in the formation of β-Al_2O_3 ($Na_2O{\cdot}11Al_2O_3$), the remaining Al_2O_3 deposit and the crucible walls were studied by X-ray phase diffraction analysis.

Results and Discussion

Before the main discussion, we considered the X-ray data to state which equilibrium is studied. The X-ray diffractogram is shown in Figure 1. It is seen that the deposit was corundum, Al_2O_3, with small inclusions of some individual alkali metal halides. There are no traces of any aluminates in the deposit, therefore, we can conclude that the equilibrium

$$Al_2O_{3,\mathrm{solid}}\downarrow = Al_2O_{3,\mathrm{dissolved}} \qquad (1)$$

is studied under the experimental conditions. For the β-Al_2O_3, it should be noted that this compound is formed if pure NaF is in contact with solid Al_2O_3. This means that the melt temperature is at least 1280 K and the mole fraction of F^- is equal to 1. For the chloride−fluoride melt, the temperature is efficiently lower, and the molar fraction of fluoride is 3−6 times as less than that in the pure fluoride melt. According to mass action law, the rate of Al_2O_3 destruction should be considerably less, and the temperature decrease leads to weakening of the destructive effect of the said ionic melt on the solid oxide.

The results of the determination of the mass fraction of Al_2O_3 in the samples and some calculated magnitudes are presented in Table 1, where x is Al_2O_3 solubility in mole fractions and S_x is the standard deviation (in mole fractions).

Spectral analysis of the samples shows that all the samples are referred to saturated solutions, and there are some oscillations from the definite average value at the same temperature caused, mainly, by features of the analysis method. This may be explained by the fact that the solid oxide starts interacting with the liquid phase from the moment of melting, and the relatively short exposition at a chosen temperature allows equilibrium conditions to be achieved. Literature data testify that a 2 h exposition at temperatures on the order of 1000 K is sufficient for the formation of the saturated solution for other oxides and other melts, which are less aggressive in respect to oxide materials.

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Table 1. Solubility of Al_2O_3 in Melts of KCl−NaCl−NaF Systems at Different Temperatures[a]

	KCl−NaCl−NaF (I) 0.425:0.425:0.15			KCl−NaCl−NaF (II) 0.38:0.38:0.24			KCl−NaCl−NaF (III) 0.35:0.35:0.30		
T (K)	x	S_x	log x	x	S_x	log x	x	S_x	log x
973				5.9×10^{-5}	4×10^{-6}	−4.23	7.9×10^{-5}	8×10^{-6}	−4.10
1023	4.5×10^{-5}	7×10^{-6}	−4.35	1.00×10^{-4}	7×10^{-5}	−4.00	1.33×10^{-4}	3×10^{-5}	−3.88
1073	5.7×10^{-5}	7×10^{-6}	−4.25	1.20×10^{-4}	6×10^{-6}	−3.92	1.57×10^{-4}	6×10^{-6}	−3.80
1123	7.7×10^{-5}	1×10^{-5}	−4.12	1.38×10^{-4}	5×10^{-6}	−3.86	1.70×10^{-4}	8×10^{-6}	−3.77

[a] x is the Al_2O_3 solubility in mole fractions, and S_x is the standard deviation in mole fractions.

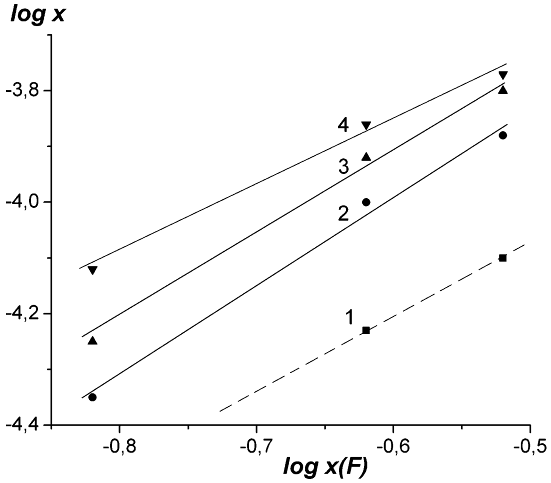

Figure 2. Dependence of Al_2O_3 solubility (log x) vs molar fraction of F^- (−log x(F)) in melts of KCl−NaCl−NaF system at different temperatures: (1) 973 K, (2) 1023 K, (3) 1073 K, and (4) 1123 K.

The data show that the solubility of alumina in the chloride−fluoride melts at the studied temperatures is low (within 0.1−0.2 g per 1 kg of the melts) and increases with increasing temperature. The increase of the F^- concentration in the molten media leads to an increase of the Al_2O_3 solubility, as shown in Figure 2. This is explained in the frames of the "hard and soft acid and base" concept by Pearson.[11−13] In essence, the interaction between the pairs formed by hard and soft acids and bases leads to the preferable formation of a "harder acid−harder base" pair as one of the products and a "softer acid−softer base" pair as another product that is presented the equation

$$\boxed{HA-SB}+\boxed{SA-HB}\rightarrow\boxed{HA-HB}+\boxed{SA-SB}, \tag{2}$$

where HA and HB are hard acid and base, respectively, and SA and SB are soft acid and base, respectively.

The fluoride ion is known to be a considerably harder base than chloride. An increase of its concentration in the chloride−fluoride melts makes them a harder basic media. Al^{3+} belongs to the hardest acids, and it forms very stable complexes with F^-; therefore, the degree of action of the melt on alumina

$$Al_2O_3\downarrow + 2nX^- = 2AlOX_n^{\ n-1} + O^{2-} \tag{3}$$

(where X is halogen) should increase if Cl^- is substituted partially or completely by F^-. The comparison of the solubility data in both studied melts shows that the increase of F^- concentration by two times leads to the increase of Al_2O_3 solubility in the chloride−fluoride system by ∼2.6 times.

Polythermal investigations allow us to solve some problems connected with the properties of the studied saturated solutions. In particular, it is possible to detect if the solution formed is ideal and trace how these deviations are changed with a temperature increase. An important practical aspect is the "log $x-T^{-1}$" plot which makes the prediction of the solubility at intermediate temperature possible.

The running solubility of a solid substance, formed of the ideal solution, with temperature is predicted by the Shreder−Le Chatelier equation[14]

$$\log x = \frac{\Delta H_m(T - T_m)}{2.3RTT_m} \tag{4}$$

where ΔH_m is the heat of melting and T_m is the melting point of the solid. After some transformations, this equation may be written as

$$\log x = \frac{\Delta H_m}{2.3R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{5}$$

This dependence presents a straight line in log $x = f(T^{-1})$ coordinates. The calculation using this equation, taking into account that $\Delta H_m = 111.4$ kJ mol^{-1} and $T_m = 2317$ K,[15] leads to the following solubility values (mole fractions): 3.4×10^{-4}(at 973 K), 6.7×10^{-4}(at 1023 K), 1.2×10^{-3}(at 1073 K), and 2.1×10^{-3}(at 1123 K). These data show that the Al_2O_3−chloride−fluoride melt is characterized by considerable negative deviation from the ideal; this means that the $Al^{3+}-O^{2-} + Na^+(K^+)F^-$ interactions are stronger than the $Al^{3+}-F^- + Na^+(K^+)-O^{2-}$ ones. (The interaction of two multicharged ions should be predominant; that behavior is also proper to other oxide−halide melt systems.) In addition to the solubility values, we obtain the theoretical slope of the log $x = f(T^{-1})$ plot as

$$\left(\frac{\partial(\log x)}{\partial(T^{-1})}\right)_p = \frac{\Delta H_m}{2.3R} = 5820K \tag{6}$$

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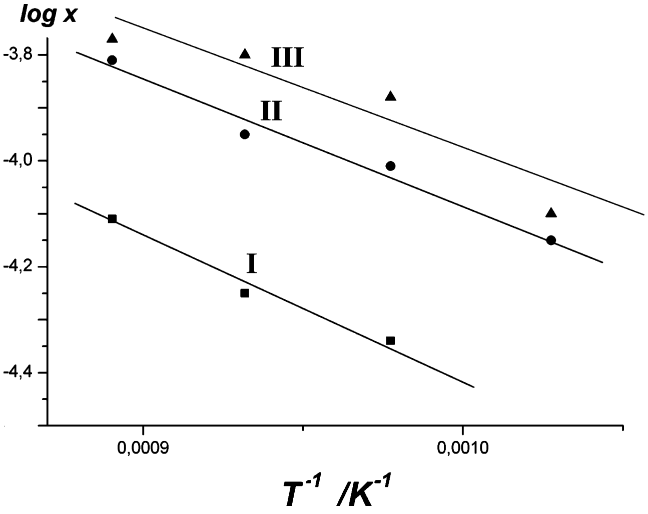

Figure 3. Dependence of Al_2O_3 solubility (log x) in melts of KCl−NaCl−NaF with the compositions 0.425:0.425:0.15 (I), 0.38:0.38:0.24 (II), and 0.35:0.35:0.30 (III) versus the inverse temperature.

Let us consider the experimentally obtained dependences presented in Figure 3. They can be approximated by the following equations:

$$\log x = 1.79\ (\pm\ 0.3) - 2630\ (\pm\ 270)T^{-1} \quad \text{for composition (I)} \quad (7)$$

$$\log x = 1.5\ (\pm\ 0.3) - 2630\ (\pm\ 400)T^{-1} \quad \text{for composition (II)} \quad (8)$$

$$log\ x = 1.63\ (\pm\ 0.6) - 2360\ (\pm\ 600)T^{-1} \quad \text{for composition (III)} \quad (9)$$

As can be seen from the presented calculations, the slopes of the dependences for both chloride−fluoride melts are practically half that of the theoretical one. This also may be explained by the negative deviations from ideal in the system studied. Moreover, the method used for the solubility investigation allows us to determine the sum of two kinds of particles: Al^{3+} and Al_2O_3. Both particles are foreign for the solvents studied; therefore, we should expect such deviations. In relation to the temperature dependence, it should be noted, that the slope of such a plot shows comparable changes of interparticle interactions with the temperature. It is clear that such an interaction weakens because of the increase of kinetic energy of the particles. It can be used to to conclude that, if the $Al^{3+}-O^{2-}$ and $Na^+(K^+)F^-$ interactions weaken to a greater degree than the $Al^{3+}-F^-$ and $Na^+(K^+)-O^{2-}$ ones, we should observe a slope that is greater than the theoretical one. If we obtain the theoretical slope, we state that the weakening of these processes occurs to practically the same degree (for the $Me^{2+}+O^{2-}$ system, it takes place in some cases). In our case, we conclude that the break down of the bonds in the solvents with temperature is more intense than that in the solid phase and the slope of the dependence log x versus T^{-1} should be less than the theoretical one. The melting of Al_2O_3 at a temperature higher than boiling points of the components of the solvent gives an information about the strength of the interparticle bonding.

For the chloride−fluoride system studied, it should be noted that melt I, as a solvent, was studied by a potentiometric method using a membrane oxygen electrode Pt-(O_2)|$ZrO_2(Y_2O_3)$.[16] It was found that the melt in the alumina crucible was polluted by oxygen-containing admixtures (~0.01 mol kg^{-1}), which could not be removed by usual purification procedures. With both $ZrO_2(Y_2O_3)$ and Al_2O_3 are considered to be possible pollutants, a sample of the obtained solution was analyzed. The former compound was found to be stable under the experimental conditions, whereas alumina underwent appreciable corrosion. The spectral analysis allowed us to estimate Al_2O_3 concentrations down to 5×10^{-3} mol/kg which corresponded to molar fractions (x) on the order of 2×10^{-4}. This value is somewhat higher than that reported in this paper and may be explained by the difference in particle sizes.

The use of the same crucible leads to its corrosion (and increase of the surface area) for different reasons. They are high acidic or basic melts, thermal shocks, melting/freezing of the studied melts in the pores, etc. Therefore, to avoid these factors, we use one crucible for one cycle of measurements. That is, we heated the crucible, for example, to 700 °C; then we obtained the samples (approximately 4−5 h), and the temperature was increased to 750 °C where the samples corresponding to this temperature were obtained. This procedure requires one working day. The next day, we took new crucible and heated it with the salt mixture to 800 °C, and the procedure was repeated.

The potentiometric data were obtained in a crucible used for some measurements, and the solubility of its walls was 2−4 times larger than that of the pounded single crystal. In view of the Ostwald−Freundlich rule (the effect of grain size on solubility), the solubility in new crucibles corresponds to true Al_2O_3 solubility in the melt.[17]

The different solubilities of Al_2O_3 in the said melt are, for system I, 0.07 g kg^{-1} at 1023 K, 0.09 g kg^{-1} at 1073 K, and ~0.12 g kg^{-1} at 1123 K; for system II, these values are 0.10 g kg^{-1} at 973 K, 0.17 g kg^{-1} at 1023 K, 0.20 g kg^{-1} at 1073 K, and 0.23 g kg^{-1} at 1123 K, and for system III, they are 0.14 g kg^{-1} at 973 K, 0.23 g kg^{-1} at 1023 K, 0.27 g kg^{-1} at 1073 K, and 0.29 g kg^{-1} at 1123 K. The cooling of the saturated melts from 1123 to 1023 K allows the crystallization of approximately 0.05 g of Al_2O_3 from 1 kg of the melts. This value is too low; therefore these solvents cannot be recommended to obtain Al_2O_3 single crystals by direct crystallization. However, the solubility values make it possible to use the chloride−fluoride melts for treatment of alumina as fluxes or media for recrystallization-like processes.

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Conclusions

Al_2O_3 is slightly soluble in the KCl−NaCl−NaF mixtures of 0.425:0.425:0.15 (I) and 0.35:0.35:0.30 (II) compositions in the 973−1123 K temperature range. Some increase of the solubility with temperature is observed, although the slope of the $-\log x_{Al_2O_3}$ versus T^{-1} plot is only half that of the theoretical one.

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Supporting Information Available: A phase diagram of the KCl−NaCl−NaF system (Kovalev, V. F.; Ioffe, V. M.; Kartsev, V. E. *Zh. Neorg. Khim.* **1970**, *15*, 1966), and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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