

Structure and Thermodynamic Properties of Molten Rare Earth-Alkali Chloride Mixtures

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The dependence of the enthalpy of mixing on the structure of molten rare earth-alkali chloride mixtures has been investigated by molecular dynamics simulation. The experimental enthalpy of the mixing with its negative and its dependence on the cation size was qualitatively reproduced. It became clear that the enthalpy of mixing depends on the structural features of short and medium range.

Key words: Molten Salt; Molecular Dynamics; Enthalpy of Mixing; Rare Earth-alkali Chloride Mixture.

1. Introduction

Molten salts may be applied in nuclear nitride fuel cycles and pyrochemical reprocessing [1], and the transmutation of minor actinides using a proton accelerator [2]. In view of this we have studied the structure and the thermodynamic and dynamic properties of molten rare-earth and uranium trichlorides, mainly single salts such as YCl_3 and UCl_3 , by both experimental [3, 4] and molecular dynamics (MD) [5, 6] methods.

The molar enthalpies of mixing of molten LaCl_3 - ACl ($A = \text{Li, Na, K, Rb and Cs}$) mixtures were reported by Papatheodorou et al. [7], and those of some rare-earth trichloride- NaCl mixtures by Blachnik et al. [8]. These studies show two interesting tendencies: the enthalpy of mixing of binary molten rare earth-alkali chlorides is negative and its minimum becomes deeper as the size of alkali metal ion increases and that of the rare earth metal ion decreases. The same tendency was observed by Gaune-Escard et al. [9, 10]. for mixtures of molten NdCl_3 and PrCl_3 with alkali chlorides. In the present work, the correlation between the enthalpy of mixing and the structure of molten rare earth-alkalichloride mixtures has been investigated by MD simulation.

2. MD Simulation

a) Pair Potentials

For the molten alkali chlorides we used the Born-Mayer-Huggins type pair potential with parameters proposed by Tosi and Fumi [11]:

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} + A_{ij} b \exp \left[\frac{\sigma_i + \sigma_j - r}{\rho} \right], \quad (1)$$

where z_i and σ_i are electric charge number and size parameter of ion i , A_{ij} is the Pauling factor between the ions i and j , and ρ the softness parameter. A_{ij} is defined as

$$A_{ij} = \frac{z_i}{n_i} + \frac{z_j}{n_j} + 1, \quad (2)$$

where n_i is the number of electrons in the outer shell of the ion i . Calculations on molten alkali chlorides by use of the Tosi-Fumi potential agree well with the experimental results [12] Tatlipinar et al. [13] reported results of computer simulations for molten rare earth trichlorides by using the Busing-type potential

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} + b(f_i + f_j) \exp \left[\frac{\sigma_i + \sigma_j - r}{f_i + f_j} \right]. \quad (3)$$

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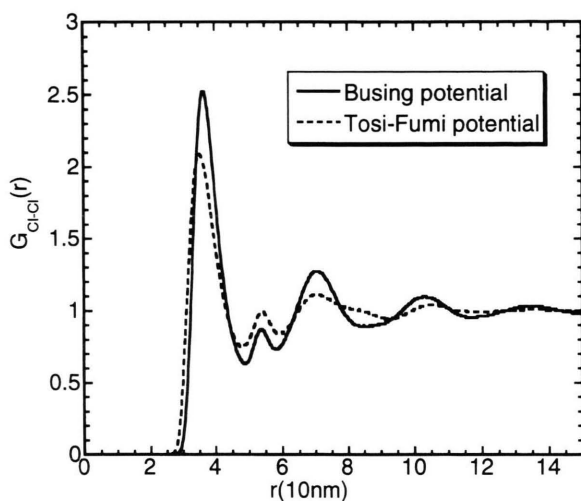


Fig. 1. Partial radial distribution functions $G_{\text{Cl-Cl}}(r)$ of molten LaCl_3 by MD simulation.

In case of alkali chloride - rare earth trichloride mixtures the Cl^- - Cl^- pair potential is a problem, since it is impossible to determine whether a particular Cl^- ion belongs to a rare earth or an alkali cation. Figure 1 shows the two theoretical partial radial distribution functions (RDF) $G_{ij}(r)$ of the Cl^- - Cl^- pair in molten LaCl_3 . The peak positions based on the Tosi-Fumi potential were similar to those based on the Busing potential. Therefore it is not a bad approximation to replace the Busing-type potential by the Tosi-Fumi potential for molten LaCl_3 . On the other hand, to use the Busing potential for molten KCl chloride resulted in poor agreement with the experimentally obtained molten structure. Thence the Tosi-Fumi potential was used for the molten rare earth-alkali chloride mixtures.

b) Procedure

In the simulation, systems of 512 particles were used for eight compositions; 0, 10.34, 19.63, 30.61, 40.66, 60.00, 80.28 and 100% RECl_3 . The number of ions in systems is given in Table 1, together with the density and the side length of the cubic basic cell. Mixtures calculated in the present work were LaCl_3 - ACl ($A = \text{Li, Na and K}$) and RECl_3 - KCl ($\text{RE} = \text{Y, Nd and La}$). The densities used in the simulations are based on the experimental data recommended by Janz [14]. The step width was 2.0 fs.

The molten structures were obtained by isothermal-choric (NVT) MD simulations of 10000 steps. Iso-

Table 1. Number of ions N , density d and side length L of the cubic cells used in the MD simulation of LaCl_3 - KCl .

No.	Mol% LaCl_3	N_{La}	N_{K}	N_{Cl}	N_{total}	d (g/cm ³)	L (nm)
1	KCl	0	256	256	512	1.4480	2.79721
2	10.34	24	208	280	512	1.6740	2.76858
3	19.63	42	172	298	512	1.8672	2.73979
4	30.61	60	136	316	512	2.0838	2.70564
5	40.66	74	108	330	512	2.2713	2.67566
6	60.00	96	64	352	512	2.6044	2.62341
7	80.28	114	28	370	512	2.9163	2.57677
8	LaCl_3	128	0	384	512	3.1854	2.53892

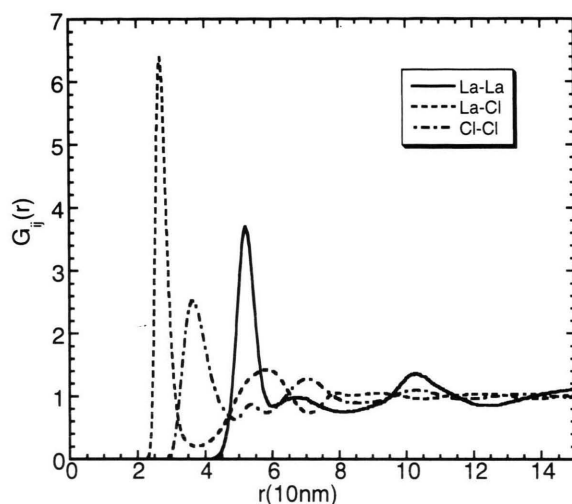


Fig. 2. Partial radial distribution functions $G_{ij}(r)$ of molten LaCl_3 by MD simulation.

thermal-isobaric (NPT) simulations were performed to obtain the thermodynamic properties. The enthalpy $H(T)$ was defined as internal energy U at zero pressure. U was deduced from the sum of the kinetic and potential energy:

$$U = \frac{3}{2}NkT + \sum_{i>j} \phi(r_{ij}), \quad (4)$$

where N is number of ions of the calculated system. The enthalpy of mixing was calculated by the equation [15]

$$\Delta H_{\text{mix}}^E = H[x \cdot \text{RECl}_3 + (1-x) \cdot \text{ACl}] - xH[\text{RECl}_3] - (1-x)H[\text{ACl}], \quad (5)$$

where x means the mole fraction of the rare earth trichloride. In the present work, 100000 steps were used to obtain the enthalpy.

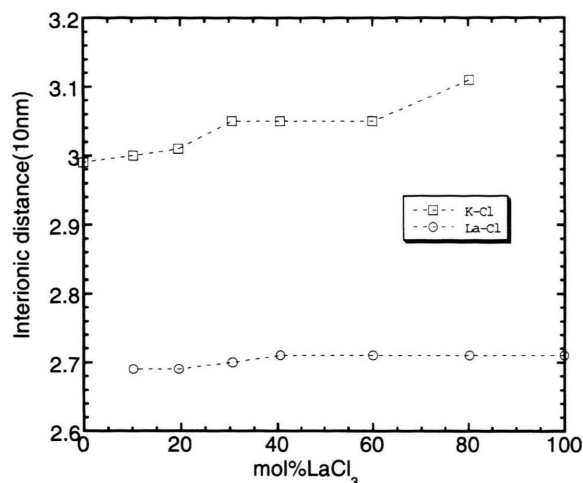


Fig. 3. The nearest neighbor distance of unlike ions in molten LaCl₃-KCl by MD simulation.

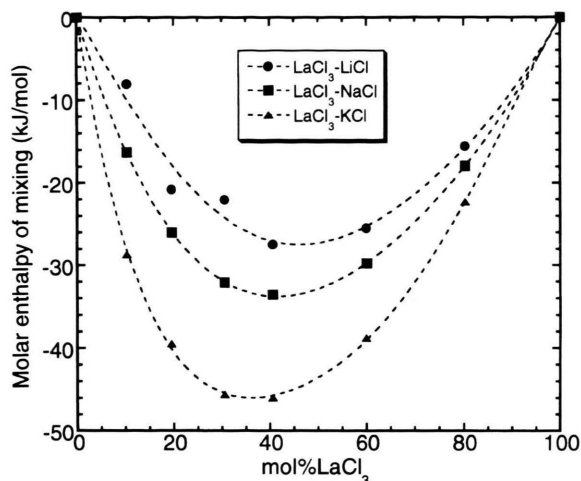


Fig. 5. Enthalpy of mixing of molten LaCl₃-ACl (A = Li, Na and K) binary systems by MD simulations.

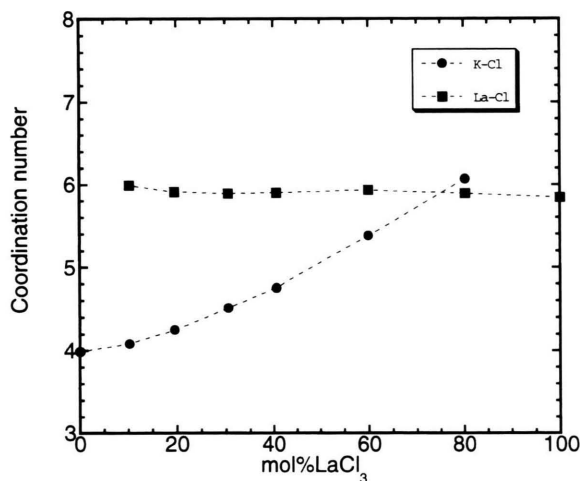


Fig. 4. Coordination numbers in molten LaCl₃-KCl binary systems by MD simulation.

3. Results and Discussion

a) Molten Structure

Figure 2 shows the obtained partial RDF's $G_{ij}(r)$ of molten LaCl₃. It has been reported [16] that most molten rare earth trichlorides have an octahedrally coordinated structure in which the rare earth metal ion is surrounded by six Cl⁻ ions. The ratio of $r_{\text{Cl-Cl}} = 0.370$ nm to $r_{\text{La-Cl}} = 0.269$ nm in the calculated partial RDF is close to $\sqrt{2}$ as calculated from the geometry

of the octahedron. The number of Cl⁻ ions around the La³⁺ ion was about 6.

The nearest La-Cl and K-Cl distances for molten LaCl₃-KCl are plotted in Figure 3. The nearest La-Cl distance is almost constant (about 0.269 nm) in the mixtures. On the other hand, the nearest K-Cl distance became shortened from 0.310 nm at 80.28%LaCl₃ to 0.299 nm in pure KCl. The variation of the Cl⁻ coordination number around the cations is shown in Figure 4. Around the La³⁺ ion it is nearly constant and is about six, which means that the octahedral structure is kept in the mixtures. Around the K⁺ ion, however, it increases from 4 in pure KCl to 6 in 80.28%LaCl₃-KCl melt.

b) Enthalpy of Mixing

The calculated molar enthalpies of mixing of molten LaCl₃-ACl (A = Li, Na and K) at 1200 K are shown in Figure 5. The calculations resulted in deeper minima for the three mixtures than found experimentally. The calculated minimum for LaCl₃-KCl is three times deeper than the reported value ca. -15.4 kJ/mol [7]. There is, however, qualitative reproducibility: negative deviation, increasing with the size of alkali ion. The calculated molar enthalpies of mixing for molten RECl₃-KCl (RE = Y, Nd and La) are shown in Figure 6. In contrast to the enthalpies of mixing of molten LaCl₃-ACl (A = Li, Na and K) shown in Fig. 5, the mixtures with a smaller rare earth metal ion gave a deeper minimum in the enthalpy of mixing.

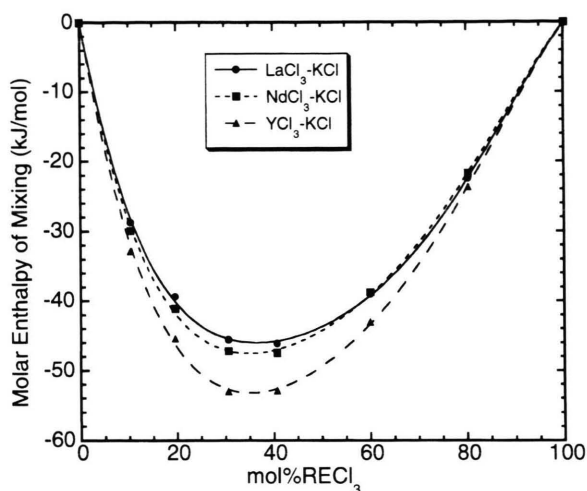


Fig. 6. Enthalpy of mixing of molten RECl_3 -KCl (RE = Y, La and Nd) binary systems by MD simulations.

The calculated enthalpies of mixing of molten LaCl_3 -KCl mixtures can be divided into two kinds of contributions based on short- and long-range interactions. The potential energy calculated in the MD simulation is a sum of pair potentials. The internal energy U given by (4) can be rewritten as

$$U = \frac{3}{2}NkT + \sum_{i>j}^{\text{short}} \phi(r_{ij} < 0.45 \text{ nm}) + \sum_{i>j}^{\text{long}} \phi(r_{ij} > 0.45 \text{ nm}). \quad (6)$$

Thus, we can distinguish two kinds of molar enthalpy, H_{short} and H_{long} corresponding to short- and long range interactions, respectively. Therefore we write

$$\Delta H_{\text{mix}}\langle \text{short} \rangle = H[x \cdot \text{LaCl}_3 + (1-x) \cdot \text{KCl}] \quad (7)$$

$$- xH[\text{LaCl}_3]_{\text{short}} - (1-x)H[\text{KCl}]_{\text{short}},$$

$$\Delta H_{\text{mix}}\langle \text{long} \rangle = H[x \cdot \text{LaCl}_3 + (1-x) \cdot \text{KCl}] \quad (8)$$

$$- xH[\text{LaCl}_3]_{\text{long}} - (1-x)H[\text{KCl}]_{\text{long}},$$

The enthalpies of mixing of molten LaCl_3 -KCl in the Fig. 5 were divided into two kinds of contributions, beyond 0.45 nm and within 0.45 nm. The results are shown in Figure 7. The reason why the cut-off distance 0.45 nm was chosen is that the nearest La^{3+} - Cl^- and Cl^- - Cl^- interactions which are considered to be closely associated with the octahedron can be separated around 0.45 nm from the nearest La^{3+} - La^{3+}

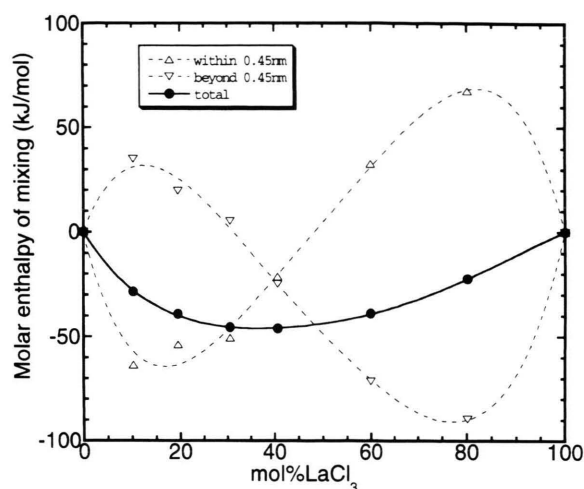


Fig. 7. Separation of the enthalpy into two kinds of contributions within and beyond 0.45 nm interactions.

interaction, as clearly indicated in the Figure 2. As for the contributions within 0.45 nm, we find the negative deviation at the KCl rich composition and the positive deviation at the LaCl_3 -rich composition. On the other hand, for the contributions beyond 0.45 nm the positive deviation is in the KCl rich region and negative one in the LaCl_3 rich region. These results are discussed in the next section.

c) Correlation Between Enthalpy of Mixing and Molten Structure

The stability of the octahedron in molten LaCl_3 may change by adding KCl, though the fundamental structure around the La ion does not change. Stability of the octahedron, ΔE_{st} defined by (9), on adding alkali chlorides is shown for LaCl_3 -LiCl and LaCl_3 -KCl in Figure 8.

$$\Delta E_{\text{st}} = \bar{E}_{\text{octa}}(\text{LaCl}_3) - \bar{E}_{\text{octa}}(\text{LaCl}_3\text{-KCl mixture}), \quad (9)$$

$$\bar{E}_{\text{octa}}(\text{LaCl}_3) = \sum \sum \phi(r) \quad (r \text{ for octahedron}), \quad (10)$$

where $\bar{E}_{\text{octa}}(\text{LaCl}_3)$ represents the average of the total potential energies of octahedra defined by (10). Relative values to the octahedra in the pure LaCl_3 melt are plotted in Figure 8. Adding alkali chlorides stabilizes the octahedron in both mixtures. In the single salt, the number of Cl^- ions is not sufficient to build a network of octahedrally-coordinated structure. On the other hand, the octahedron becomes stable by supplying Cl^- ions from alkali chloride. The composition

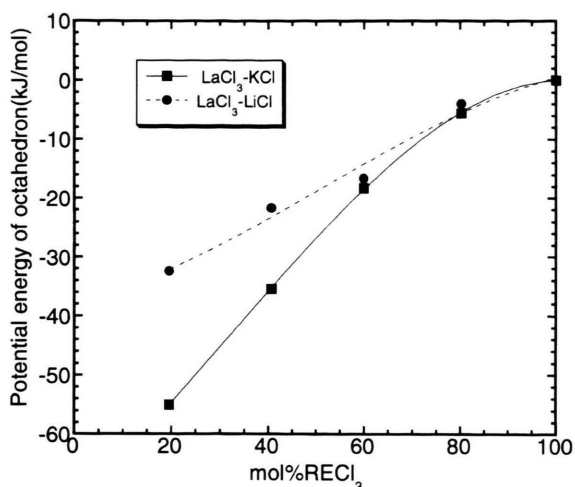


Fig. 8. Stability changes of the octahedron in molten LaCl_3 - LiCl and LaCl_3 - KCl binary systems by MD simulations.

dependence of the energy of the octahedron corresponds to that of the partial molar enthalpy of mixing for LaCl_3 - KCl mixtures shown in the Figure 7. The octahedron (LaCl_6)³⁻ is more strongly stabilized by the larger K^+ ion compared with the smaller Li^+ ion as shown in the Figure 8.

In the pure LaCl_3 melt, some Cl^- ions are considered to be connected with two La^{3+} ions to compensate the lack of Cl^- ions. Saboungi et al. [17] suggested from neutron diffraction analysis that there is a medium range order (MRO) in molten YCl_3 . The MRO may be due to the coordination of octahedrons with each other via bridging- Cl^- ions. The ratio of bridging- Cl^- ion to total Cl^- ions may be almost proportional to the MRO. The bridging- Cl^- ion is easily detected by counting the coordination number of rare earth ions around a Cl^- ion in the simulation, because the number of rare earth ions around the bridging- Cl^- ion is 2 or more. Figure 9 shows ratio of the bridging- Cl^- ions to total Cl^- ions for molten YCl_3 - KCl and LaCl_3 - KCl . In the pure trichloride melts, most Cl^- ions (over 80%) are bridging- Cl^- ions. The amount of bridging- Cl^- ions, however, decreases with increasing KCl fraction. This means that bridging- Cl^- ions are not required for building the octahedra due to the Cl^- ions from KCl . The decreasing in the MRO by adding KCl is considered to be responsible for the minimum of the enthalpy of mixing found in the LaCl_3 -rich region for the long range contribution in Figure 7. The smaller Y^{3+} ion results in a higher fraction of bridging- Cl^- ions in the

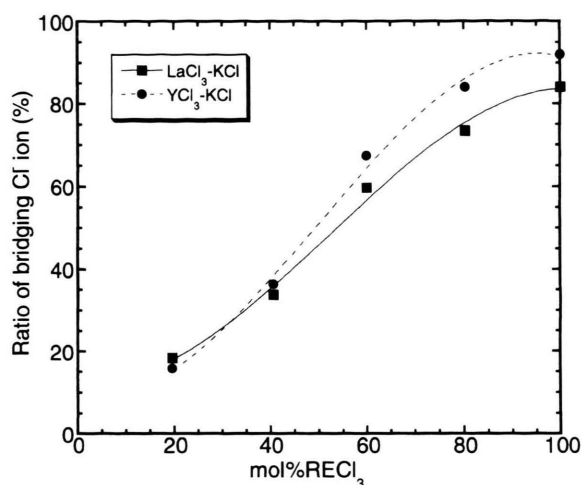


Fig. 9. Ratio of the bridging- Cl^- ions to total Cl^- ions in molten YCl_3 - KCl and LaCl_3 - KCl binary systems.

RECl_3 -rich region compared with the larger La^{3+} ion. This suggests that smaller rare-earth ions produce a higher range of MRO in molten rare-earth trichloride-alkali chloride mixtures.

The structural features in the mixtures found by the above simulations are compatible with the behavior of the enthalpy of mixing discussed in the previous section. This stability of the octahedron and the medium range structural order are strongly affected by the ionic size. In the simulation, a combination of larger alkali and smaller rare-earth ions was found to produce more negative values of the enthalpy of mixing. The quantitative discrepancy between the experimental and calculated values, remains unexplained. Papatheodorou et al. explained the behavior of the enthalpy of mixing of LaCl_3 -alkali chloride binary systems by electrostatic interactions with polarization between the octahedron and the alkali ions. Better accuracy will be obtained by considering the polarization effect in further simulations.

4. Conclusion

The enthalpy of mixing of molten rare earth-alkali chloride mixtures has been correlated to their structural features by a molecular dynamics method. In the simulations, the dependence of the enthalpy of mixing on the ionic sizes and composition of the mixtures was qualitatively reproduced. It was found that the enthalpy of mixing is largely determined by changes in the short and medium range orders in the mixtures.

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- [1] T. Ogawa, M. Akabori, Y. Suzuki, F. Kobayashi, T. Otsugi, and T. Mukaiyama, Proc. Int. Conf. on Emerging Nuclear Fuel Cycle Systems, Global-'97, (1997).
- [2] M. Mizumoto et al. Proc. Int. Conf. on Emerging Nuclear Fuel Cycle Systems, Global-'93, p. 357, 1993.
- [3] H. Hayashi, Y. Okamoto, T. Ogawa, Y. Sato, and T. Yamamura, MS-5 conference, Dresden, Germany 1997.
- [4] Y. Okamoto, F. Kobayashi, and T. Ogawa, J. Alloys Comp. **271-273**, 355 (1998).
- [5] Y. Okamoto, H. Hayashi, and T. Ogawa, J. Non-Cryst. Sol. **205-207**, 139 (1996).
- [6] Y. Okamoto, H. Hayashi, and T. Ogawa, J. Nucl. Mater. **247**, 86 (1997).
- [7] G. N. Papatheodorou and T. Østfold, J. Phys. Chem. **78**, 181 (1974).
- [8] R. Blachnik and D. Selle, Z. Anorg. Allg. Chem. **454**, 90 (1979).
- [9] M. Gaune-Escard, L. Rycerz, and W. Szczepaniak, A. Bogacz, Thermochemica **236**, 59 (1994).
- [10] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, Thermochemica **236**, 67 (1994).
- [11] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids, **25**, 45 (1964).
- [12] L. V. Woodcock, Chem. Phys. Lett. **10**, 257 (1971).
- [13] H. Tatlipinar, Z. Akdeniz, G. Pastore, and M. P. Tosi, J. Phys.: Condens. Matter. **4**, 8933 (1992).
- [14] G. J. Janz, J. Phys. Chem. Ref. Data **17**, 1 (1998).
- [15] R. Takagi, L. Rycerz, and M. Gaune-Escard, Proceedings of the 9th International Symposium on Molten Salts (1994), p. 99.
- [16] G. N. Papatheodorou, Inorg. Nucl. Chem. Lett. **11**, 483 (1975).
- [17] M.-L. Saboungi, D. L. Price, C. Scamehorn, and M. P. Tosi, Europhys. Lett. **15**, 173 (1991).