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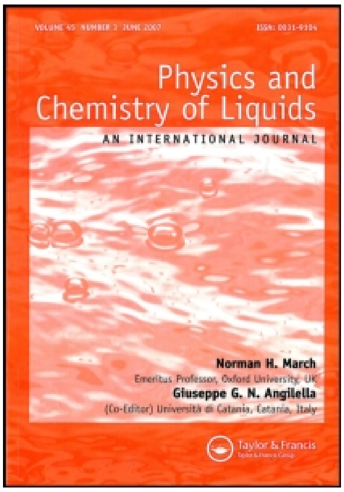

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Microstructure of mixed-nitrate melts and glasses

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We evaluate the stability of various structures for a $Ca_2(NO_3)_7$ core unit compensated by K or Rb ions, as a basic constituent of the glass-forming melts of CKN and CRbN compounds [$3ANO_3 \cdot 2Ca(NO_3)_2$ with $A = K$ or Rb]. We find that three alternative structures are stable for the core unit and lie at approximately the same energy, provided the Ca-NO_3 overlap repulsion is stiff enough as suggested by the planar structure of the NO_3 group, but independent of the amount of electronic charge transfer to these groups. In these structures, each Ca ion can lie in a fourfold or a fivefold coordination by NO_3 groups, so that the two Ca ions can be bridged by one, two, or three NO_3 groups. This picture is compatible with the accepted view of CKN as a prototype fragile glass-former and with the stability of mixed-nitrate glasses over a broad range of composition.

Keywords: Ionic glasses; Molten Salts; Nitrates

1. Introduction

Mixed-nitrate glasses are formed by quenching a molten mixture of a divalent-metal nitrate and an alkali nitrate and are stable over a broad range of composition [1]. The stoichiometric $3KNO_3 \cdot 2Ca(NO_3)_2$ compound, known as CKN, has been studied in depth as a prototype of these materials, and in particular its transport properties in the melt have been accurately measured over very broad temperature ranges [2,3]. The measured temperature dependence of the shear viscosity shows strong deviations from the simple Arrhenius law [2] and classifies the melt as a fragile glass-former, implying that its structure may reorganize itself over a variety of particle orientations and coordination states [4]. The structure of molten CKN should thus be viewed as a disordered array of strong chemical units, rather than as an extended disordered network of chemical bonds. Parallel measurements of the ionic conductivity of molten CKN have displayed strong deviations from a linear Stokes–Einstein law [3], indicating that the elementary mechanisms of momentum and charge transport are basically different in this material as in many other glass-forming systems.

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The evidence that we have recalled above suggests a model in which the electrical conduction in CKN is due to the motions of alkali ions through a disordered array of strongly bound $Ca_2(NO_3)_7$ units, while the latter are mainly responsible for the viscosity of the material. In this work, we approach a microscopic implementation of this model by proposing suitable interionic force laws and using them to evaluate the structural features of monomeric units for both CKN and CRbN.

Specifically, we evaluate the stability of three alternative structures for the $Ca_2(NO_3)_7$ unit compensated by three K or Rb ions. In these structures, the Ca ions share either one, two or three NO_3 groups. Two rather different values of the charge transfer to the NO_3 groups are examined, thus allowing for different amounts of ionic character, and the overlap repulsive forces between first neighbours are taken to be quite stiff, consistently with the structure of the NO_3 groups. In brief, section 2 presents the model and its parameters, and section 3 reports our main results. Our conclusions are given in section 4.

2. The model

Various structural and dynamic evidence indicate that the pure components of the nitrate mixtures conform reasonably well to an ionic model, with the NO_3 group acting as the negative ion [5]. To our knowledge, the essential available data for alkali nitrates are the value of the Rb–N distance in $RbNO_3$ ($r_{\mathrm{Rb–N}} = 3.10$ Å [6]) and the frequency of an infrared-active vibrational mode in the melt of these materials [7]. In our previous work [5] we found that these data are compatible with rather different values for the amount of electronic charge transfer from the alkali to the NO_3 group. We also examined two alternative choices for the relative stiffness of the alkali-NO_3 overlap repulsion, corresponding to values appropriate for a soft spherical anion such as chlorine in an alkali chloride [8] or for a much stiffer polyvalent ion [9]. In fact, the NO_3 group is a very stable unit in the shape of a planar equilateral triangle with nitrogen at its center [10], possessing internal vibrational modes that are almost independent of its metal-ion partners [1,7] as well as a low-frequency Raman-active mode associated with torsional oscillations around its axis in both the melt and the hot-solid phase of alkali nitrates [7,11]. We concluded that the second above-mentioned choice of the relative-stiffness parameter is more appropriate to describe the overlap repulsion between the flat NO_3 group and an alkali ion or a divalent Ca ion. We then reported finding a new stable structure for a $Ca_2(NO_3)_7$ unit, which consists of two fivefold-coordinated Ca ions sharing three NO_3 bonding groups. A previous work had already proposed another structure for $Ca_2(NO_3)_7$ in vitreous CKN [12], in which the two Ca ions are fourfold-coordinated and share a single NO_3 group.

Following our previous work [5] we use interionic pair potentials to construct the potential energy $U(\{r_{ij}\})$ of an $A_3Ca_2X_7$ molecular cluster (where A = K or Rb and X = NO_3) as a function of the set of bond lengths r_{ij} between pairs of ions. We write

$$U(\{r_{ij}\}) = \sum_{i \neq j} \left[\frac{Z_i Z_j}{r_{ij}} + \Phi_{ij}(r_{ij}) \right], \qquad (1)$$

where Z_i are the ionic valences and $\Phi_{ij}(r)$ are the overlap repulsive potentials. These are taken in the Busing form,

$$\Phi_{ij}(r) = f(\rho_i + \rho_j)\exp\left[\frac{R_i + R_j - r}{\rho_i + \rho_j}\right] \tag{2}$$

where R_i are the ionic radii, ρ_i are the ionic inverse-stiffness constants, and $f = 0.05\,\mathrm{e}^2/\text{Å}^2$. Contributions from electronic polarization are, in general, associated mainly with the anion [13] and are omitted in the present context, as they are expected to be small and to mainly affect the details of the shape of the cluster.

The parameters that we have used for the model given in equations (1) and (2) are indicated in table 1. The interested reader is directed to [5] for an exhaustive presentation of their assessment. In brief, we have fixed the repulsive parameters for the alkali ions by taking R_A as the Tosi–Fumi radii [8] and by determining ρ_A from a fit of the bond lengths in diatomic alkali chloride molecules [14]. The corresponding values of the parameters for the Ca ion are from the work of Yuen *et al.* [15]. Finally, the repulsive parameters of the $\mathrm{X} = \mathrm{NO_3}$ ion and the two values of its effective valence are from our previous analysis of data on the Rb–N distance in $\mathrm{RbNO_3}$ [6] and on the infrared-active mode frequency in nitrate melts from the review of Brooker and Papatheodorou [7]. In all cases we have taken $R_\mathrm{X}/\rho_\mathrm{X} = 18.6$, yielding rather stiff repulsive interactions between cations and anions. The repulsions between nitrate ions are governed by their Coulomb interactions, their magnitude being determined by the amount of charge transfer.

The highest value of the ionic valence yields a deeper potential energy minimum for the $\mathrm{ANO_3}$ group, yielding at equilibrium a binding energy $-U_\mathrm{AX} \approx 3.1$–$3.3\,\mathrm{eV}$ for $Z_\mathrm{X} = -0.86$ against $-U_\mathrm{AX} \approx 1.7$–$1.8\,\mathrm{eV}$ for $Z_\mathrm{X} = -0.63$. The magnitude of these estimates is not substantially altered in an important manner when one accounts for the difference between the electron affinity of $\mathrm{NO_3}$ (3.94 eV [16]) and the first ionization potential of Rb or K (4.2–4.3 eV) in estimating the binding energy of an alkali nitrate unit relative to its separated neutral components. Barring strong chemical contributions to the bonding associated with the detailed distribution of valence electrons on the $\mathrm{NO_3}$ ion, a rather high ionicity of alkali nitrates is suggested by these results.

3. Structure of the $\mathrm{Ca_2K_3(NO_3)_7}$ and $\mathrm{Ca_2Rb_3(NO_3)_7}$ units

We use the interionic force laws reported in table 1 to evaluate the possible structures of a $\mathrm{Ca_2A_3(NO_3)_7}$ unit in a state of mechanical equilibrium, by starting from several alternative initial configurations and searching for minima of the potential energy in configuration space. We find a variety of $\mathrm{Ca_2(NO_3)_7}$ core structures in which each of the

Table 1. Model parameters for nitrates.

System		$-Z_\mathrm{X}$	R_A (Å)	ρ_A (Å)	R_Ca (Å)	ρ_Ca (Å)	R_X (Å)	ρ_X (Å)
$\mathrm{KNO_3}$	(1)	0.86	1.46	0.18	1.32	0.071	1.64	0.088
	(2)	0.63	1.46	0.18	1.32	0.071	1.44	0.078
$\mathrm{RbNO_3}$	(1)	0.86	1.59	0.20	1.32	0.071	1.64	0.088
	(2)	0.63	1.59	0.20	1.32	0.071	1.44	0.078

Table 2. Energy of the single-bond (U_1) and double-bond (U_2) configurations of a $Ca_2(NO_3)_7$ unit, relative to the triple-bonded ground state (eV).

System	$-Z_X$	U_1	U_2
CKN	0.63	0.21	0.23
	0.86	0.22	0.29
CRbN	0.63	0.16	0.22
	0.86	0.21	0.30

Ca ions are either in a fivefold or in a fourfold coordination by NO_3 groups, so that the two Ca ions can share any one, two, or three NO_3 groups. The three alkali ions can lie at several different sites around each of the above core structure, the various low-energy configurations of the compensating alkali counterions being all at essentially the same energy within a few hundredths of an eV. In essence, for each core structure, the seven negatively charged NO_3 groups effectively screen the two Ca ions from each other as well as from the surrounding alkali counterions, and at the same time provide a multiplicity of correlated minima for the distribution of the latter around the core structure. This also implies that the core units that can coexist in a dense disordered phase will be effectively screened from each other and will be in this sense quite independent from each other.

Our quantitative estimates show that in all cases the triple-bond configuration of the $Ca_2(NO_3)_7$ unit lies deeper in energy, but the single-bond and double-bond configurations lie at only about 0.2 eV above it for either value of the electronic charge transfer measured by Z_X (table 2). Higher NO_3 sharing evidently gives better screening of the Coulomb repulsions between the Ca ions, with the NO_3 ions inside a multiple bond being kept apart from each other by their mutual Coulomb repulsions. It is also seen from table 2 that an increase in the amount of charge transfer increases the energy separation of the double-bonded configuration from the others.

We have also carried out calculations using much softer repulsions between the positive ions and the NO_3 group, corresponding to $R_X/\rho_X = 6.9$ as for a spherical anion such as Cl^- [8]. Such softer repulsions favour a tetrahedral coordination of the Ca ion and hence the single-bond configuration of the $Ca_2(NO_3)_7$ unit. However, this configuration is higher in energy by 1.5–2 eV relative to those entering table 2. We find that higher-bonded configurations are not stable in this case.

4. Conclusions

In summary, our extensive calculations indicate that the CKN and CRbN melts may contain $Ca_2(NO_3)_7$ units having competing internal structures from three different types of NO_3 sharing between the Ca ions. These units are compensated by alkali counterions, which are quite free to transport charge by correlated hops joining a multiplicity of local-equilibrium sites. This structural picture is consistent with high electrical conductivity combined with a relatively high viscosity in these melts. The mechanisms of the two transport processes are basically different, but are in coexistence as shown by the experimental evidence [2,3]. The general mechanism that is commonly invoked for these behaviours is the different weighting of the waiting-time distribution for different dynamical variables, which in the present specific case we suggest, arises from the different structural components responsible for viscosity and for electrical transport. From these structural features we can expect quenching of momentum transport to be more effective than that of charge transport, thus implying that (i) viscosity and diffusion become decoupled at low temperatures, and (ii) a larger apparent activation energy governs viscosity at lower temperatures.

The above qualitative picture of the structure of the melt is consistent with the fact that CKN and CRbN are fragile glass-formers. Quenching of the melt can be expected to yield a superionic glass in which the three types of $Ca_2(NO_3)_7$ units are intermingled in an almost random fashion. This is also compatible with the stability of the vitreous state as the composition of the mixed-nitrate melt is varied over a broad range away from stoichiometry. Changes in composition would merely affect the relative concentration of the component microstructures without substantially affecting the glass forming ability of the melt. The interionic force models that we propose could be used to ascertain these proposed features of the dense melt through numerical simulation studies.

Finally, we stress once again that the stability of the various $Ca_2(NO_3)_7$ core units reported here depends in a crucial manner on the nature of the nitrate group as an essentially lamellar (rather than spherical) object, endowed with a rather stiff overlap repulsion against a polyvalent ion such as Ca. Only the single-bonded species formed by two fourfold-coordinated Ca ions survives an appreciable softening of this repulsion.

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References

[1] T. Furukawa, S.A. Brawer, W.B. White. *J. Chem. Phys.*, **69**, 2639 (1978).
[2] A. Voronel, E. Veliyulin, T. Grande, H.A. Øye. *J. Phys.: Condens. Matter*, **9**, L247 (1997).
[3] A. Voronel, E. Veliyulin, V.Sh. Machavariani, A. Kisliuk, D. Quitmann. *Phys. Rev. Lett.*, **80**, 2630 (1998).
[4] C.A. Angell. *Science*, **267**, 1924 (1995).
[5] Z. Akdeniz, M.P. Tosi. *Zs. Naturforsch.*, **59a**, 957 (2004).
[6] V.A. Kulikov, V.V. Ugarov, N.G. Rambidi. *Russ. J. Struct. Chem.*, **22**, 446 (1981).
[7] M.H. Brooker, G.N. Papatheodorou. In *Advances in Molten Salt Chemistry*, G. Mamantov (Ed.), Vol. 5, p. 26, Elsevier, Amsterdam (1983).
[8] M.P. Tosi, F.G. Fumi. *J. Phys. Chem. Solids*, **25**, 45 (1964).
[9] Z. Akdeniz, Z. Çiçek, M.P. Tosi. *Z. Naturforsch.*, **55a**, 861 (2000).
[10] T. Ishiwata, I. Tanaka, K. Kawaguchi, E. Hirota. *J. Chem. Phys.*, **82**, 2196 (1985).
[11] Z. Akdeniz, M.P. Tosi. *Phys. Chem. Liq.*, **43**, 361 (2005).
[12] Y.B. Wang, D.H. Ryan, G.P. Johari. *J. Non-Cryst. Solids*, **205–207**, 221 (1996).
[13] Z. Akdeniz, M.P. Tosi. *Z. Naturforsch.*, **54a**, 180 (1999).
[14] M.P. Tosi, M. Doyama. *Phys. Rev.*, **160**, 716 (1967).
[15] P.S. Yuen, R.M. Murfitt, R.L. Collin. *J. Chem. Phys.*, **61**, 2383 (1974).
[16] A. Weaver, D.W. Arnold, S.E. Bradforth, D.M. Neumark. *J. Chem. Phys.*, **94**, 1740 (1991).