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Seven-coordinated scandium(III) chloroions in $ScCl_3$–CsCl molten mixtures at 600–900 °C

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Raman spectroscopic measurements of $ScCl_3$–CsCl molten mixtures in the temperature range of 600–900 °C and compositions up to 25 mol% $ScCl_3$ indicate that the predominant scandium(III) chloroions in these melts are $ScCl_6^{3-}$ and a novel all chloride highly coordinated $ScCl_7^{4-}$.

The structural properties of a large number of trivalent rare earth halide (LX_3)–alkali halide (AX) molten mixtures have been investigated directly by scattering experiments (neutron, X-ray, Raman) or indirectly from their thermodynamic and transport properties.[1,2] Furthermore, during the past few years computer simulations have been used to study the structure of these melts.[3] Detailed Raman spectroscopic measurements of a series of LX_3–AX (X = F, Cl, Br)[4] mixtures indicate that the spectral behavior and structure of these melts are very similar, especially in mixtures dilute in rare earth halide. At LX_3 mole fractions near and below 0.25 the spectra show two main bands, P_1 (polarized) and D_1 (depolarized), which are assigned to the $\nu_1(A_{1g})$ and $\nu_3(F_{2g})$ modes of the LX_6^{3-} octahedra which are the predominant species in these melts. The octahedra are present at all compositions up to 25 mol% in LX_3 and at all temperatures studied above the binary liquidus. The melting of the solid compounds A_3LX_6, having the trivalent rare earth as isolated LX_6^{3-} octahedra occurs with no drastic changes in the vibrational modes of the octahedra (*i.e.* the vibrational modes of the LX_6^{3-} octahedra in the solid are transferred into the melt).[4]

In the present note we show that the $ScCl_3$–ACl (A = Cs) binary system with $x_{ScCl_3} < 0.25$ behaves differently to the other rare earth halide–alkali halide melts. Furthermore, we give evidence for the existence of $ScCl_7^{4-}$ species at compositions below 25 mol% in $ScCl_3$ and in the temperature range between 600 and 900 °C. The coordination chemistry of scandium(III), including highly coordinated Sc species, has been recently reviewed.[5]

The sources and methods for preparation and purification of $ScCl_3$ and CsCl are described in ref. 6. The Raman apparatus with the optical furnace and the procedures for measuring high-temperature spectra of melts were the same as before.[4,6]

Raman spectra were measured at $ScCl_3$ compositions of 4, 6.5, 14.5 and 25 mol% and at temperatures from the liquidus temperature up to 900 °C for each composition. Fig. 1 shows the composition dependence of the spectra measured at temperatures a few degrees above the liquidus temperature for each composition. At 25 mol% $ScCl_3$ the spectra are characterized by a strong polarized P_1 band at 275 cm^{-1} and a depolarized D_1 band at 145 cm^{-1}. Based on our previous work[4] these bands are assigned to the $\nu_1(A_{1g})$ and $\nu_5(F_{2g})$ modes of the $ScCl_6^{3-}$ octahedra. Further support for the assignment is our recent work[6] concerning the changes of the vibrational modes upon melting the $Cs_2NaScCl_6$ and Cs_3ScCl_6 solid compounds. It has been shown that the vibrational modes of the independent $ScCl_6^{3-}$ octahedra existing in these solids are transferred into the melt giving the P_1 (ν_1, A_{1g}) and D_1 (ν_5, F_{2g}) bands. The weak bands at 340 and 310 cm^{-1} (Fig. 1) are associated with the $Sc_2Cl_9^{3-}$ and $ScCl_4^-$ species, respectively, as discussed elsewhere.[6,7]

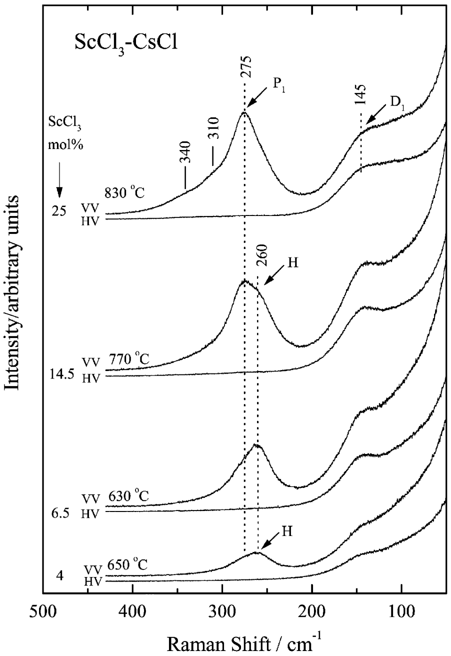

Fig. 1 Composition dependence of the Raman spectra of $x ScCl_3$–$(1 - x)$CsCl ($0 < x < 0.25$) molten mixtures a few degrees above the binary liquidus temperature. Conditions: laser wavelength λ_0 = 488.0 nm, laser power = 200 mW, spectral slit width = 4 cm^{-1}, time constant = 0.3 s, scan rate = 0.8 cm^{-1} s^{-1}.

As the $ScCl_3$ mole fraction is lowered from 25 to 4 mol% the rather symmetric P_1 (ν_1, A_{1g}) band changes. A shoulder, marked as H in the spectra of Fig. 1, appears at ≈260 cm^{-1} whose intensity increases relative to the P_1 band intensity with decreasing $ScCl_3$ mole fraction. In the very dilute $ScCl_3$ melts the H band predominates. The frequency of the new band is at lower energies than that of $ScCl_6^{3-}$ indicating a species with scandium coordination higher than six.

The situation and the observed spectral changes are similar to the behavior of the $ThCl_4$–CsCl[8] and ZrF_4–KF[9] melt mixtures. It has been shown that dissolution of the tetravalent metal halide in the corresponding alkali halide leads to the establishment of an equilibrium of the type:

$$MX_7^{3-} \leftrightarrows MX_6^{2-} + X^- \qquad (1)$$

(M = Th, Zr; X = halide) where both a six-coordinated (O_h) and a seven-coordinated (D_{5h}) species are present. Equilibrium (1) shifts to the right with increasing temperature and alkali halide mole fraction. The frequency ratio of the stretching modes of the six- and seven-coordinated species is $\nu_1(MX_6^{2-})/\nu_1(MX_7^{3-}) \approx 1.07$ for both the thorium and the zirconium anions. The frequency ratio for the TF_6^- and TF_7^{2-} (T = Sb, Bi) anions is similar,[10] giving $\nu_1(TF_6^-)/\nu_1(TF_7^{2-}) \approx 1.08$. In the case of the

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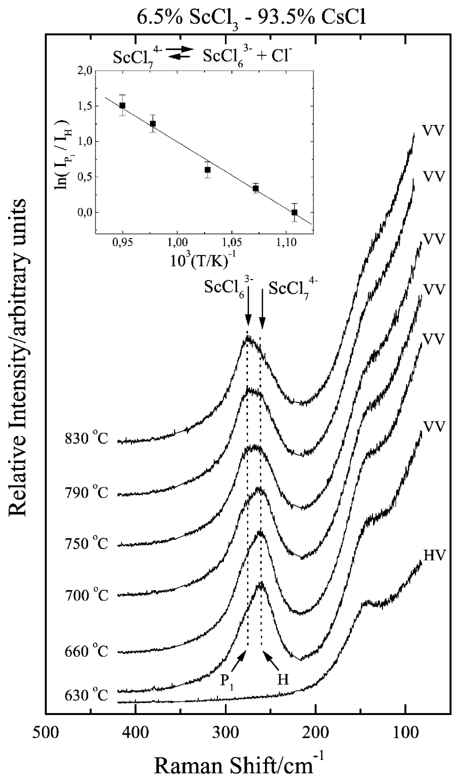

Fig. 2 Temperature dependence of the Raman spectra of a 6.5 mol% $ScCl_3$–93.5 mol% CsCl molten mixture. Conditions as in Fig. 1. Inset: ΔH calculation from an Arrhenius-like plot.

scandium system the ratio $\nu_1(ScCl_6^{3-})/\nu(H, band) \approx 1.06$, *i.e.* smaller, but close to the ratios of the above four sets of anions. We consider this as an indication that the new species giving rise to the H band is a seven-coordinated scandium chloroanion and we assign the H band to the $\nu_1(A_1')$ vibrational mode of $ScCl_7^{4-}$ species. By assuming, as before,[8,9] a D_{5h} symmetry for the seven-coordinated species, the main expected Raman active modes, apart from the $\nu_1(A_1')$, are the $\nu_{10}(E_2')$ and $\nu_8(E_1'')$.[8–10] By scaling the frequencies of this scandium(III) chloroion to the frequencies of other seven-coordinated metal halide compounds (*i.e.* Cs_3ThCl_7,[8] Na_3ZrF_7,[9] Cs_2BiF_7 and Cs_2SbF_7[10]) we can estimate that the $\nu_{10}(E_1')$ and $\nu_8(E_1'')$ bands of the scandium species lie in the frequency range of 120–180 cm⁻¹ and presumably overlap with the D_1 band of the octahedra. The vertical intensity changes of the H and P_1 bands with composition (Fig. 1) imply that an equilibrium:

$$ScCl_7^{4-} \leftrightarrows ScCl_6^{3-} + Cl^- \qquad (2)$$

is established and that the structure of melts dilute in $ScCl_3$ is predominated by the six- and the seven-coordinated scandium species.

In support of the proposed equilibrium (2) are the temperature dependent measurements of the relative Raman intensities. This is shown in Fig. 2 for the 6.5 mol% $ScCl_3$ melt studied over a temperature range of 200 °C. The relative intensity changes of the H and P_1 bands indicate that the seven-coordinated species predominate in the melt structure at lower temperatures while the six-coordinated species are favored at higher temperatures. Similar changes with temperature were also observed in the spectra of mixtures with compositions of 4 and 14.5 mol% $ScCl_3$.

By resolving the overlapping H and P_1 bands for all compositions studied we could measure the integrated relative intensities and then from an Arrhenius-like plot (see *e.g.* inset of Fig. 2) we could calculate the enthalpy of equilibrium (2). An average value of $\Delta H \approx 70 \pm 10$ kJ mol⁻¹ was found. This value is higher than that of equilibrium (1) for the $ThCl_4$–CsCl (≈35 kJ mol⁻¹) and ZrF_4–KF (≈37 kJ mol⁻¹) systems indicating a decreased stability for the $ScCl_6^{3-}$ anion relative to the $ScCl_7^{4-}$ anion. An account of the relative stabilities of the six- and seven-coordinated species participating in equilibria (1) and (2), in terms of the relative ionic radii of both the cations and anions involved, will be presented elsewhere.[7]

It is evident from the above that the structural properties of dilute solutions of $ScCl_3$ in caesium chloride deviate from the systematics established for the other rare earth trihalides.[4] Two predominant coordination geometries ($ScCl_6^{3-}$, $ScCl_7^{4-}$) are present instead of one (LX_6^{3-}). Thus, it seems that the $ScCl_3$–ACl melts may be good candidates for testing theoretical and computer simulation models[3] of ionic liquid mixtures.

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