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Raman Spectra of Solute Species in Molten Florides; O_2^-, CrO_4^{2-} and CO_3^{2-} *

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Raman spectra were observed in molten LiF–NaF–KF (46.5-11.5-42.0 mole %) at 500°C. The following bands were observed: O_2^-, *1107* cm^{-1}, *polarized;* CO_3^{2-}, *1053* cm^{-1}, *polarized;* CrO_4^{2-}, *840* cm^{-1}, *polarized, 348, 880, 378* cm^{-1}. *The frequencies were compared with observations made of these ions in other environments.*

Introduction

Raman studies of several solute species in molten LiF–NaF–KF (46.5-11.5-42.0 mole %) were undertaken to obtain additional evidence for the existence of the superoxide ion, O_2^-, in this basic fluoride melt.[1] In addition to the spectrum of the O_2^- ion, spectra of several other ions were obtained.

Experimental Section

The solvent used in these experiments was a lithium fluoride-sodium fluoride-potassium fluoride eutectic (46.5-11.5-42.0 mole %, liquidus temperature 454°). The fluoride mixture was prepared from analytical reagent grade salts and was purified by treatment of the fused melt with anhydrous HF and hydrogen. High purity sodium superoxide (NaO_2) and potassium superoxide (KO_2) were synthesized by D. E. Lavalle of Oak Ridge National Laboratory. Samples were prepared by loading a quartz cell with the solvent in a helium-filled dry box. An atmosphere of helium was maintained over the sample while it was melted. Additions of salts could be made to the melt by means of ball valves attached to the top of the assembly. Excess salt was added to attain a saturated solution, and the residual undissolved material was allowed to settle. The sample was cooled, and a portion of the clear solid crushed in an inert atmosphere and placed in a quartz tube (4 mm O.D., 5 in. long) sealed at one end. After evacuating and flushing with helium several times, the quartz tube, with slightly less than an atmosphere of helium above the sample, was sealed off by means of a torch. The use of quartz as a short-term container for molten LiF–NaF–KF was investigated by comparing the absorption spectra of Ni^{II} and Cu^{II} solutions in molten LiF–NaF–KF at 500°C contained in quartz with spectra of similar solutions contained in graphite captive-liquid cells.[2] Identical spectra were obtained in both cases.

The Raman spectrophotometer used was a Cary model-81 monochromator, coupled with an E.M.I. 9558 photomultiplier tube and a photon counting system. Raman excitation was achieved with a Spectra-Physics, model 141, argon ion laser utilizing the laser lines at 4880 or 5145 Å, or with the 6328 Å line from a Spectra-Physics, model 125, helium-neon gas laser. Polarization measurements were made qualitatively by rotating the plane of polarization of the laser beam. The salt was melted inside the sample compartment of the Raman spectrophotometer by passing a current through a coil of platinum wire wrapped around the section of the quartz tube which contained the sample. The temperature of the sample was ~500°.

Results and Discussion

The Raman spectrum of O_2^- in molten LiF–NaF–KF consists of a single, strongly polarized band at 1107 cm^{-1}, as shown in Figure 1. This band was produced in samples made by dissolving KO_2 or NaO_2 in the fluoride melt. The weak shoulder around 1050 cm^{-1} is due to CO_3^{2-} ion which will be discussed later. We also observed a band at ~1105 cm^{-1} in molten LiF–NaF–KF to which Na_2O_2 had been added. We attribute this also to O_2^-, as the commercial Na_2O_2 used contained some NaO_2. Values for the superoxide (O_2^-) frequency in solids are given in the literature.[3-5] Our values for solid samples of KO_2 (1143 cm^{-1}) and NaO_2 (1154 cm^{-1}) are in agreement. Our spectrum of solid Na_2O_2 showed a pair of sharp Raman lines at 736 and 791 cm^{-1} and a medium strength line at 1136 cm^{-1} in agreement with Evans.[5]

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Holzer *et al.*[6] have reported an especially interesting series of observations of the Raman spectrum of O_2^- ion in alkali halide crystals. Here the O_2^- frequency varied from 1123 in KI to 1145 cm^{-1} in KCl. It was shown that the vibrational frequency decreased with an increase in unit cell size of crystals having a common cation. By extrapolation Holzer and coworkers estimated the frequency for an isolated O_2^- ion to be 1090 cm^{-1}. In the LiF–NaF–KF melt, the O_2^- ion would not be isolated and yet would not be subjected to the same type of rigid repulsion experienced in crystals. Thus we observe the symmetrical stretching vibration of O_2^- ion in the fluoride melt between that for the free O_2^- ion and that for the ion embedded in a crystal lattice.

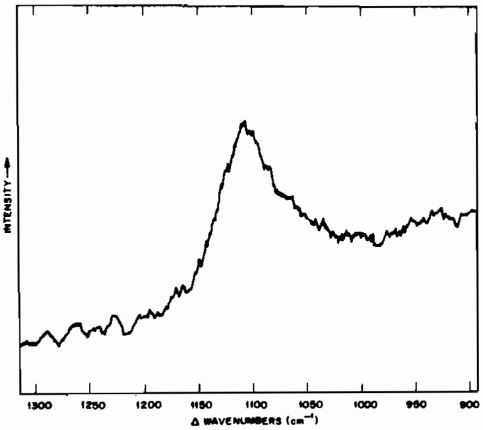

Figure 1. Raman spectrum of O_2^- at ~ 500° in molten LiF-NaF-KF, 4880 Å argon ion laser excitation. Slit width at 4880 Å, 5 cm^{-1}.

Raman spectra were also obtained for LiF–NaF–KF solutions of other species which may have been present in the melt as a result of the reaction of molten LiF–NaF–KF with quartz, or which may have been added along with NaO_2 or KO_2 as an impurity. In order to test the possibility of OH^- existing as an impurity in our melts, we added anhydrous NaOH to LiF–NaF–KF at 500°. A violent reaction occurred. The Raman spectrum of a sample of the melt showed no bands that could be atributed to OH^-. The Raman spectrum of a solution of Na_2CO_3 in molten LiF–NaF–KF gave a single polarized band at 1053 cm^{-1} which we assign to the symmetrical stretching frequency of CO_3^{2-} (ν_1). It is interesting to compare this frequency with the value for aqueous carbonate ion which is observed[7] at 1060 cm^{-1}. In both aqueous and molten fluoride solutions, the other Raman active bands of the CO_3^{2-} ion are difficult to observe because they are weak and broad. Maroni and Cairns[8] recently reported Raman values for the ν_1 stretching frequency of CO_3^{2-} in fused carbonates. They observed lines at 1064 and 1066 cm^{-1} in melts having the compositions Li_2CO_3–K_2CO_3–Na_2CO_3 (42-27-31 mole %) and Li_2CO_3–K_2CO_3 (59-41 mole %), respectively. For the mixture, Li_2CO_3–LiBr (13-87 mole %), they obtained 1080 cm^{-1}. The large shift in the latter value was attributed to the presence of excess Li^+ ions. However, our melt contained considerable Li^+ and the shift was in the other direction. This indicates that the shift is due to an anion effect since our system differed from that of Maroni and Cairns[8] in the use of fluoride rather than bromide salts.

Several other experiments were performed to test the possibility of reactions taking place between the LiF–NaF–KF melt and the quartz Raman cells. We found that enough Na_2SiF_6 would not dissolve in molten LiF–NaF–KF at 500° to give the Raman bands of SiF_6^{2-}. However, bands at 670, 480, and 410 cm^{-1} were observed in the Raman spectrum of a solid piece of the insoluble product formed by the reaction of SiF_4 with molten LiF–NaF–KF. These band positions, intensities and polarizations are in agreement with those reported for Na_2SiF_6 by Begun and Rutenberg.[9] Na_2O_2 is reported[10] to react at an elevated temperature with quartz to form Na_4SiO_4 or Na_2SiO_3. We were unable to locate any bands[11] which could be assigned to SiO_4^{4-} in our spectra. Sodium metasilicate appeared to be very insoluble in LiF–NaF–KF at 500°, and the Raman spectrum of a molten sample above undissolved Na_2SiO_3 showed only a weak broad band in the 900-950 cm^{-1} region. Solid Na_2SiO_3 gave a band at 930 cm^{-1}. Broad, weak, Raman bands attributable to the quartz sample tube were seen at approximately 430, 495, 605, 800, and 1056 cm^{-1} in some of the samples but could be identified because they occurred simultaneously.

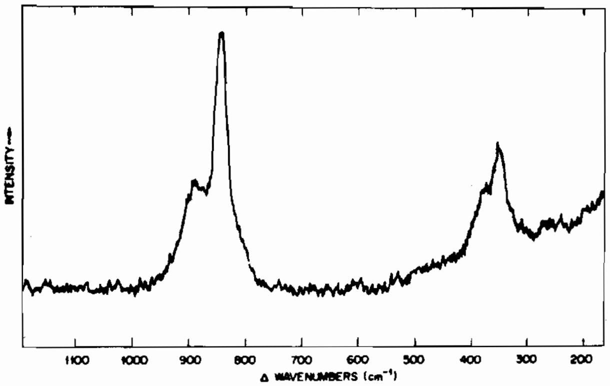

Figure 2. Raman spectrum of CrO_4^{2-} at ~ 500° in molten LiF-NaF-KF, 6328 Å helium-neon laser excitation. Slit width at 6328 Å, 5 cm^{-1}.

Since CrO_4^{2-} ion occurred occasionally as an impurity in molten fluoride solutions, a Raman spectrum of K_2CrO_4 dissolved in LiF–NaF–KF was obtained. This spectrum is reproduced in Figure 2. The band assignments and positions as seen in the present investigation are: $\nu_1(A_1)$, 840 cm^{-1}; $\nu_2(E)$, 348 cm^{-1}; $\nu_3(F_2)$, 880 cm^{-1}; $\nu_4(F_2)$, 378 cm^{-1}. The peak at 840 cm^{-1} is polarized, and the 378 cm^{-1} band is almost hidden on the side of the 348 cm^{-1} peak. The band

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assignments were made in accordance with those reported by Stammreich and coworkers.[12] There is a very close agreement between our values in molten LiF–NaF–KF and the values reported for aqueous CrO_4^{2-} ion (ν_1, 847 cm^{-1}; ν_2, 348 cm^{-1}; ν_3, 884 cm^{-1}; ν_4, 368 cm^{-1}). As in the case of CO_3^{2-} ion, we find a slight lowering of the symmetrical stretching frequency. In the absence of strong, specific interactions, ions in molten fluoride solutions seem to be quite analogous to ions in aqueous solutions.

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