RAMAN SPECTROSCOPIC STUDIES OF ZnF₂-AF (A;K,Cs) MOLTEN MIXTURES

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ABSTRACT

Raman spectra of liquid ZnF₂-AF (A:K, Cs) mixtures have been measured at different ZnF₂ compositions and at temperatures up to 950°C. The spectral changes upon melting of polycrystalline K₂ZnF₄ were also measured. The strong polarized band in molten K₂ZnF₄ was found to be ~120 cm⁻¹ higher relative to the high frequency band of the corresponding solid; this indicates that the coordination number of Zn²⁺ in the melt is lowered. The liquid mixtures with ZnF₂ content less than 33 mol% show similar spectral characteristics as molten K₂ZnF₄ indicating that the coordination number of Zn²⁺ in mixtures rich in alkali fluoride is probably close to four. For melts rich in ZnF₂ (X_{ZnF₂} > 0.6) a new polarized band appears at ~350 cm⁻¹ which shifts slightly to the red with increasing ZnF₂ mole fraction. This new band is close to that expected for six fold coordinated Zn²⁺. The data are interpreted in terms of equilibria between different coordinated species of Zn²⁺ in these melt mixtures.

INTRODUCTION

Zinc fluoride is one of the main components in a series of fluoride multicomponent systems which are used for the production of new infrared transmitting glasses. Thus, the structural entities formed in the liquid are of particular interest to the understanding of the vibrational spectra and the structure of fluoride glasses.
The structural properties of the pure zinc halides (chlorides, bromides, iodides) as well as their mixtures with alkali halides have been investigated by several spectroscopic methods. Raman scattering, neutron and x-ray diffraction, EXAFS studies as well as molecular dynamics simulation data show that in rich in alkali halide mixtures the zinc cation is tetrahedrally coordinated by the halogen anions while in concentrated in zinc halide mixtures independent tetrahedra are bound by vertices, edges and/or faces to form a three-dimensional network like liquid structure.

In contrast no structural information is available for zinc fluoride and its mixtures with alkali fluorides. The only indirect information comes from calorimetric measurements of ZnF$_2$-AF (A= Li-K) melts where ZnF$_3^-$ anions have been proposed as the only stable complexes in these liquids.

This work concerns with the systematic investigation of the Raman spectra of ZnF$_2$-AF (A= K, Cs) mixtures at different compositions and temperatures. Also, the structural changes upon melting of the polycrystalline compounds formed in the binary phase diagram were studied. The spectroscopic data are correlated and discussed in terms of the structural properties of these fluoride melts.

**EXPERIMENTAL**

Zinc fluoride (99%) and caesium fluoride (99%) were purchased from Alfa Chemicals Co. Potassium fluoride was purchased from Merck Co. (99%). Potassium and zinc fluoride were further purified by slow crystallization from the melt. Caesium fluoride was dried overnight under vacuum at 300°C. All the crystallization procedures took place into glassy carbon crucibles in an inert atmosphere high temperature furnace. All the room temperature procedures were carried out into a N$_2$ dry box with low water content (< 0.2 ppm H$_2$O).

A new high temperature furnace with optical openings, for recording the spectra, was constructed; the design was similar to that reported previously. Two heating resistances were used, one through the central vertical hole and the other through the optical windows. A temperature gradient of ± 5°C was obtained around the center of the furnace where the cell was placed and the maximum operational temperature was ~1100°C.

The 488 nm line of an argon ion laser (Spectra Physics, Model 2017), was used for exciting the spectra. For collecting and analyzing the scattered light a T-64000 (Jobin Yvon) Raman system, equipped with a Spectraview - 20 2D liquid N$_2$ - cooled...
CCD detector was used, in the triple configuration. The spectral resolution was 5-6 cm\(^{-1}\) and the integration time was 5 secs. The spectral window centered at 430 cm\(^{-1}\) in the Stokes region was ~770 cm\(^{-1}\) wide for 1022 valued pixels of the CCD detector. Before each experiment two liquid samples were used for adjusting the optics and the polarization characteristics of the spectra; CCl\(_4\) at room temperature and a mixture of 0.3ZnCl\(_2\)-0.7CsCl at 800°C. The system was interfaced with a personal computer and the spectra were saved in digital form.

Two different polarizations were used for recording the spectra namely VV and HV. All the mixtures were premelted into a high temperature furnace to ensure homogeneity. The graphite windowless cell technique was used for recording the spectra. Before use the cells were degassed at 1000°C for ten hours.

**RESULTS AND DISCUSSION**

Table I lists the main observed frequencies at different compositions and temperatures for all the zinc fluoride-alkali fluoride mixtures studied by Raman spectroscopy. The spectra of the solid K\(_2\)ZnF\(_4\) were also measured from room temperature to temperatures above melting point. A large number of spectra were recorded and kept in digital form but only a part of them are presented here in order to give a description of the overall picture of the liquid systems studied.

Spectral changes upon melting of K\(_2\)ZnF\(_4\)

The K\(_2\)ZnF\(_4\) crystal is tetragonal (D\(_{4h}^{17}\)/I4/mmm) and isostructural\(^{10,11}\) to K\(_2\)NiF\(_4\). The Zn cations possess crystal sites of an octahedral symmetry. The ZnF\(_6\) octahedra form a two-dimensional corner sharing array in a layer structure. Factor group analysis of the vibrational modes of the K\(_2\)ZnF\(_4\) crystal shows that only four Raman active modes are expected:

\[
\Gamma(\text{Raman}) = 2 A_{ig} + 2 E_g
\]  

[1]

The K\(_2\)ZnF\(_4\) compound melts incongruently at 737°C. In Fig. 1 we present the Raman spectra of K\(_2\)ZnF\(_4\) at 25 and 850°C. In the room temperature spectrum three of the four expected Raman active modes were observed and the measured frequencies are in good agreement with the literature data.\(^{12}\)

In the liquid the Raman spectra are characterized by a strong polarized band at 471 cm\(^{-1}\) and a broad depolarized band at about 170 cm\(^{-1}\). The high frequency band in

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the melt is about \(-120 \text{ cm}^{-1}\) higher relative to the high frequency band at \(356 \text{ cm}^{-1}\) observed in the solid. The depolarized band is in the same frequency range as the low frequency bands of the solid. If the coordination number of Zn\(^{2+}\) cation in the liquid was similar to that of the solid then a rather small "red" shift of the \(356 \text{ cm}^{-1}\) band of the solid is expected as we go into the melt. In contrast the relative large (\(-140 \text{ cm}^{-1}\)) "blue" shift observed in the spectra (Fig. 1) indicates that the coordination number of Zn\(^{2+}\) in the melt is lower than six.

**Composition and temperature dependence of the Raman Spectra of ZnF\(_2\)-AF molten mixture.**

Figure 2 shows the Raman spectra of a series ZnF\(_2\)-KF liquid mixtures at 950°C. The following general observations can be made:

(i) in the composition range \(0 < X_{\text{ZnF}_2} \leq 0.33\) the spectra are characterized by a broad polarized band centered at \(470 \text{ cm}^{-1}\) (PT\(_1\)) and a broad depolarized at (DT\(_1\)) \(-170 \text{ cm}^{-1}\). The relative intensities of these bands did not change with temperature variations.

(ii) in the region \(0.33 < X_{\text{ZnF}_2} \leq 0.9\) the spectra are characterized by a polarized liquid wing which probably overcomes one or more depolarized bands and by two polarized bands one at \(-474 \text{ cm}^{-1}\) (OT\(_1\)) and another at \(-350 \text{ cm}^{-1}\) (O\(_1\)). The O\(_1\) band exhibits a small red shift with increasing ZnF\(_2\) content while the OT\(_1\) frequency position seems to be invariant to composition changes.

(iii) for 0.66 ZnF\(_2\) - 0.33 CsF liquid mixture the relative intensities of the two polarized bands are affected by temperature variations. This is seen in Fig. 3 where the spectra at two different temperatures are superimposed. Thus with increasing temperature the intensity of OT\(_1\) band increases relative to that of the O\(_1\) band, while the frequencies at both bands remain constant. Such a variation of the relative intensities with temperature characterizes melt mixtures where two or more different species are in equilibrium.

Observation (i) implies that in melt mixtures rich in alkali fluoride, rather stable ZnF\(_x\)\(^{x-}\) species are present. The previous discussion regarding the spectra changes upon melting K\(_2\)ZnF\(_4\) implies that \(x<6\). Furthermore, semiquantitative spectra measurements indicate that the PT\(_1\) band intensity increases with increasing ZnF\(_2\) mole fraction. The increase is definitely observed up to 33 mol % ZnF\(_2\), but within experimental error an intensity increase up to 50 mol % ZnF\(_2\) cannot be excluded. Thus, the complex ions with stoichiometries either ZnF\(_4\)\(^{2-}\) or/and ZnF\(_3\)\(^{1-}\) are the predominant species in these melts.
The appearance of stable tetrahedral $\text{ZnX}_4^{2-}$ ($X=\text{Cl}, \text{Br}$) in liquid mixtures of $\text{ZnX}_2$ with alkali halides is well established \(^3\)\(^7\) and support the presence of $\text{ZnF}_4^{2-}$ tetrahedra in the fluoride systems. On the other hands the enthalpy of mixing data\(^2\) supports the view that the $\text{ZnF}_3^{1-}$ configuration (or better the 1:3 stoichiometry) stabilizes the mixture. It is noteworthy that for the $\text{HgCl}_2$-$\text{ACl}$ melt mixtures both the $\text{HgCl}_4^{2-}$ and $\text{HgCl}_3^{2-}$ complexes are known to exist\(^1\)\(^3\). Since the ionic radii ratios are $\text{Zn}^{2+}/\text{F}^- < \text{Hg}^{2+}/\text{Cl}^-$ = 0.56 then we may conclude that the structural behavior in the alkali halide rich region of the $\text{ZnF}_2$-$\text{KF}$ and the $\text{HgCl}_2$-$\text{KCl}$ melts may be similar. The tetrahedral $\text{ZnF}_4^{2-}$ are the predominant species up to 33 mol % $\text{ZnF}_2$ while at higher mole fractions the $\text{ZnF}_3^{1-}$ configurations may be also present.

From observations (ii) and (iii) and the above discussion it appears that in the mole fraction region $0.5 < X_{\text{ZnF}_2} < 1$ a new structural entity may be present in the melt mixtures. The $O_1$ band at ~350 cm\(^ {-1}\) is assigned to this entity which presumably in the predominant "species" in compositions rich in $\text{ZnF}_2$.

Due to volatility and surface tension problems we were unable to obtain Raman spectra of pure $\text{ZnF}_2$ using the windowless graphite cell. However, from the systematics of the spectra in Fig. 2 it is expected that the spectra of molten $\text{ZnF}_2$ to be similar to those of the 90 mol % $\text{ZnF}_2$ mixture. Following semiquantitative the spectral trends (Fig. 2) we have calculated in Fig. 4 the spectra of the 100% molten $\text{ZnF}_2$ and we compare them with the spectrum of polycrystalline $\text{ZnF}_2$ at room temperature. Crystalline $\text{ZnF}_2$ is isostructural to rutile having the $\text{Zn}^{2+}$ ions in a six-fold (near octahedral) site. Factor group analysis shows that four Raman active modes are expected

$$\Gamma(\text{Raman}) = A_{1g} + E_g + B_{1g} + B_{2g}$$ \[2\]

Three of the four modes are well defined in the spectra (Fig. 4) while the fourth one ($B_{1g}$) is superimposed on the rotational spectrum of air. The $A_{1g}$ vibrational mode of the crystal is mainly a $\text{Zn-F}$ stretching frequency of the six-fold coordinated $\text{Zn}^{2+}$. This frequency also, coincides with the maximum of the broad polarized band of molten $\text{ZnF}_2$ (Fig. 4). In other words the "species" associated with the $O_1$ band can be assigned to a fluoride configuration where the $\text{Zn}^{2+}$ is six-fold coordinated. Due to the broadness of the main polarized band a wide range of distortions from octahedral symmetry is presumable present in molten $\text{ZnF}_2$. 

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CONCLUSIONS

From the above discussion it follows that in mixtures rich in ZnF$_2$ the Zn$^{2+}$ is most probably six-fold coordinated, while in the alkali fluoride rich mixtures the four-fold coordinated ZnF$_2^{2-}$ are the predominant species.

At intermediate composition an equilibrium exists where the Zn$^{2+}$ ions distribute themselves between the above two coordinations plus another rather stable coordination (probably three-fold) arising in the 50/50 binary mixture.

Neutron diffraction as well as molecular dynamics simulation studies could be useful for a better understanding and verification of the structural behavior of these fluoride melts.

REFERENCES

1. R.M. Almeida, J.C. Pereira and R. Alcala, Phys. Chem. Glasses, 33 (5), 187 (1992)
2. O.J. Kleppa and M. Wakihara, J. Inorg. Nucl. Chem., 38, 715 (1979)
3. E.A. Pavlatou and G.N. Papatheodorou, in Eighth International Symposium on Molten Salts/1992, R.J. Rube, G. Blongren and H. Kojima Editors, Vol. 92-16, 72 The Electrochemical Society Proceedings Series, Pennington, NJ (1992) and references therein.
4. S. Biggin and J.E. Enderby, J. Phys. C., 14, 3129 (1981); D.A. Allen, R.A. Howe and N.D. Wood, J. Chem. Phys., 94, 5071 (1991)
5. R. Triolo and A.H. Narten, J. Chem. Phys., 74, 703 (1981)
6. K. Kadono, H. Kageyama, N. Kamijo and H. Tanaka, J. of Non-Cryst. Solids, 123, 291 (1990)
7. E.A. Pavlatou, P.A. Madden and M. Wilson, J. Chem. Phys., 107(24), 10446 (1997)
8. B. Gilbert and T. Mutterne, Appl. Spectr., 44, 299 (1990) and references therein
9. K. Andrikopoulos, D. Vlassopoulos, G.A. Voyiatzis and Y.D. Yannopoulos and E.I. Kamitosos, (submitted to Macromolecules 1997)
10. Von O. Schmitz and H. Bornefeld, Z. Anorg. All. Chem., 287, 120 (1956)
11. E. Herdtweck and D. Babel, Z. Kristall., 153, 189 (1980)
12. K. Strobel and R. Geick, J.Phys. C: Solid State Phys. 15,2105 (1982)
13. G.A. Voyiatzis and S. Boghosian, in Ninth International Symposium on Molten Salts 1994; C.L. Hussey, D.S. Newman, G. Mamantov and Y. Ito Editors, Vol. 92-16, 242, The Electrochemical Society Proceeding Series, Pennington NJ, (1994), and references therein
Table I: Main Raman frequencies in the mixtures at different composition and temperatures

| Composition / ZnF₂ mol % | Temperature / °C | Main frequencies (cm⁻¹) |
|-------------------------|------------------|------------------------|
| KF-ZnF₂                 |                  |                        |
| 21                      | 750              | 469ᵃ (170)ᵇ           |
|                         | 800              | 469 (170)             |
|                         | 950              | 469 (170)             |
|                         | 950              | 470 (170)             |
| 33                      | 850              | 471 (170)             |
|                         | 950              | 469 (170)             |
| 50                      | 930              | 474 (170)             |
|                         | 950              | 474 (170)             |
|                         | 970              | 474 (170)             |
| 66                      | 880              | 469 (353)             |
|                         | 950              | 474 (350)             |
| 80                      | 800              | (480) 350 (222)       |
|                         | 950              | (480) 351             |
| 90                      | 950              | 340 (174)             |
| CsF-ZnF₂                |                  |                        |
| 33                      | 800              | 474 (174)             |
|                         | 950              | 474 (176)             |
| 50                      | 800              | 480 (160)             |
| 66                      | 820              | 480 (341)             |
|                         | 870              | 480 (341)             |
|                         | 950              | 480 (338)             |

ᵃ Frequencies with an estimated error of 1 cm⁻¹
ᵇ Numbers in parenthesis indicate shoulder bands and frequencies with an estimated error of 10 cm⁻¹
Fig. 1: Raman spectra of K$_2$ZnF$_4$ at 25°C and at 850°C. Laser wavelength $\lambda_0=488$nm, spectral slit width $w=5$cm$^{-1}$, integration time $t=5$secs.

Fig. 2: Composition dependence spectra of ZnF$_2$-KF liquid mixtures at 950°C. Spectra conditions as in Fig. 1.
Fig. 3: Temperature dependence of the VV spectra of 0.66 ZnF$_2$-0.33 CsF molten mixture. Spectra conditions as in Fig. 1.

Fig. 4: Raman spectra of polycrystalline and of molten ZnF$_2$. The calculation of the spectra of molten ZnF$_2$ was based on the trends of Fig.2.