STRUCTURAL PROPERTIES OF ZINC HALIDE MELTS

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ABSTRACT

Vibrational Raman spectroscopy has been used to identify and determine the structure of species formed in the binary mixtures ZnCl₂-ACL (A=Cs, Li) and ZnCl₂-ZnBr₂. The data indicate that the network-like structure of the zinc halide melts breaks up with the addition of alkali metal halide and with increasing temperature. The tetrahedral structure around the Zn is preserved but one, two, three or four "terminal" halogen atoms having A⁺ as nearest neighbors are formed. Different bridging bonding states are proposed to exist in the pure ZnCl₂ glass and liquid.

INTRODUCTION

The structural properties of zinc halide melts and glasses, including their mixtures with alkali halides, have been extensively investigated by a variety of spectroscopic techniques (1). Pure ZnCl₂ has been studied by x-ray scattering (2), EXAFS (3) and neutron diffraction (4,5) while Raman, IR and inelastic neutron scattering spectroscopy have been used for studying both pure ZnCl₂ (6-11) and its mixtures with alkali halides (7,12,13) and with ZnBr₂ (13). All these studies have revealed a commonly adapted structural model for glassy-ZnCl₂ and liquid-ZnCl₂, where the small Zn²⁺ ions occupy tetrahedrally coordinated "sites" in a closely packed ion structure with strong intermediate range ordering. For melt mixtures rich in alkali halide, tetrahedral ZnX₄²⁻ (X=halide) entities ("complexes") have been argued to exist.
(7,12,13) as in general is the case for most first row divalent transition metal halide-alkali halide melts (14,15). For melt mixtures rich in \( \text{ZnX}_2 \), the structure is described in terms of either polynuclear in Zn aggregates (7,10) or bridging and non bridging states of the halogen atoms (8,10,12,13). The depolarized low frequency Raman spectra of molten and glassy \( \text{ZnCl}_2 \) have been associated with the vibrational density of states (10,11), having contributions from internal modes of the local symmetry, some of which are splitted as a consequence of long range interactions (LO-TO splitting (9,11)).

Quasielastic light scattering spectroscopy in \( \text{ZnCl}_2 \) at temperatures from below \( T_g \) to above \( T_m \) have pointed out, that the present structural entities are important in determining the dynamic processes occurring near \( T_g \) (16-19). In a recent photon correlation spectroscopic study (20), at least two dynamic processes have been observed, implying peculiar features for the structure and bonding in \( \text{ZnCl}_2 \).

In the present work we have undertaken a detailed Raman spectroscopic study of \( \text{ZnCl}_2 \) melts and glasses, as well as, of the binary mixtures of liquid \( \text{ZnCl}_2-\text{CsCl} \), \( \text{ZnCl}_2-\text{LiCl} \) and of glassy \( \text{ZnCl}_2-\text{ZnBr}_2 \). Systematic temperature and composition dependence measurements are reported, and the data are interpreted in terms of different bonding states of the “network” like structure of these melts.

**EXPERIMENTAL**

The reagent grade chemicals \( \text{ZnCl}_2 \), \( \text{ZnBr}_2 \), \( \text{LiCl} \) and \( \text{CsCl} \) were purchased from Merk Chemical Co. or Cerac Pure Inc. The starting materials were further purified by bubbling gaseous HCl or HBr through the corresponding halide melt and then filtering it under nitrogen atmosphere. All operations with the anhydrous chemicals were carried out in a nitrogen filled glove box (\(<1 \text{ ppm } \text{H}_2\text{O}\)) or in sealed fused silica containers.

The Raman cells were made from fused silica tubes of constant diameter (OD=6 mm, ID=4 mm). The clean and anhydrous chemicals were transferred into the cells and sealed under vacuum. The cell was between 2-3 cm long and was attached to a fused silica manipulation rod of \( \approx 10 \) cm length. The mixtures \( \text{ZnCl}_2-\text{CsCl} \), \( \text{ZnCl}_2-\text{LiCl} \) and \( \text{ZnCl}_2-\text{ZnBr}_2 \) were made by
mixing into the Raman cell preweighed amounts (0.2 to 0.6 gr total) of the component salts. For making the ZnCl$_2$-ZnBr$_2$ glasses the cells containing the mixtures, were heated at ~550° C for several hours, and then quenched in water at room temperature. All melts and glasses obtained were clear, transparent and did not fluoresce. when the Ar$^+$ lines were used to excite the spectra.

The Raman spectroscopic system and the techniques for measuring relative Raman intensities from samples in different cells were the same as before (21,22). The spectrometer was interfaced with a P.C. for recording the spectra and for directly calculating the reduced Raman intensity and the depolarization ratios.

RESULTS AND DISCUSSION

The measured Raman intensity $I(\omega)$ at frequency $\omega$ is related to the reduced Raman intensity $R(\omega)$ (15) as follows:

$$R(\omega) = I(\omega) \frac{\omega}{(\omega_0 - \omega)^4} \left[ n(\omega) + 1 \right]^{-1}$$

where $\omega_0$ is the excitation laser frequency and $[n(\omega)+1]=\exp^{\frac{\hbar \omega}{kT}} - 1 + 1$ the Boltzmann thermal population factor.

For amorphous materials the $R(\omega)$ is related to the vibrational density of states (23), and an advantage for using it especially at elevated temperatures, is that it suppresses the Rayleigh and Boson peaks and emphasizes the low frequency ($\omega<100$ cm$^{-1}$) features of the spectra (15). The effect of the thermal population factor is also important for quantitative measurements of the relative intensities of species in equilibrium, with Raman bands in the intermediate frequency region ($\omega<500$ cm$^{-1}$) (21).

Most of the Raman spectra reported in the present work are at elevated temperatures, and it is necessary for quantitative comparisons of the intensities to use the $R(\omega)$ representation of the spectra. Frequency and intensity distortions of the bands due to the thermal population factor are thus removed, and temperature dependent effects are revealed.
Temperature Dependence of the ZnCl₂ spectra

Figure 1 shows the Raman spectra of glassy and liquid ZnCl₂ at different temperatures. Details for the low frequency spectra of the glass at 130° C are given in Fig. 2. Our spectra are very much in agreement with the spectra reported before (9-11). Apart from the Boson peak measured in our I(ω) spectra at ~25 cm⁻¹, a weak polarized band was present in the VV spectra at ~530 cm⁻¹ which has been also reported in ref. 9. Three strongly polarized bands were measured at 230, ~280 and ~380 cm⁻¹ and two depolarized bands at ~75 and ~105 cm⁻¹ are seen in the low frequency region. A third low frequency band, which is deconvoluted in the isotropic spectra of fig. 2 at ~125 cm⁻¹, is polarized.

Increasing temperature did not change drastically the overall intensity of the "raw" I(ω) spectra, and minor variations of the relative intensities were observed. However, in the thermal factor population free R(ω) spectra, discreet changes in the relative intensities appear to occur (Fig. 1). The overall R(ω) intensity decreases with rising temperature, but the band intensities at 280 cm⁻¹ and 380 cm⁻¹ increase relatively to the 230 cm⁻¹ band. These observations indicate that, structural changes occurring with increasing temperature, affect the vibrational frequencies of the ZnCl₄ tetrahedra participating in the "network" like structure.

The only crystalline stable form of pure anhydrous ZnCl₂ is an orthorhombic h.c.p. structure (24) having ZnCl₄ tetrahedral groups, each sharing vertices with four others. A vertex sharing structure of single bridged Cl atoms has been also accepted for the glass and the liquid. Such structure implies that the coordination sphere of Zn would have four Zn atoms as second nearest neighbors. The diffraction studies (5) however, show that in the liquid the Zn-Zn coordination number is 4.7, indicating that on the average there are more than four ZnCl₄ groups around each ZnCl₄ group. Such coordination can be achieved by having more than two tetrahedral groups bound by a common vertex and/or by connecting the tetrahedra by edges. Structures of the MY₂ salts, having either double bridged (edges) Y atoms in infinite chains (e.g BeCl₄ groups) or layers of tetrahedra sharing vertices and edges (e.g. GaS₄ and PS₄ groups), are rather rare but known to exist (24). If the assumption is made, that the distance between the Y atoms of different MY₄ groups is not less than the edge-length of the tetrahedra.
(this restricts the M-Y-M angle to 102°), then the maximum number of tetrahedra that can be met at a common vertex is eight, but the number is reduced to four if edge sharing is not permitted.

The space topology of the tetrahedra and the 4.7 Zn-Zn coordination number, imply that it is possible in the ZnCl₂ network to have one Cl atom sharing the vertices with more than two ZnCl₄ groups and/or two Cl atoms bound in a common edge of two tetrahedra(edge sharing). In Figure 3 we present schematically three such structures, one having single vertex sharing (SV), the other with a double vertex sharing (DV) and the third with edge sharing (E). These structures create non-equivalent chlorine atoms of the ZnCl₄ groups and thus, different Zn-Cl stretching vibrational frequencies are expected.

The temperature dependence of the Raman spectra (Fig. 1) supports the above model (Fig.3). Thus, the 230 cm⁻¹ band could be assigned to a Zn-Cl stretching mode, which is weakened by either double bridged Cl atoms (edge sharing, structure E) or, single bridging of more than two tetrahedra at a common Cl atom (i.e. structure DV). Increasing temperature tends both to break the double bridges and to reduce the number of tetrahedra bound to a common Cl atom, which in turn strengthens the Zn-Cl bond and moves the vibrational frequency to higher values (i.e the 280 cm⁻¹ band). An equilibrium between species of the type DV and E with SV gives an account for the reversible temperature changes of the relative Raman intensities shown in Fig. 1. In this context, the 380 cm⁻¹ band, seen better in the high temperature spectra, is attributed to Zn-Cl vibrations of non bridged Cl atoms (structure TB in Fig. 3). Such a possible structure is supported by the neutron scattering measurements (5), where a decrease of the coordination number of Zn-Cl occurs with increasing temperature, implying the creation of voids or equivalently the formation of ZnCl₃ units (i.e. structure TB).

The low frequency region of the spectra of ZnCl₂ (Fig. 2) was also influenced by the temperature. An overall intensity drop and broadening of the bands was observed, but the relative intensities of the three bands involved did not change drastically. The isotropic spectra show the presence of the ~125 cm⁻¹ polarized band at all temperatures with no shifts of its frequency. It seems that this region of the spectra is not affected by the local thermostructural changes occuring in the "network" structure.
The ZnCl$_2$-CsCl and ZnCl$_2$-LiCl liquid systems

Raman spectra of these binary systems were measured at different compositions and at various temperatures above the liquidus and up to 670° C. Figures 4 and 5a show the composition dependence of the R(ω) spectra at 660° C for the ZnCl$_2$-CsCl system and at 622° C for the ZnCl$_2$-LiCl system.

For the mixtures rich in CsCl ($X^{\text{Zn}} < 0.33$), the predominant feature of the spectra is a polarized band at 275 cm$^{-1}$ with intensity that increases proportionally to the amount (mole fraction) of the ZnCl$_2$ in the melt. With increasing temperature small "red" shifts of the 275 cm$^{-1}$ band were observed but no drastic changes in the intensities and the spectra profile were detected. In agreement with previous investigations (6,7,12), the polarized bands at 275 cm$^{-1}$ in the CsCl melts and at 282 cm$^{-1}$ in the LiCl melts are assigned to the stretching $\nu_1$ frequency of ZnCl$_4^{2-}$ tetrahedral "complexes" formed in the alkali chloride rich mixtures. The red shift in the Li to Cs sequence is also in agreement with the general behavior of the vibrational spectra of the MX$_n^+\cdot AX$ (A = Li...Cs) binary melts (14, 15). The depolarized band at ~120 cm$^{-1}$ presumably covers the $\nu_2$ and $\nu_4$ modes of the tetrahedra, while the $\nu_3$ mode as in other cases (15) is too weak to be seen in the spectra. The ZnCl$_4^{2-}$ "complex" is visualized as a Zn atom having a tetrahedral coordination of chlorines as first nearest neighbors, and only alkali metal ions as counter cations in the second coordination with no bridging Cl atoms (Fig. 6, S4). The lifetime of such species is much longer than 10$^{12}$ sec (14,15) and their presence in the melt has been supported by electronic absorption spectroscopy (25) and enthalpy of mixing measurements (26).

For the mixtures rich in ZnCl$_2$, the following composition and temperature dependent changes are noted in the spectra (Fig. 4,5 and 7):

i. Small additions of CsCl diminish the intensity of the 230 cm$^{-1}$ ZnCl$_2$ band and give rise to two new polarized bands $\nu_{S1}$=350 cm$^{-1}$ and $\nu_{S2}$=290 cm$^{-1}$. The intensities of these bands increase relatively to the 230 cm$^{-1}$ band with increasing CsCl content and at ~66 % ZnCl$_2$ mixture the predominant band is the $\nu_{S2}$ (Fig. 4b).

ii. Similar composition effects are observed in the LiCl mixtures but the $\nu_{S1}$ and $\nu_{S2}$ bands are broader, weaker and red shifted by ~20 cm$^{-1}$ relatively to those of the CsCl mixtures (Fig. 5a)
iii. Increasing temperature decreases the 230 cm\(^{-1}\) band intensity relatively to the \(v_{51}\) and \(v_{52}\). The effect is more pronounced at 66-90% ZnCl\(_2\) (Fig. 7) for the CsCl mixtures, and at \(\sim 77\%\) ZnCl\(_2\) (Fig. 5b) for the LiCl mixtures.

A possible account for the appearance of the \(v_{51}\) and \(v_{52}\) bands could be the formation of polynuclear in Zn "complexes" formed by two or more ZnCl\(_4\) groups bound by a vertex, an edge or a plane (e.g. Zn\(_2\)Cl\(_7^2\), Zn\(_2\)Cl\(_6^2\), Zn\(_2\)Cl\(_5^2\)). However, it should be noted that, the enthalpy of mixing interaction parameter (26) of the ZnCl\(_2\)-CsCl binary possesses a minimum at 33% ZnCl\(_2\) composition, and changes almost linearly with increasing ZnCl\(_2\) composition from 33 to 100%. These thermodynamic observations have indicated (26) that: (a) the ZnCl\(_4^2\) is the only thermodynamically stable "complex" and (b) the addition of alkali metal chloride brings up continuous changes in the ZnCl\(_2\) "network" structure. Such changes can be visualized as a sequential breakage of the bridging chlorine bonds and the formation of partially charged ZnCl\(_4\) groups, which are bound to segments of the network. Thus, breaking off one bridging chlorine bond gives a charged ZnCl\(_4\) structure, which is bound to the "network" by three bridging Cl atoms and has the alkali metal cation as nearest neighbor (structure S1, Fig. 7). Similarly, breakage of two, three, or four bridges gives structures S2, S3, or S4 respectively. Structure S4 corresponds to the ZnCl\(_4^2\) "complex" that predominates the rich in alkali metal chloride mixtures, while structure S1 is formed with the first small additions of alkali metal chloride in ZnCl\(_2\). In intermediate compositions, an equilibrium mixture of these structures is anticipated with relative concentrations that depend on both temperature and composition.

The Raman activity of the S1 to S4 structures will reflect the non-bridging Zn-Cl "stretching" mode and the frequencies are expected to decrease in the sequence \(v_{51} > v_{52} > v_{53} > v_{54}\). Thus, for the ZnCl\(_2\)-CsCl system the 350 and 290 cm\(^{-1}\) bands, observed in the ZnCl\(_2\) rich mixtures, are assigned to the S1 and S2 structures, while the most intense band seen in the 50/50 mixture at \(\sim 280\) cm\(^{-1}\) is presumably the frequency corresponding to the S3 structure. As the temperature is raised, the "network" structure of ZnCl\(_2\) breaks up giving configuration mainly with single bridged (SV) and terminal bridged Cl atoms (TB). Consequently, when the mixture is formed, the S2 structure will be more favorable at higher temperatures than the S1 structure. For example the addition, of chloride ions, transforms the high
temperature TB structure (Fig. 3) into the S2 structure (Fig. 6). Such changes favor, for certain compositions, the ZnCl$_4$ charged groups with a maximum number of non-bridging Cl atoms, and give an account for the experimental observations in Figure 7.

**The ZnCl$_2$ - ZnBr$_2$ glassy system**

Liquid mixtures of ZnCl$_2$-ZnBr$_2$ can be quenched to room temperature to form glasses at different compositions. Figure 8 shows the "raw" I(ω) Raman spectra of these glasses and compares them with the spectra of the pure components.

In the frequency region above 100-150 cm$^{-1}$, the spectra of the mixtures show new bands that shift with composition, while the main bands of the pure components appear to either shift or lose their intensity in the mixtures. For example, the ~130 cm$^{-1}$ ZnBr$_2$ band is completely absent from the 75% ZnCl$_2$ spectra. A possible assignment (13) of these bands is to the presence of mixed zinc halide tetrahedral groups of the type ZnCl$_x$Br$_{4-x}$, which participate as basic units in the "network" structure of the glass.

However, the absence from the spectra of bands due to pure components, indicate that not all tetrahedral groups are present in the mixture, or in other words, that the mixed glass is not formed by a random distribution of five ZnCl$_x$Br$_{4-x}$ (x=0-4) tetrahedral groups. This is in contrast with Raman spectroscopic studies of other mixed halide systems both in the gaseous state (27), and in molecular (28) or ionic melts (29), where the exchange and bonding of the halide to the metal structural group is random.

The enthalpy of mixing of the liquid ZnCl$_2$-ZnBr$_2$ binary is zero (26), which implies that the Cl and Br sizes and polarizabilities do not affect the overall "lattice" energies of the mixed system relatively to those of its components (14). Thus, there is no preferential structural arrangement of the halogen atoms in these mixtures and moreover, the system can be described in terms of a random closest packing of chlorine and bromine atoms which offers tetrahedral sites for the formation of the ZnCl$_x$Br$_{4-x}$ groups. In such an arrangement, it is rather unlikely to find clusters of the same halogen atoms so as to have one Zn atom sharing vertices with four (or more)
tetrahedral groups, all having the same halogen atoms. A cluster of, say, 16 Cl atoms are needed to form one ZnCl$_4$ group bound to four other ZnCl$_4$ groups and thus, giving rise to Raman bands in the mixture, which are close to the bands of the pure ZnCl$_2$. The spectra in Figure 8 exclude the formation of such kind of clusters in the mixed glasses.

In the view of the above proposed model for the bonding in the ZnCl$_2$ "network" (i.e. Fig. 3), it is difficult, just from the room temperature spectra, to make assignments for different types of bridging groups in the mixed glass systems. Detailed temperature and composition dependence studies (30) would be useful for both making the assignment and verifying the proposed model.

In the frequency region below 150 cm$^{-1}$ the spectra presented in Figure 8, show three bands plus the "Boson" peak. In Figure 9 the R(ω) form of the low frequency spectra is given for the pure components and for the mixed glasses. The spectra show remarkable similarities, all having a polarized band in the isotropic spectra and two depolarized bands in the anisotropic spectra. The low frequency vibrational spectra of glasses and liquids are not well understood yet (31), but the similarities and systematics followed in the spectra (Fig. 9), indicate a collective character of the vibrational modes in this frequency region.

CONCLUSIONS

Raman spectroscopic studies of ZnCl$_2$ glasses and melts and of the binary mixtures of liquid ZnCl$_2$-ACl (A=Li,Cs) and glassy ZnCl$_2$-ZnBr$_2$ have shown that:
(a) The reduced Raman intensity of pure ZnCl$_2$ changes drastically with temperature. This was interpreted to indicate the presence of different bonding states in the network structure where vertex and/or edge sharing of the ZnCl$_4$ tetrahedral groups occur.
(b) In the ZnCl$_2$-ACl mixtures the breaking of the network structure occurs both with increasing temperature and AC1 composition. With the addition of ACI breakage of certain bridging chlorine bonds occur and charged "tetrahedral" ZnCl$_4$ groups are formed which are bound to segments of the network by one, two or three bridging chlorines atoms. In ACI rich mixtures
$\text{ZnCl}_4^2$ tetrahedral "complexes" are formed.

(c) The glassy $\text{ZnCl}_2\cdot\text{ZnBr}_2$ mixtures are formed by a random closest packing of chlorine and bromine atoms. The formation of clusters having locally large numbers of the same atoms (i.e. chlorines or bromines) is excluded.

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Figure 1. Temperature dependence of the reduced Raman spectra of ZnCl$_2$.

Figure 2. Low frequency reduced Raman spectra of ZnCl$_2$ at 130 °C. Polarizations VV, ANISO=HV, ISO=VV-4/3HV.
Figure 3. Structural models for bonding of the ZnCl$_4$ groups in liquid/glass ZnCl$_2$. SV: Single Vertex, two ZnCl$_4$ groups bound to one bridging Cl atom. DV: Double Vertex, three ZnCl$_4$ groups bound to one bridging Cl atom. E: Edge, two ZnCl$_4$ groups bound to two common bridging Cl atom. TB: Terminal Bond, indicates the presence of non-bridging Cl atom.

Figure 4. Composition dependence of the reduced Raman spectra of ZnCl$_2$–CsCl at 660 °C.
Figure 5. Reduced Raman spectra of ZnCl₂-LiCl.
   a) Composition dependence at 660 °C.
   b) Temperature dependence of the 77% ZnCl₂ mixture.

Figure 6. Structural models of charged ZnCl₄ groups formed sequentially by breaking the ZnCl₂ 'network' with increasing additions of alkali chlorides.
Figure 7. Temperature dependence of the reduced Raman spectra of the 80/20 ZnCl₂–CsCl mixture.

Figure 8. Raman spectra of ZnCl₂–ZnBr₂ glassy mixtures at room temperature.
Laser line: 488 nm
Laser power: 60 mW
Spectral slit width: 2 cm⁻¹
Scan rate: 0.25 cm⁻¹/sec
Figure 9. Composition dependence of the low frequency reduced Raman spectra of ZnCl$_2$-ZnBr$_2$ glasses.