

The Simple and the Complex: Revealing the Structure of Molten Salts

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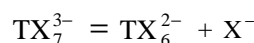
The understanding of the physicochemical properties of molten salts requires knowledge of their structure. Simplified structural models like that of Temkin¹ served as a first means of understanding the thermodynamics of mixing of molten salts. However, a better understanding of both the thermodynamic and the transport properties required more complex models where concepts of molecular behavior, clustering of ions, networking, long range, partial ionizations, dispersion interaction etc were introduced (see e.g. ref. 2). All these lead to an indirect information about the structure of the melts. Direct evidence was also provided mainly by scattering experiments (neutron, electron, X-ray)² by absorption spectroscopy (UV, VIS or IR)^{1,2} and later after the commercialization of CW lasers, by Raman spectroscopy^{3,4}. For the careful researcher definite structural conclusions are not easily obtained and it is necessary that the results from both the indirect (thermodynamic and transport) and the direct (spectroscopy) methods should be compatible after accounting for the lifetime of the proposed local and/or long range structure. Finally, in recent years computer simulations have been used rather successfully for predicting the molten salt structures⁵.

In the following some selected examples of molten salt structures are presented which are based on Raman spectroscopic measurements. It should be emphasized that such measurements require the development of specialized experimental spectroscopic set-ups but laboratory techniques for making and handling super clean chemicals is of almost importance as well.

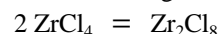
Changes of vibrational modes upon melting⁴. In a series of studies the changes of vibrational modes upon melting solid compounds have been examined. Crystalline solids with internal vibrational modes due to isolated structural units have been the main subject of these studies. The elpasolite like crystalline solids with the general formula A_3LX_6 (A= alkali metal, L=trivalent metal, X=halide) possess the isolated LX_6^{3-} octahedra whose vibrational modes are transferred into the melt. Similar is the behavior of other compounds like A_2MX_4 (M=Zn, Be, Mg....), ALX_4 (L= Fe, Al), $A_3L_2Cl_9$ (L= Sc, Cr) where the tetrahedra MX_4^{2-} , LX_4^- and the $L_2Cl_9^{3-}$ units are present in the solid and liquid phases of the corresponding salts. However, in other cases (e.g. A_3FeCl_6 , K_2ZnF_4) the melting of the solid may lead to drastic changes of the vibrational modes implying drastic structural changes (e.g. octahedral to tetrahedral).

Dilute solutions of metal halides in alkali halides. The dissolution of divalent (M^{2+}), trivalent (L^{3+}) tetravalent (T^{4+}) and pentavalent (R^{5+}) halides in molten alkali halides gives rise to vibrational modes that in most cases can be associated with highly symmetric ion clusters in tetrahedral or octahedral symmetry. The tetrahedral species predominate the structure of melt mixtures involving divalent halides (MX_4^{2-} ; M= Mg, Zn, Hg....)

and in certain cases of mixtures involving trivalent halides (LX_4^- ; L=Al,Fe,Sc..). The octahedral species are usually found in mixtures with trivalent (LX_6^{3-} ; L = rare earth)⁶, tetravalent (TX_6^{4-} ; T= Zr, Th)^{7,8} as well as pentavalent (RX_6^- ; R= Ta, Nb) halides. In certain cases fluoride melts behave differently while in other cases different type of equilibria may be established:



Molecular, chain and network like structures of pure melt halides. Raman spectroscopic studies of binary melt mixtures $AX-NX_n$ (N= M^{2+} , L^{3+} , T^{4+} , R^{5+}) at different composition and temperatures as well as study of the NX_n pure component and the observed changes of vibrational modes upon melting the NX_n crystalline or/and glass forming solids revealed a variety of structures. Thus, melts with molecular character have been found in the cases of HgX_2 , $FeCl_2$, AlX_3 (X≠F), $ZrCl_4$, NbX_5 and TaX_5 . Dimerization of the molecular melt and establishment of molecular equilibria⁹ and/or partial ionization¹⁰ are rather common e.g.:



A few molten divalent halide melts have been found to form chain like and/or network like structures. Typical examples are the tetrahedral chains and clusters in $BeCl_2$ melts¹¹ and the rather strong network of tetrahedra formed in ZnX_2 (X≠F) melts which can be correlated to the similar SiO_2 like glass structure. The existence of weak network-like structures has been argued in LX_3 (L= rare earth) melts^{4,6}.

References

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