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DIELECTROSCOPIC STUDIES ON DISSOLUTION OF AGGREGATES IN Mn^{2+} DOPED ALKALI HALIDE SYSTEM

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This paper reports the results of dielectroscopic studies in pellets of Mn^{2+} - doped $KCl0_{.9}$ $Br_{0.1}$ crystals grown from aqueous solution, at different temperatures and frequencies.

The water groups have been found to have a role to contribute to increased dielectric constant upto 400K and also to dielectric loss due to jumps of water created defects upto this temperature.

The divalent manganese ions seem mainly to occupy Suzuki phase arrangement in heavily doped $KCl_{0.9}$ $Br_{0.1}$ lattice. The Suzuki phase aggregates seem to break into individual I-V pairs near 580K and contribute to large dielectric constant. The I-V pairs also contribute to appreciable dielectric loss above 580K. Further increase in dielectric loss is observed above 690K and this seems to be due to movement of Br^-/Cl^- ions in the lattice, when the melting points of component halides are approached.

KEYWORDS : Mixed alkali halides, dielectroscopic studies, dissolution of aggregates.

INTRODUCTION

Alkali halide crystals contain Schottky and Frenkel defects even in the pure form. However, when these are doped with divalent cation impurities, vacancies are created at host cation sites. A vacancy could be at nearest neighbour or next nearest neighbour site, depending upon the energy considerations [1-3].

The impurity vacancy pairs are termed as I-V pairs and could group together at low temperatures and are said to form aggregates or precipitates [4-5]. On heating, the precipitates, however, dissolve to form separate I-V pairs. Such I-V pairs could break into cation impurities and vacancies at further higher temperatures.

So far electrical conduction at highest temperatures near the melting point, in doped alkali halides is concerned [6-7], this is achieved through Schottky defects without any role of cation impurities. This is intrinsic conduction and is identified as region-I [6] in log(T) vs. I/T graph. On lowering the temperature, the number of Schottky pairs decreases; however, till the temperature the number of I-V pairs is quite small the conduction is through cations of broken I-V pairs and this region-II is termed as unassociated extrinsic. At further lower temperatures, when vacancies are under the influence of impurities, resulting conduction is termed as extrinsic associated ionic conduction. At much lower temperatures, however, the I-V pairs form aggregates as stated earlier and the conduction values are further lowered and ionic conduction even disappears and at times only scantly electronic conducton may survive.

A sophisticated form of aggregates in doped alkali halides is termed as Suzuki phase [8-9]. Such a phase has the composition of type $6NaCl.MCl_2$, M being the impurity divalent cation. Tewari and Pandey [10] were able to identify six line electron paramagnetic resonance (EPR) of Mn^{2+} trapped in the Suzuki phase of Pb^{2+} in KBr single crystal lattice. Watkins [11] who was the pioneer to report the EPR of Mn^{2+} in NaCl crystals, had also attributed a broad peak due to aggregation involving manganese ions. Again, Pandey *et al* [12] have reported a narrow EPR line with g approximately 2 in RbCl heavily doped with $MnCl_2$ and this is probably due to 6 $RbCl.MnCl_2$ Suzuki phase, the narrowing being effective due to spin-spin exchange between manganese ions.

Electrical measurements have been made by Mahadevan and Jay Kumari [13] on mixed alkali halide crystals. Again, so far dielectrocscopic studies are concerned Kamiyoshi and Nigara [14] have reported results of experimental studies with regard to variation of dielectric constant in some mixed alkali halides with respect to relative composition.

The dielectric loss studies do have been reported in some alkali halides with divalent cation impurities [15]; however the problem of heavily doped cations has not been attempted, so far.

In this work, we are reporting the results of experimental studies with regard to both dielectric constant and dielectric loss in mixed system of $KCl_{0.9}$ $Br_{0.1}$ with heavy (1%) doping of manganese impurities.

EXPERIMENTAL

The Mn^{2+} -doped $KCl_{0.9}$ $Br_{0.1}$ crystals were grown by evaporation of aqueous solution of mixed potassium chloride and potassium bromide in 9 : 1 ratio. The manganese was added as $MnCl_2$ in the mother solution, being one percent by weight of the potassium halide mixture. The polycrystalline mass of $KCl_{0.9}$ $Br_{0.1}$ was converted into pellets with a suitable die and hydraulic press arrangement.

The pellet of the material under study was then kept at a suitable place in the sample holder and the C_p and D values were directly read with a HP 4194A-impedance bridge. The C_p values were then divided by C_0, the capacitance of the empty cell with the electrode arrangement. As the capacitance of the leads was not considered, this resulted in an apparent value of dielectric constant, Ka. Such values of Ka were estimated at various frequencies and temperatures to yield frequency and temperature variation of dielectric constant. The variation of dielectric loss (loss tangent) also as a function of frequency and temperature was plotted directly with the data for D as read with the impedance bridge.

RESULTS AND DISCUSSION

Dielectric constant studies : Fig. 1, gives the plot of variation of apparent dielectric constant in Mn^{2+} - doped mixed KCl : KBr system as a function of temperature. The measurements pertain to six different frequencies 100 kHz, 200 kHz, 300 kHz, 500 kHz, 700 kHz and 100 kHz. As is evident from this figure, the dielectric constant maintains a constant large value upto 400 K, perhaps due to water molecules trapped inside the crystal, during growth from acqueous solution.

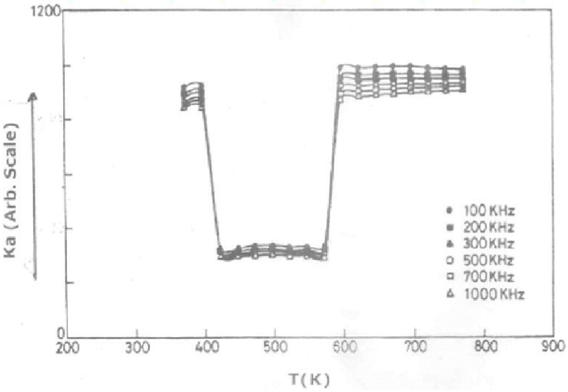

Fig. 1. Temperature variation of apparent dielectric constant in KCl$_{0.8}$ Br$_{0.1}$: Mn^{2+}.

The dielectric constant further shows a sharp fall from 400 K to 425 K. The effect of trapped water seems to be eliminated during such a heating. Beyond 425 K, the dielectric constant shows no variation upto 580 K and then a sharp increase occurs.

The sharp rise in dielectric constant (Ka) beyond 580 K is attributed to breaking of Suzuki phase, formed in mixed alkali halide system due to heavy manganese ion doping. The Suzuki phase aggregate will break into individual I-V pairs on heating and this probably occurs in a narrow temperature range beyond 580K. The abundance of I-V dipoles created thus leads to large value of Ka as observed.

Dielectric loss studies :

Fig. 2 gives the plot of variation of loss tangent (tan) in Mn^{2+} - doped mixed KCl : KBr system as a function of temperature. The measurements pertain to six different frequencies 100 kHz, 200 kHz, 300 kHz, 500 kHz, 700 kHz and 1000 kHz.

The dielectric loss shows a small peak due to some water borne defects upto 425 K. From 425 K to 580 K, the dielectric loss maintains a constant value. However, above 580 K the breaking up of Suzuki phase aggregates in mixed potassium halides is realized due to observation of a strong dielectric loss peak. The loss is due to plentiful of individual I-V pairs. It will be worth to mention that Cook and Dryden [16] had also observed a similar effect in lightly doped alkali halides and they assessed the formation of only dimers and trimers of I-V pairs in their system. In the present work, however, we have observed dissolution of Suzuki phase into individual I-V pairs, through dieletroscopic studies.

The dieletric loss further indicates an increase when the temperature is raised beyond 690 K. This is probably due to movement of Br^- (Cl^-) ions in the mixed lattice as the melting points of KBr (7340C) and that of KCl (7700C) are approached. Thus the unique features observed in the temperature variation of dielectric loss of mixed alkali halide system are uniquely explained.

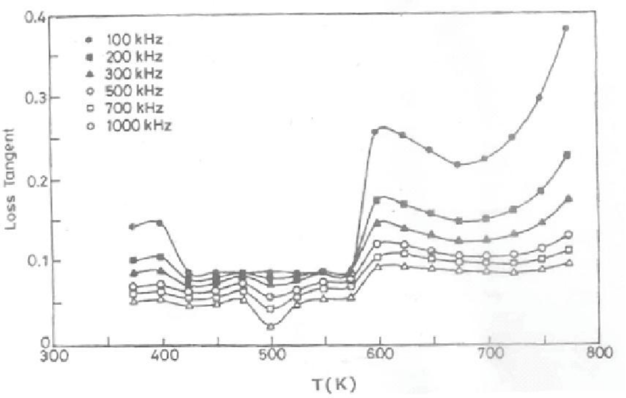

Fig. 2. Temperature variation of dielectric loss in $KCl_{0.9}Br_{0.1}$: Mn^{2+}.

It would, however be interesting if the dielectroscopic results as above are corroborated with EPR studies.

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