

## Dielectric properties of nanophase $\text{Ag}_2\text{HgI}_4$ and $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$ nanocomposites

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**Abstract.** The dielectric properties of nanophase  $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites at different frequencies have been studied over a temperature range covering the stability range of *b* phase of  $\text{Ag}_2\text{HgI}_4$  and beyond the *b* to *a* phase transition temperature.  $\epsilon'$ ,  $\tan \delta$  and  $s_{\text{a.c.}}$  of nanophase  $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites were found to be larger than the reported values for polycrystalline pellets of  $\text{Ag}_2\text{HgI}_4$ . The dielectric properties of the nanocomposites were found to be a function of the wt.% of nano alumina. The observed changes are attributed to the grain boundary properties of nanophase materials and to the microsize space charge effects.

**Keywords.** Nanophase materials; nanocomposites; dielectric properties.

### 1. Introduction

Physical properties of nanophase materials are presently of great scientific interest (Gleiter 1989; Siegel 1994). Enhanced electrical properties of nanophase materials compared to their bulk counterparts have been reported in the literature (Puin and Heitjans 1995; Chiang *et al* 1997). The electrical properties of nanostructured superionic conductors have not been investigated extensively.

$\text{Ag}_2\text{HgI}_4$  existing in tetragonal (*b*) phase at room temperature and in cubic phase (*a*) at higher temperature is one of the oldest known superionic conductors first studied by Ketelaar in 1938. *b*- $\text{Ag}_2\text{HgI}_4$  is a normal ionic conductor with defined lattice positions for the Ag and Hg ions. But *a*- $\text{Ag}_2\text{HgI}_4$  is a highly conducting phase in which the three cations have four equivalent lattice sites where the cations are continuously distributed. In both the phases the charge transport is predominantly by silver ions (Leute and Rusche 1981). Many authors (Neubert and Nichols 1958; Browall and Kasper 1975; Kezionis *et al* 1984) have studied the electrical properties of this material. Several authors have attempted dispersion in a superionic conductor of small particles of the dielectric material  $\text{Al}_2\text{O}_3$  as a method of enhancing the electrical conductivity (Jow and Wagner 1979; Chang *et al* 1984; Kumar and Shahi 1995). It would be of interest to investigate the effect of reduction in the size of the grains of ionic conductors on their electrical properties. As far as the authors know the dielectric properties of nanoparticles of  $\text{Ag}_2\text{HgI}_4$  have not been investigated. The authors report here the results of a detailed study of the dielectric pro-

erties of nanophase  $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites. The dielectric constant and a.c. conductivity of these materials have been studied at a frequency range 5 Hz–13 MHz and over a temperature range from 300 K to 370 K covering the stability range of *b* phase of  $\text{Ag}_2\text{HgI}_4$  and beyond the *b* to *a* phase transition temperature.

### 2. Experimental

Nanoparticles of  $\text{Ag}_2\text{HgI}_4$  were prepared by chemical precipitation from aqueous solutions of  $\text{AgNO}_3$  and  $\text{K}_2\text{HgI}_4$ . The particles of  $\text{Ag}_2\text{HgI}_4$  were separated from the suspension, washed repeatedly by suspending them in distilled water and using an ultrasonic disintegrator to remove adsorbed ions.  $\text{Al}_2\text{O}_3$  particles were of commercial origin and were used as received. The crystal structure of the particles was determined by X-ray powder diffraction using a Bruker AXS D5005 X-ray diffractometer with Ni filtered  $\text{CuK}_\alpha$  radiation. High temperature X-ray studies of nanoparticles of  $\text{Ag}_2\text{HgI}_4$  were performed to determine the *b* to *a* phase transition.  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites were prepared by wet mixing of suitable weight percentage of  $\text{Ag}_2\text{HgI}_4$  and  $\text{Al}_2\text{O}_3$  in the presence of acetone. For the purpose of reference, sample codes were assigned to the pellets as in table 1. X-ray diffraction analyses of  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites were also carried out and the insolubility of  $\text{Al}_2\text{O}_3$  in  $\text{Ag}_2\text{HgI}_4$  was verified by the presence of the characteristic peaks corresponding to both  $\text{Ag}_2\text{HgI}_4$  and  $\text{Al}_2\text{O}_3$ . The nanoparticles were consolidated into pellets of diameter 11 mm and thickness 1–2 mm at a pressure of ~ 0.3 GPa. Both faces of the discs were coated with colloidal silver electrodes. Conducting leads were attached to the electrodes and the samples were then

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encapsulated using nonconducting epoxy powder. For electrical conductivity measurements, the encapsulated pellets were immersed in an oil bath the temperature of which could be regulated with an accuracy of  $\pm 0.1^\circ\text{C}$ . Capacitance ( $C$ ) and dielectric loss ( $\tan d$ ) were measured using a Hewlett-Packard 4192A impedance analyser and the dielectric constant ( $\epsilon'$ ) and a.c. conductivity ( $S_{\text{a.c.}}$ ) were calculated knowing the geometrical dimensions of the sample. The measurements were carried out at different frequencies from 5 Hz to 13 MHz over a temperature range from 300 K to 370 K.

### 3. Results

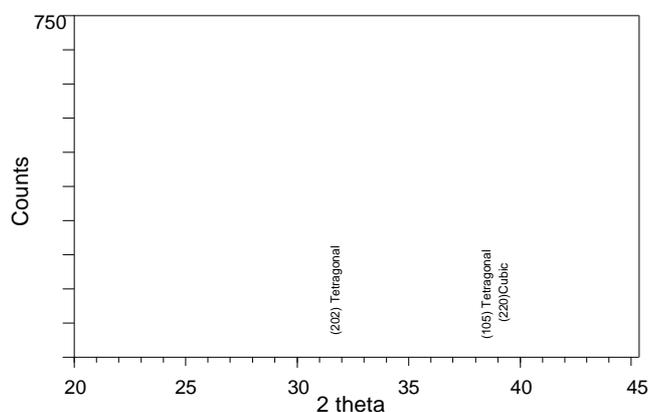
The X-ray diffraction pattern of the nanoparticles of  $\text{Ag}_2\text{HgI}_4$  is shown in figure 1. The overlapping peaks were deconvoluted using a software. The diffraction peaks of the nanoparticles of  $\text{Ag}_2\text{HgI}_4$  revealed the presence of cubic ( $a$ ) phase in addition to the tetragonal ( $b$ ) phase at room temperature (figure 1). In polycrystalline  $\text{Ag}_2\text{HgI}_4$ , the cubic phase exists only at high temperature ( $> 324$  K). The particle sizes were estimated from the line broadening of the diffraction lines using Scherrer's equation (Taylor 1961),

$$L = kl/b \cos q,$$

where  $L$  is the particle diameter,  $k$  a constant nearly equal to 1,  $l$  the wavelength of the X-ray radiation,  $b$  the full width at half maximum of the powder diffraction peak in radians and  $q$  the reflection angle of the peak, and were

**Table 1.** Sample identification codes.

Sample	Wt.% of $\text{Al}_2\text{O}_3$	Sample code
	0	SM-0
$\text{Ag}_2\text{HgI}_4$	5	SM-1
	10	SM-2
	15	SM-3

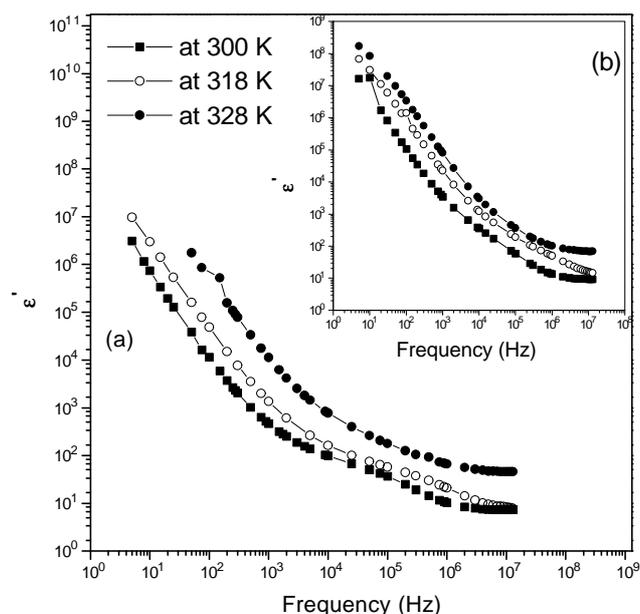


**Figure 1.** X-ray diffraction pattern of nanoparticles of  $\text{Ag}_2\text{HgI}_4$ .

found to be 20 and 16 nm respectively for  $\text{Ag}_2\text{HgI}_4$  and  $\text{Al}_2\text{O}_3$  nanoparticles.

The real part of dielectric constant ( $\epsilon'$ ) of nano- $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites was found to have very high values at low frequencies which decreased rapidly with the applied frequency irrespective of the temperature of measurement. The typical variation of  $\epsilon'$  of two samples with frequency of the applied field is represented in figure 2. It was found that at 300 K the value of  $\epsilon'$  of bare nano  $\text{Ag}_2\text{HgI}_4$  (SM-0) decreased from  $\sim 10^6$  at 100 Hz to  $\sim 10$  at 13 MHz. The variation of dielectric constant with temperature of bare nano- $\text{Ag}_2\text{HgI}_4$  and the  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites at 1 kHz is shown in figure 3. In general,  $\epsilon'$  increased almost linearly with temperature. There is a small upward shift in the value of  $\epsilon'$  near the  $b$  to  $a$  transition temperature of  $\text{Ag}_2\text{HgI}_4$ , but the slope of the graph before and after the transition remains the same (figure 3). Numerically, at 1 kHz,  $\epsilon'$  of sample SM-0 had a value of  $\sim 400$  at 300 K which increased with temperature and reached a value of  $\sim 11200$  at 328 K.

The variation of dielectric loss ( $\tan d$ ) of the samples with frequency and temperature is shown in figure 4. It can be seen that  $\tan d$  decreases rapidly with increase in the frequency and at higher frequencies the loss angle has almost the same low value at all temperatures. For the sample SM-0, the value of the dielectric loss at 300 K is  $\sim 7$  at 100 Hz and  $\sim 0.07$  at 13 MHz. The same behaviour is observed in the case of the nanocomposites also. At 300 K, for the sample containing 5 wt.% of nano alumina (SM-1), the value of  $\tan d$  at 100 Hz is  $\sim 13.8$  and that at



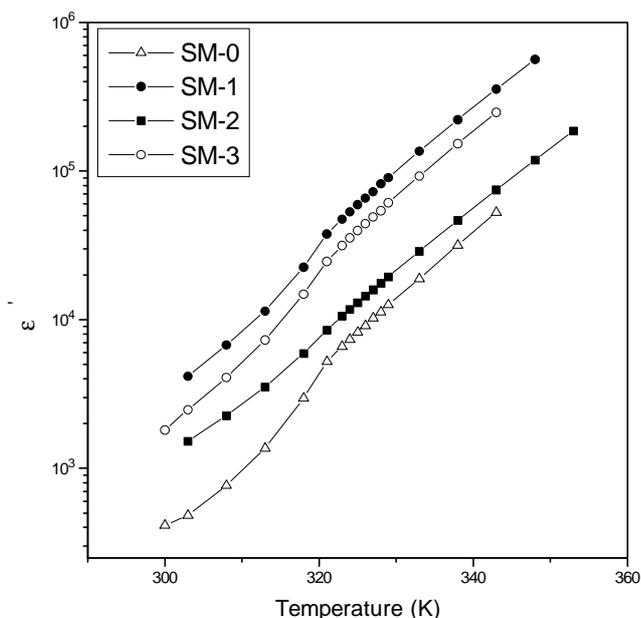
**Figure 2.** Variation of  $\epsilon'$  of (a) nanophase  $\text{Ag}_2\text{HgI}_4$  and (b) a typical  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposite sample (SM-1) with frequency.

13 MHz is  $\sim 0.06$ . For SM-2 the value of  $\tan d$  at 300 K was found to vary from  $\sim 6.7$  to  $\sim 0.78$  when the frequency was increased from 100 Hz to 13 MHz. For SM-3 this variation was from 19 to 0.075.

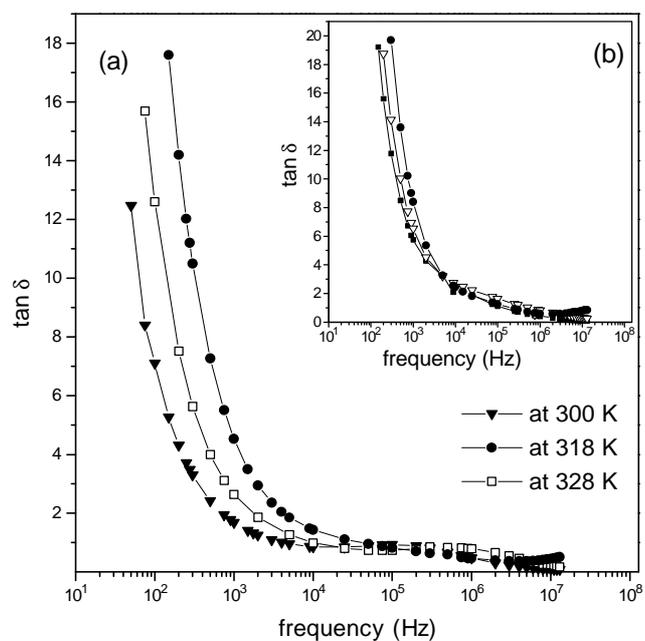
The variation of  $\epsilon'$  and  $\tan d$  with wt.% of nano alumina is shown in figures 5 a–b.  $\epsilon'$  was found to increase initially, then to decrease and again to increase with wt.% of nano alumina. Numerically,  $\epsilon'$  at 300 K and at 1 kHz was found to increase from  $\sim 465$  for SM-0 to  $\sim 3490$  for

SM-1, and then to decrease to a value of  $\sim 1400$  for SM-2 and again increase to  $\sim 4500$  for SM-3. Similar variation in  $\epsilon'$  was observed at higher temperatures also. The nature of variation of  $\tan d$  with wt.% of nano alumina was found to be similar to that of  $\epsilon'$ .

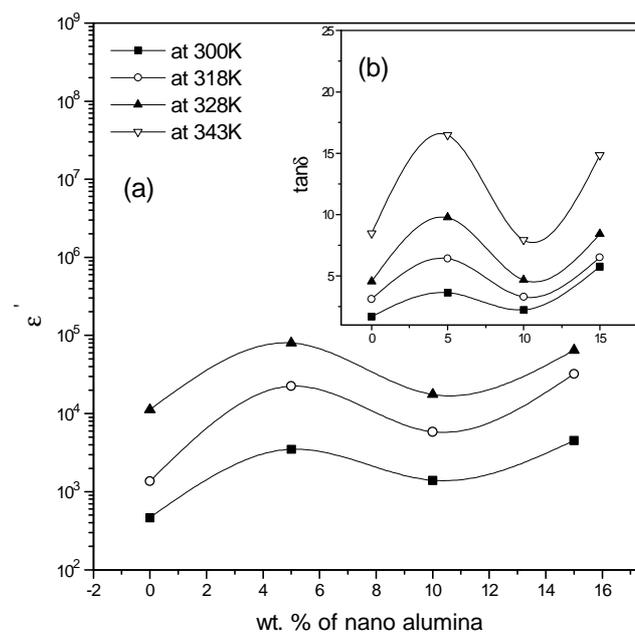
The variation of a.c. electrical conductivity ( $s_{a.c.}$ ) of the samples with frequency at different temperatures is shown in figure 6. The conductivity was found to decrease with frequency initially and thereafter it increased with



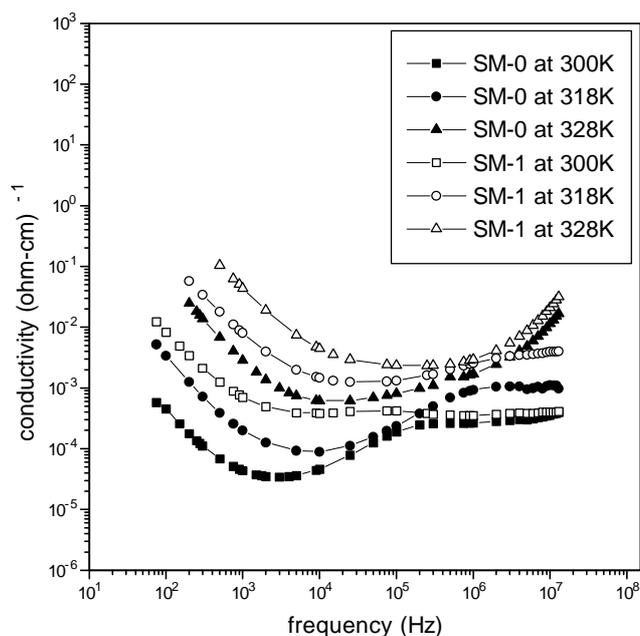
**Figure 3.** Temperature dependence of  $\epsilon'$  of the nanophase  $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites.



**Figure 4.** Variation of  $\tan d$  of (a) nanophase  $\text{Ag}_2\text{HgI}_4$  and (b) a typical  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposite sample (SM-3) with frequency.



**Figure 5.** Variation of (a)  $\epsilon'$  and (b)  $\tan d$  with the wt.% of nano alumina.



**Figure 6.** Variation of  $s_{a.c.}$  of nanophase  $\text{Ag}_2\text{HgI}_4$  and a typical  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposite (SM-1) with frequency.

frequency. Numerically, at 300 K,  $S_{a.c.}$  of SM-0 was found to decrease with frequency from a value of  $4.5 \times 10^{-4}$  (ohm-cm) $^{-1}$  at 100 Hz to a value of  $4 \times 10^{-5}$  (ohm-cm) $^{-1}$  at 5 kHz, and then to increase steadily up to a value of  $1.9 \times 10^{-4}$  (ohm-cm) $^{-1}$  at 100 kHz. Beyond about 100 kHz,  $S_{a.c.}$  was found to increase slowly with frequency. Typical variation of  $S_{a.c.}$  of  $Ag_2HgI_4-Al_2O_3$  nanocomposites with wt.% of nano  $Al_2O_3$  at 1 kHz is shown in figure 7. The nature of variation of  $S_{a.c.}$  with the wt.% of nano alumina is similar to that of  $e'$  and  $\tan d$ .

The temperature dependence of a.c. conductivity of nano  $Ag_2HgI_4$  and other nanocomposites at 1 kHz are shown in figure 8. The sample SM-1 showed the highest conductivity compared to the other samples. The activation energies calculated were 1.39 for the  $a$  phase and 1.42 for the  $b$  phase for the sample SM-0, and 1.29 and 1.21 respectively for SM-1. The value of  $S_{a.c.}$  of SM-0 at 1 kHz increased by about three orders of magnitude from a value of  $3.31 \times 10^{-5}$  ( $\Omega$  cm) $^{-1}$  at 300 K to a value of  $2.4 \times 10^{-2}$  ( $\Omega$  cm) $^{-1}$  at 343 K compared to value of  $\sim 10^{-6}$  at room temperature and  $\sim 10^{-3}$  ( $\Omega$  cm) $^{-1}$  above 325 K for polycrystalline samples of  $Ag_2HgI_4$  (Neubert and Nichols 1958). The a.c. conductivity of sample SM-1 at 1 kHz increased by about 19 times compared to that of the sample SM-0 under the same conditions.

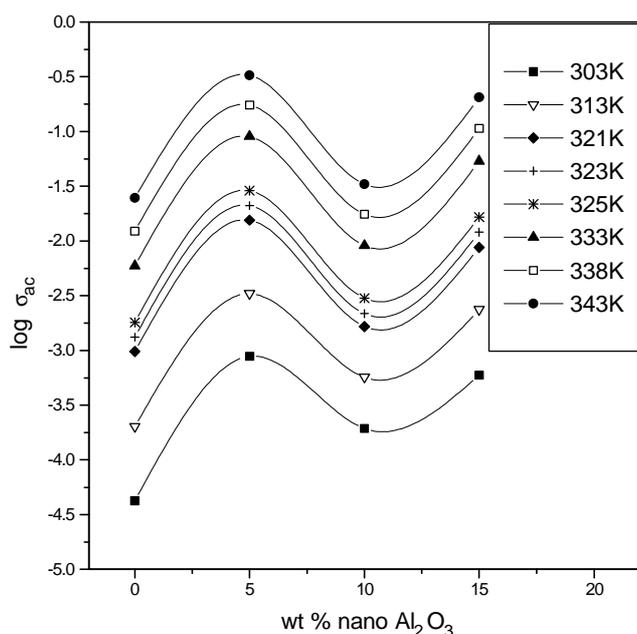
## 4. Discussion

### 4.1 Dielectric constant and $\tan d$

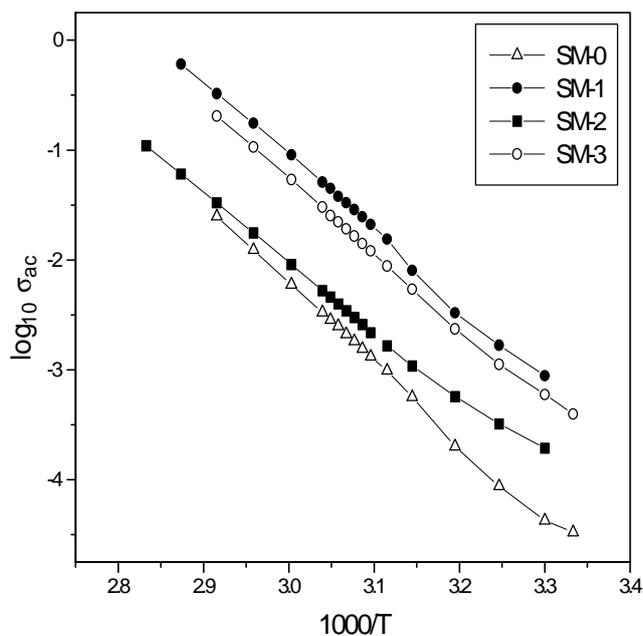
The dielectric constant of polycrystalline  $Ag_2HgI_4$  over the frequency range from 200 kHz to  $10^8$  Hz and for the

temperature range of 293 to 333 K has been reported (Benguigui and Weil 1977). The reported value of  $e'$  at 0.25 MHz was less than 10 whereas in the present investigation, the nanoparticles of  $Ag_2HgI_4$  showed a value of  $\sim 20$  and the sample containing 5 wt.% of nano  $Al_2O_3$  showed a value of  $\sim 29$  at this frequency and at 300 K. The high frequency dielectric constant of polycrystalline  $Ag_2HgI_4$  in the disordered phase ( $a$ ) is reported to be 5.1 (Kezionis *et al* 1984). In the present study, the value of  $e'$  of nano  $Ag_2HgI_4$  at 13 MHz and at 328 K ( $a$  phase) was found to be  $\sim 100$ . According to Samara (1984), the higher the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects. Since the grain boundary of nanoparticles contain a large density of defects (Halperin 1986; Gleiter 1989), it can be argued that the dielectric constant of nanoparticles should have higher values.

A large vol.% of a nanocrystalline material consists of grain or interphase boundaries. These boundaries contain defects such as dangling bonds, vacancies, vacancy clusters etc (Chi-mei *et al* 1995). These defects can cause a positive or negative space charge distribution in interfaces. The space charges can move under the application of an external field and when they are trapped by the defects, lots of dipole moments are formed (space charge polarization). Hence the space charge effect will be an important factor which decides the dielectric properties in materials with small particle sizes (Maier *et al* 1988). In addition, ion jump polarization may also be greater in nanocrystalline materials since there will be a number of positions in the grain boundaries for the ions to occupy. The high values of the dielectric constant in the present



**Figure 7.** Conductivity ( $S_{a.c.}$ ) as a function of the wt.% of nano alumina at different temperatures.



**Figure 8.** Temperature dependence of a.c. conductivity ( $S_{a.c.}$ ) of nanophase  $Ag_2HgI_4$  and  $Ag_2HgI_4-Al_2O_3$  nanocomposites.

study may be attributed to the increased ion jump orientation effect and the increased space charge effect exhibited by nanoparticles. Along with these, the d.c. conductivity effects can also enhance the value of the dielectric constant (Kingery 1976). The large d.c. conductivity observed in fast-ion conductors is interpreted in terms of random hopping of mobile ions from site to site (Kimball and Adams 1978). In a nanocrystalline material, the presence of high density of trap sites will enhance hopping and thereby increased d.c. conductivity can be expected. Also, at low frequencies the dielectric loss is inversely proportional to frequency which indicates large d.c. conductivity (Yadav *et al* 1980) and hence increased value of dielectric constant.  $\epsilon'$  was found to decrease with frequency since as frequency increases a point will be reached where the space charge cannot sustain with the field and hence the polarization decreases, which results in the decrease of  $\epsilon'$ .

The dielectric constant was found to increase with temperature. Molecules cannot orient themselves in dielectrics. As temperature rises, the orientation of dipoles is facilitated and  $\epsilon$  increases (Tareev 1979). The ionic polarization also increases as temperature increases (Kingery 1976). At higher temperatures, the d.c. conductivity due to the hopping of mobile ions becomes important and enhanced dielectric constant results. X-ray diffraction analysis of the  $\text{Ag}_2\text{HgI}_4$  nanoparticles revealed the presence of cubic phase in addition to the tetragonal phase at room temperature. The co-existence of two phases in nanoparticle samples has been reported (Garvie 1985). In polycrystalline  $\text{Ag}_2\text{HgI}_4$ , the dielectric constant is higher for *a* phase (cubic) compared to the *b* phase (tetragonal structure). It has been reported (Takeuchi *et al* 1999) that the relatively higher tetragonal content in addition to the cubic in single crystal grains of  $\text{BaTiO}_3$  would lead to higher permittivity. The presence of the cubic phase at low temperature in the nanoparticles of  $\text{Ag}_2\text{HgI}_4$  may also be a reason in addition to the factor mentioned in the preceding paragraph for the high value of the observed dielectric constant.

The resultant dielectric constant of a composite system of two or more components has been studied by many workers (Kingery 1976; Tareev 1979; Bhimasankaran *et al* 1998). It is easy to calculate  $\epsilon'$  for a composite material simply by considering it as a layer material consisting of layers either parallel or normal to the applied field. According to these analyses, a dielectric constant intermediate between the dielectric constants of  $\text{Ag}_2\text{HgI}_4$  and  $\text{Al}_2\text{O}_3$  should be obtained for the nanocomposites in the present study. But the experimentally obtained value of  $\epsilon'$  of the nanocomposites was found to be about one order of magnitude higher than the corresponding value for SM-0. Hence it is clear that the nanocomposite system is not obeying such mixing rules.

The variation in dielectric constant  $\epsilon'$  of the nanocomposites of  $\text{Ag}_2\text{HgI}_4$  and  $\text{Al}_2\text{O}_3$  with frequency were similar to that of bare  $\text{Ag}_2\text{HgI}_4$ . The addition of alumina nanopar-

ticles enhanced the value of dielectric constant of nano- $\text{Ag}_2\text{HgI}_4$  and the enhancement was found to be a function of the concentration of nano alumina. The insolubility of  $\text{Al}_2\text{O}_3$  in  $\text{Ag}_2\text{HgI}_4$  as evidenced by X-ray diffraction studies show that the dispersion of alumina nanoparticles in nanoparticles of  $\text{Ag}_2\text{HgI}_4$  influenced the polarization processes and caused an increase in  $\epsilon'$ .

Dielectric loss of polycrystalline  $\text{Ag}_2\text{HgI}_4$  (Benguigui and Weil 1977) at different temperatures has been reported over the frequency range of 0.25 and 50 MHz. It is reported that below the *b* to *a* phase transition temperature,  $\tan \delta$  decreases with frequency, starting from a maximum value at 0.3 MHz.  $\tan \delta$  in the present study was found initially to decrease rapidly with frequency and then to decrease at a slower rate. In nanophase materials, inhomogeneities like defects, space charge formation etc in the interface layers together produce an absorption current resulting in a dielectric loss. Also, enhancement in d.c. conductivity will give rise to currents which in an a.c. field are in phase with applied voltage and hence cause dielectric loss (Tareev 1979). The absence of dielectric loss peaks in the frequency versus dielectric loss curves of the present samples show the wide distribution of relaxation times (Kingery 1976). The values of  $\tan \delta$  of the  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites depend on the concentration of alumina nanoparticles. This result may be attributed to the modification in the grain boundaries of nanoparticles which has to be a function of the wt.% of nano alumina.

#### 4.2 A.c. conductivity

The a.c. conductivity ( $S_{a.c.}$ ) of the samples was found to be strongly dependent on the frequency of the applied field (figure 6). The conductivity was found initially to decrease and then to increase with frequency for all samples. It has been reported that a dispersion in the conductivity is a direct evidence for the hopping of charge carriers around lattice imperfections (Snowden and Saltsburg 1965). Dispersion in conductivity will occur when the carriers are not free to move throughout the sample. Conductivity decay with frequency was observed in NiO by oxygen adsorption and this phenomena has been explained on the basis of the multiple trapping of the charge carriers by the adsorbed species (Saltsburg *et al* 1964). The conductivity decrease in the present study at low frequency may be due to the trapping of charge carriers in the defects of the grain boundaries.

The frequency dependence of conductivity above 1 kHz can be represented by the relation  $S(w) = Aw^s$  (Sayer and Mansingh 1972; Mansingh 1980), where *s* is close to unity and the parameter *A* shows little dependence on temperature. The value of *s* is the slope of the log *S* versus log *w* plot, where *w* is the angular frequency. The graph at all temperatures above 1 kHz can be divided into

three linear sections with different slopes. The  $\log s$  versus  $\log w$  plot for SM-0 at 300 K has slopes  $\sim 0.5$ ,  $\sim 0.04$  and  $\sim 0.3$  between 5 kHz and 13 MHz. The strong dependence of  $s_{a.c.}$  on frequency in the high frequency range is typical of highly correlated ionic motion in structurally disordered solid electrolytes (Puin and Heitjans 1995). It is important to note that the value of  $s$  becomes  $\sim 1.2$  in the high frequency region for the sample SM-0 at 328 K. A value of  $s > 1$  was reported for borate glasses (Cramer and Funke 1992) and was explained on the basis of an additional localized reorientational ionic motion.

Temperature dependence of the a.c. conductivity of polycrystalline  $\text{Ag}_2\text{HgI}_4$  was reported by Neubert and Nichols (1958) to contain two regions corresponding to the  $b$  and  $a$  phases. The conductivity versus inverse temperature plot in the present study was found to be conspicuously different from that of the polycrystalline sample. The Arrhenius plot (figure 8) shows that there is no sudden but only a small and gradual upward shift at the phase transition temperature indicating the absence of a sharp transition temperature. Also, the transition temperature is not sharp. The portions of the graph before and after the phase transition have almost identical slopes. In polycrystalline  $\text{Ag}_2\text{HgI}_4$ , the  $s_{a.c.}$  above 325 K ( $a$  phase) was almost independent of temperature. Rice *et al* (1974) suggested that it is the interaction of the interstitial cation defects with the strain field they induce which is primarily responsible for the phase transition. In the present study, the phase transition is modified compared to the bulk sample suggesting a modified interaction involving the cation defects.

The conductivity enhancement observed in the present investigation can be explained on the basis of the space charge model reported by Maier *et al* (1988). In thermal equilibrium, the surface and grain boundaries of an ionic crystal may carry an electric charge resulting from the presence of excess ions of one sign. This charge is just compensated by a space charge cloud of the opposite sign adjacent to the boundary. For a pure material, this charge arises if the energies to form anion and cation vacancies or interstitials at the boundary are different. The magnitude and sign of the boundary charge changes if there are aliovalent solutes present in the matrix which alter the concentration of the lattice defects in the crystal. Space charge effects will be predominantly important in very small crystals since the grain boundaries contain a large number of defects compared to the coarser grained polycrystalline materials. The model proposed by Maier *et al* (1988) for  $\text{AgCl}$  and  $\text{AgBr}$  is used to explain the enhancement of conductivity in the present study.

If the grain size of the sample is reduced continuously, the space charge regions become predominant and additional conductivity increases can be expected when the size of the particles is no longer large compared to the Debye length ( $l$ ). In this case, the defect profile will be

significantly different from that of the bulk case. The conductivity enhancement can be roughly taken account of by a 'micro size factor',  $g \cong 4l/L$ , where  $L$  is the sample thickness. That is, if the sample thickness is of the order of  $\sim 0.4 l$ , the space charge effects are enhanced by an additional order of magnitude. In the present investigation, the a.c. conductivity of the nanoparticles of  $\text{Ag}_2\text{HgI}_4$  is found to be increased by one order of magnitude compared to the bulk polycrystalline material. The space charge model satisfactorily explains this enhancement of one order of magnitude. The enhancement of conductivity by the addition of fine particles of alumina to  $\text{LiI}$ ,  $\text{AgCl}$  etc is also explained on the basis of space charge effects induced by an internal adsorption of ions at the oxides surface (Maier *et al* 1988; Maier 1992). The increased cation vacancy concentration can lead to highly conducting interfacial layers short circuiting the grains. Here also, if the grain size of the particles is of nanometer size scale, size effects are observed and conductivity increases. However, a moderate increase of nano alumina content does not result in more local segregation and hence the observed variation of the conductivity with wt.% of nano alumina.

## 5. Conclusions

The dielectric properties of nanophase  $\text{Ag}_2\text{HgI}_4$  and  $\text{Ag}_2\text{HgI}_4\text{-Al}_2\text{O}_3$  nanocomposites were investigated for a wide range of frequencies from 5 Hz to 13 MHz over a temperature range from 300 K to 370 K.  $\epsilon'$ ,  $\tan d$  and  $s_{a.c.}$  were found to be larger than the reported values for polycrystalline pellets of  $\text{Ag}_2\text{HgI}_4$ . The addition of  $\text{Al}_2\text{O}_3$  particles in nanoparticles of  $\text{Ag}_2\text{HgI}_4$  samples enhanced the values of  $\epsilon'$ ,  $\tan d$  and  $s_{a.c.}$  compared to the bare nano  $\text{Ag}_2\text{HgI}_4$  and the enhancement was found to be a function of the wt.% of nano alumina. The observed changes in the dielectric properties are attributed to the grain boundary properties of nanophase materials and to the microsize space charge effects.

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