CHAPTER 6

ELECTRICAL PROPERTIES OF NANOPHASE $\text{Ag}_3\text{PO}_4$

6.1 Introduction

Nanostructured materials or nanophase materials are formed by the assembling of a large number of nanoparticles. These materials are important since their properties are considerably different from those of corresponding bulk materials due to large volume of interface between grains.\textsuperscript{1-7} The morphology and in particular the connectivity of random networks of nanoparticles influences both the mechanical restoring forces and the transport properties.\textsuperscript{8} Nanoparticle materials exhibit greatly altered electrical properties compared to their coarser grained counter parts.\textsuperscript{9-13}

Nanophase materials consist of grains, grain boundaries and grain interfaces which play important roles in determining the electrical properties.\textsuperscript{14-17} In these materials the majority of atoms, molecules or ions reside in the grain boundaries or within one or two layers from the boundary. These grain boundaries having high density of defects like dangling bonds, vacancies, micropores, etc. can control the transport properties of the materials in a decisive manner.\textsuperscript{17}

Impedance spectroscopy (IS) is an appropriate experimental technique to obtain information about the electrical characteristics of polycrystalline materials and nanomaterials.\textsuperscript{14-19} IS has also been used for the characterisation of the electrical behaviour of solid electrolytes\textsuperscript{20,21} and ceramic materials.\textsuperscript{22,23} This technique probes the electrical response as a function of frequency, of components, the grains and grain boundaries.\textsuperscript{24} This method is capable of revealing the structural uniformity, variation in electrical conduction paths, stability, etc.\textsuperscript{17} IS can be effectively used to study the inter-granular electrical
barriers, origin of resistance or capacitance and their dispersion with small signal frequencies and the role of defects within the regime of the electric field.25

The overall dielectric properties arise due to intragrain, intergrain and sample-electrode processes in the nanophase materials.25,26 The motion of charges could take place in any fashion, viz. charge displacements, dipole re-orientation, space charge formation, etc.25,26 IS study of nanophase ZnO,17,18 CaF$_2$14 and CeO$_2$11 has been reported.

The study of dielectric properties of nanophase materials has been found to be interesting. Enhanced electrical properties of nanophase materials compared to their bulk counterparts have been reported in the literature.10,11 For example, nanophase AgI has been found to have high ionic conductivity compared to its bulk counterpart due to the defect structure of nanoparticles.12 The ionic conductivity of nano CaF$_2$ is found to be increased by four orders of magnitude compared to the conductivity of single crystalline CaF$_2$.14 In nanostructured yttria stabilized zirconia, increased ionic conductivity was observed.19 In the case of nanophase Ag$_2$Hgl$_4$, increase in dielectric constant, loss tangent and a.c. conductivity was reported compared to polycrystalline pellets of Ag$_2$Hgl$_4$.10 When we consider the dielectric behaviour of a material, the two factors that are of practical interest are frequency range and temperature range, that is being applied to the material.

The ionic conduction and dielectric behaviour of silver phosphate glasses have been studied by Cutroni and co-workers.27,28 The hopping mechanism of silver ions in Ag$_3$PO$_4$ glasses has been reported by Haque et. al29. Solid electrolytes are materials having high ionic conductivity and relatively small electronic conductivity. These materials are important for their unique transport properties and potential applications in solid state batteries. The electrical behaviour of several nanophase ionic conductors are studied and
The electrical behaviour of nanophase $\text{Ag}_3\text{PO}_4$ has not been studied.

In the present chapter electrical conductivity studies and impedance spectroscopic studies of consolidated nanoparticle $\text{Ag}_3\text{PO}_4$ are described. Depending upon the concentration of the reacting components, duration and temperature, the precipitated particles may vary in size, shape and uniformity and hence the electrical properties. Electrical studies of nanophase $\text{Ag}_3\text{PO}_4$ were conducted for three reactant concentrations (0.015M, 0.01M and 0.005M) in order to understand how it affects the particle size and hence electrical properties. This study was carried out to understand the basic electrical nature of nanophase $\text{Ag}_3\text{PO}_4$ which has not been hitherto reported. Room temperature complex impedance spectra, dielectric behaviour and a.c. conductivity of nanophase $\text{Ag}_3\text{PO}_4$ were studied over a range of frequencies from 100Hz to 13MHz and in the temperature range 300-525K.

6.2 Experimental

Nanoparticles of $\text{Ag}_3\text{PO}_4$ were prepared by chemical precipitation from aqueous solution of $\text{AgNO}_3$ and $\text{Na}_2\text{HPO}_4$ as described in section 3.2.1 of Chapter 3. Three powder samples of $\text{Ag}_3\text{PO}_4$ of reactant concentrations 0.015M, 0.01M and 0.005M were prepared. The crystal structure of the particles was determined by X-ray powder diffraction using Philips 1710 PW powder X-ray diffractometer using $\text{CuK}_\alpha$ radiation over a wide range of Bragg angles fitted with nickel filter. The particle size variation with reactant concentration was not visible in the XRD patterns of the three samples. The particle size varied from 40-60nm as calculated from the line broadening of XRD peaks using Scherrer’s equation for all three samples. But from TEM image, for 0.015M $\text{Ag}_3\text{PO}_4$ sample the particle size was 20nm, and for 0.005M sample the particle size was 15nm. This shows that the particle size decreases with decrease in reactant concentration. SEM image of nanoparticle
Ag$_3$PO$_4$ shows that the clusters are in the form of fractal aggregates or in the form of coral reefs. Each particle is oval shaped and the aggregate have a fluffy nature with considerable porosity. The details are given in sections 3.4.1 and 3.5.1 of Chapter 3. For IS measurements and dielectric measurements the powder samples of Ag$_3$PO$_4$ nanoparticles were consolidated into pellets of diameter 12mm and thickness 1-2mm at a pressure of ~ 0.5 GPa. Both faces of the discs were coated with air drying silver paste which act as electrodes. Conducting leads were attached to the electrodes and these samples were used for the IS and dielectric measurements. For IS analysis, real part (Z') of the total complex impedance $Z = Z' - j Z''$ and imaginary part (Z'') were measured for frequencies ranging from 100Hz to 13MHz at room temperature. For dielectric measurements, capacitance values and loss tangent (tanδ) were measured. The apparatus used for electrical measurement was HP 4192A LF impedance analyser.

6.3 Results and Discussion

6.3.1 Impedance Spectroscopic Analysis

There are a number of studies dealing with the complex impedance analysis of nanophase as well as polycrystalline materials.$^{11,14-21}$ Based on these reports, the IS study of nanophase Ag$_3$PO$_4$ has been carried out by the author to know the electrical conduction mechanism in this sample. The application of IS to the characterisation of ceramic ionic conductors started with the work of Bauerle.$^{25,31}$ He presented an equivalent circuit model for the polarisation processes of grain interiors, grain boundaries and electrode sample interface for zirconia with platinum electrodes. From then onwards this model was proved to be typical of most solid electrolytes. Recently ionic conductivity studies of ultrafine grained yttria stabilized zirconia (YSZ) pellets were carried out using impedance spectroscopy by Ramamoorthy et al.$^{15,19}$ The ionic conductivity of nanophase zirconia is found to be greater than that of its
coarser grained counterparts. IS studies of polycrystalline Mn-Zn ferrites revealed an increase in resistivity and it was found to be from the increase in resistivity of the grain boundary, which originated from the increase in the microscope shape factor of the grain boundary. Complex impedance spectra analysis of polycrystalline Mg-Zn ferrites has shown that the capacitive and resistive properties of the material are due to grain and grain-boundary processes. The impedance analysis of polycrystalline Ni-Zn ferrites and the observed impedance response was attributed to a series combination of highly resistive grain boundary component and a less resistive grain component.

For polycrystalline BaTiO₃, the impedance spectrum has shown a small arc due to grain and a large arc due to grain boundary. The large grain boundary arc was explained on the basis of the presence of air gaps and high impedance electrical inhomogeneity in the region between grains. The impedance spectrum of high purity ZrO₂ stabilized with CaO, for different grain sizes were studied and two well-separated semicircles were presented. These two semi-circles at high frequencies were attributed to grain and grain boundary processes in electrical conduction and a portion of the third semicircle present at low frequencies was due to sample-electrode interface impedance. For polycrystalline CeO₂ which is electronically conducting, the impedance spectra showed a small arc due to grain contribution and a large arc due to grain boundary contribution. For nanophase ZnO having grain size 60nm the impedance spectrum has shown only one semicircle which was explained on the basis of grain boundary contribution. But recently IS study of nanophase ZnO having grain size 13nm has shown two partially overlapping semicircles with large arc for grains and smaller arc for grain boundaries. In the case of nano CaF₂, three semicircular arcs are seen. The smallest arc in the high frequency region due to grain, the large middle arc due to grain boundary and a third arc in the lowest frequency region due to electrode processes. The charge transport in this sample is explained as due to defective parallel space charge layers, parallel interfaces and grains whereas
more resistive grain boundary arc is due to resistive interfaces and space charge layers perpendicular to the current.

**Impedance Spectrum of Nanophase Ag₃PO₄**

Fig. 6.1, 6.2 and 6.3 show the impedance spectra (Cole-Cole plots) obtained at room temperature for nanophase Ag₃PO₄ for three reactant concentrations 0.015M, 0.01M and 0.005M respectively. Three semi-circular arcs (regions 1, 2 and 3) are observed in all the plots. These three semi-circular arcs correspond to three different relaxation processes in the grains, grain boundaries and sample-electrode interfaces. Real materials usually do not exhibit impedance spectra of the simple semicircular form, but exhibit a distorted or depressed semicircle in the complex plane, which may arise from not one but several relaxation times or from a continuous distribution of relaxation times arising from microstructural inhomogeneity or disorder. Arcs which are depressed with origin below the real axis are usually observed in measurements on solid electrolytes. The contribution of each of the components, grain, grain boundary and sample electrode interface can be represented by a suitable combination of resistance and capacitance in parallel. The sample can thus be represented by an equivalent circuit (fig 6.4) containing three, parallel R-C element connected in series.

The appearance of three overlapping semi-circular arcs in the plot indicates the presence of three polarization processes in the system with different response times, the grain response being at the high frequency side and electrode response at low frequency side. One parallel R-C circuit has one time constant and hence can be conveniently used a model to represent one polarisation process. The Z' vs Z" plot for such a R-C model containing semi-circular arcs with its intercept on the Z' axis gives resistance value R for each element. Capacitance values can be calculated by using the relation \( \omega RC = 1 \), where \( \omega = 2\pi f \), f being the frequency corresponding to the
maximum of each circular arc. A depressed circular arc in the impedance plot with its centre of curvature below the $Z'$ axis shows a distribution of relaxation times for the above mentioned process. Thus $R_g$, $R_{gb}$ and $R_s$ represent grain resistance, grain boundary resistance and sample-electrode resistance respectively. Then the capacitance $C_g$, $C_{gb}$ and $C_s$ can be calculated. The contribution to the conductivity due to grain ($\sigma_g$) was calculated by measuring the dimensions of the pellets. The mean relaxation time for the grain and the grain boundary processes $\tau_g = R_g C_g$ and $\tau_{gb} = R_{gb} C_{gb}$ are the inverse of the peak frequencies $\omega_g$ and $\omega_{gb}$. It is reported that the semi-circular arc present in the low frequency region (electrode response) represents the blocking nature of metal electrodes on ionic conductors.

The overall impedance behaviour of the three samples is mainly constituted of the contributions from the grain boundaries. The SEM image (fig 3.7 of Chapter 3) shows that nanophase $\text{Ag}_3\text{PO}_4$ is porous having large volume of interface. The intergranular porosity largely alters the diameter of the grain boundary arc ($R_{gb}$) in the impedance spectrum. In nanophase materials, a large number of atoms reside in the grain boundary where they occupy positions relaxed from normal sites. The grain boundary resistance may also be attributed to partial or complete blocking of charge carriers due to the presence of defects at the grain boundaries or because of space charge regions depleted of charge carriers or mismatching of lattice. The diameter of region 1, a measure of grain contribution to the total resistivity ($R_g$) is comparatively small in all the three samples. The grain contribution to the impedance spectrum by three samples of nanophase $\text{Ag}_3\text{PO}_4$ is given in table 6.1. Since the grain boundary resistance $R_{gb}$ (intercept of region 2) is very large compared with grain resistance, conductivity is mainly through grains, which is characteristic of ionic conductors. From table 6.1 it can be noticed that grain conductivity decreases with decrease in reactant concentration, which may be due to decrease in particle size. In nanoparticles, the surface
atoms will have higher diffusion coefficient than that of the bulk, we normally expect higher conductivity and lower activation energy in the grain boundary region. But in the present study, the high impedance and small conductivity in the grain boundaries may be due to large area of grain boundary region, porosity, presence of defects, space charge regions depleted of charge carriers, etc. The low value of conductivity in 0.005M sample compared to other two samples may be due to the confined passage of Ag$^+$ ions within the small grains. The ionic conductivity is directly proportional to the jump attempt frequency and the square of the jump distance. The jump distance may be smaller in lower concentrated sample having smaller particle size.

Fig. 6.1: Impedance spectrum of 0.015M Ag$_3$PO$_4$
Fig. 6.2: Impedance spectrum of 0.01M Ag$_3$PO$_4$

Fig. 6.3: Impedance spectrum of 0.005M Ag$_3$PO$_4$
### Table 6.1: Variations of grain resistance, grain capacitance and grain conductivity with reactant concentration for nanophase Ag₃PO₄

<table>
<thead>
<tr>
<th>Reactant concentration (M)</th>
<th>Rg (kilo ohm)</th>
<th>Cg (pF)</th>
<th>σg (ohm⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>36.5</td>
<td>77.6</td>
<td>2.550E-4</td>
</tr>
<tr>
<td>0.01</td>
<td>112</td>
<td>42.4</td>
<td>0.935E-4</td>
</tr>
<tr>
<td>0.005</td>
<td>250</td>
<td>22.5</td>
<td>0.404E-4</td>
</tr>
</tbody>
</table>

### 6.3.2 Dielectric Properties

Dielectric (essentially non-conducting) characteristics of ionic conductors are important in solid state batteries as solid-electrolytes whereas that of ceramic materials are of increasing importance in solid-state electronics.\(^{41}\) The dielectric properties that are of practical interest are dielectric constant, dielectric loss factor and dielectric conductivity. When we consider the dielectric behaviour of a ceramic material, the two factors that are of practical interest are frequency range and the range of environmental conditions, particularly temperature. It has been shown that alternating current response as a function of frequency gives valuable information about the dynamic response of the system and makes it possible to characterise many materials.\(^{42}\)
6.3.2.1 Dielectric Constant

The complex dielectric constant is given by the equation \( \varepsilon = \varepsilon' - j \varepsilon'' \)
where \( \varepsilon' \) is the real part of the dielectric constant and \( \varepsilon'' \) is the imaginary part of the dielectric constant.

\[
\varepsilon' = \frac{Cd}{\varepsilon_0A} \quad \text{............... 6.1}
\]

\[
\varepsilon'' = \varepsilon' \tan\delta \quad \text{............... 6.2}
\]

where \( C \) is the capacitance of the sample measured, \( d \) the thickness of the sample, \( A \) the cross-sectional area of the sample, \( \varepsilon_0 \) the permittivity of free space and \( \tan\delta \) (loss tangent) is the dielectric loss measured with the sample. The dielectric loss factor is given as \( \varepsilon' \tan\delta \).\(^{41}\)

The variation of real part of the dielectric constant \( \varepsilon' \) of nanophase \( \text{Ag}_3\text{PO}_4 \) (0.015M and 0.005M) with frequency of the applied electric field at room temperature is shown in fig. 6.5. It is found that for both the samples high values of dielectric constant are observed at low frequencies, which decreased rapidly with increasing frequency. It is also found that dielectric constant varies with reactant concentration and is higher for higher concentrated sample (0.015M). Among the three samples of \( \text{Ag}_3\text{PO}_4 \) studied, the particle size is maximum for higher concentrated sample. Fig. 3.1 and 3.2 of chapter 3 have shown that RLA fractal structure may also have a role in determining the dielectric constant of nanophase \( \text{Ag}_3\text{PO}_4 \).\(^{43}\) It has been reported that dielectric constant depends almost linearly on the grain sizes in the case of materials having a barrier layer at grain grain-boundary interface.\(^{44,45}\) The formation of barrier layer in the above case was confirmed by impedance analysis.\(^{45}\)
High values of dielectric constant at low frequencies are observed in many nanophase materials.\textsuperscript{10,12,33,46} The high value of dielectric constant below 1kHz frequency may be due to electrode polarisation, which is common in ionic conductors.\textsuperscript{41} Therefore the dielectric property of the ionic material is significant for frequencies greater than 1kHz. In the case of nanophase AgI,\textsuperscript{12} $\varepsilon'$ was found to be greater than that of crystalline AgI and it is explained on the basis of defect structure of nanoparticles. In the case of PbF$_2$, the high value of $\varepsilon'$ was reported at 10kHz and is attributed to the decrease in the number of polarizable ions per unit volume as a result of thermal expansion with temperature.\textsuperscript{47}

The dielectric constant of a material is controlled by four kinds of polarisation, namely electronic, ionic, rotation or orientation and space charge polarisation.\textsuperscript{41} One process common to all materials is the electronic polarisation and is the only process sufficiently rapid to follow the alternative fields and is in the range of optical frequencies (visible region). Ionic polarisation is the displacement of positive and negative ions in relation to one another and is able to follow an applied high frequency field and contribute to the dielectric
constant at frequencies up to the infrared region of the spectrum. Dipolar or orientation polarisation arises from molecules with a permanent electric dipole moment that is able to change their orientation with the influence of an applied electric field. Orientation polarisation usually occurs in glasses and crystals when two or more equivalent positions for an ion are present. When an external field is applied, the ion and the vacancy can be exchanged in positions by a simple jump of the cation to the nearest vacancy. So orientation polarisation is also known as ion jump polarisation, which is normally observed at higher temperatures. Space charge polarisation or interfacial polarisation is caused by the mobile charges which are present at interfaces. These mobile charges are impeded by interfaces, because they are not supplied or discharged at an electrode, or because they are trapped in the material. Space charges resulting from these phenomena appear as an increase in capacitance as far as the exterior circuit is concerned. Orientation and space charge polarisation have relaxation times corresponding to the particular material and process but, in general, participate only at lower frequencies.

The observed high values of dielectric constant in nanophase $\text{Ag}_3\text{PO}_4$ at room temperature can be attributed to space charge polarisation based on the polarisation effects explained above. Nanoparticles contain a large number of defects such as dangling bonds, vacancies and micropores at the grain boundaries causing a change of positive and negative space charge distribution in interfaces. When an external electric field is applied, the space charge moves under this field and they are trapped by the defects in interfaces forming lots of dipole moments (space charge polarisation). Therefore space charge polarisation is the main factor that gives a high value of dielectric constant for nanophase $\text{Ag}_3\text{PO}_4$. The polarisation is maximum for DLA clusters ($0.015\text{M} \text{Ag}_3\text{PO}_4$) showing high value of dielectric constant.

Fig. 6.6 shows the variation of $\varepsilon'$ with temperature for $0.01\text{M} \text{Ag}_3\text{PO}_4$ at different frequencies. The same pattern is obtained for other two
concentrations of the sample, with the value of the dielectric constant minimum for 0.005M, which is having smallest particle size. The effect of temperature on electronic and ionic polarisation is small while there is a considerable contribution due to ion jump orientation polarization to the dielectric constant.

![Graph](image)

**Fig. 6.6:** Variation of $\varepsilon'$ with temperature for 0.01M Ag$_3$PO$_4$

The dielectric loss or loss tangent of a material can be written as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{4\pi\sigma}{\varepsilon'\omega} \tag{6.3}$$

or $$\varepsilon' = \frac{4\pi\sigma}{\omega \tan\delta} \tag{6.4}$$

At higher temperatures, the d.c. conductivity will increase exponentially with temperature as $$\sigma = \sigma_0 \exp (-E/k_B T) \tag{6.5}$$

At sufficient high temperatures, the loss tangent ($\tan\delta$) becomes overpowered by the conductivity $\sigma$ of the sample giving an increased value of
\( \varepsilon' \) at high temperatures. Thus at higher temperatures, the combined effect of ion jump polarisation and the d.c. conductivity effects at low frequencies contribute towards dielectric constant and give a sharp rise in \( \varepsilon' \) value.

From fig. 6.6 it is observed that as temperature increases \( \varepsilon' \) increases and at low frequencies there is a peak in the plot indicating ion jump orientation effects and d.c. conductivity effects.\(^{41}\) At higher frequencies this peak disappears. It is reported that the higher the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects.\(^{48}\) Since the grain boundary of nanoparticles contain a large density of defects, it is expected that the dielectric constant of nanoparticles will be much more higher than that of bulk crystals. At higher temperatures and at lower frequencies mobile ions can make random hopping from site to site in the case of ionic conductors.\(^{49}\) In the case of nanophase materials, the high density of trap sites will increase hopping motion and thereby increased d.c. conductivity. Thus ion jump orientation effects and space charge effects resulting from the increased concentration of charge carriers contribute to \( \varepsilon' \) at low frequencies and at higher temperatures. The defect concentration increases with temperature and at a particular high temperature, the charges get depleted resulting in a peak\(^{37}\) as in fig. 6.6. This may be due to the fact that the charges can get over the potential barrier set up by the regions of charge accumulation with increase in temperature.\(^{37}\) It can be noted that there is a shift in the peak positions with higher frequencies as temperature increases, which are characteristic of ionic conductors.\(^{37}\) It is reported that the characteristic of space charge polarisation and rotation direction polarisation is the appearance of peak in the \( \varepsilon' \) vs T graph.\(^{37}\) \( \varepsilon' \) was found to decrease with frequency because a point will be reached when space charge cannot sustain with the field and polarization decreases resulting in a small value of \( \varepsilon' \).
Fig. 6.7 shows the variation of $\varepsilon'$ with temperature for different reactant concentrations of $\text{Ag}_3\text{P}0_4$ at 10kHz frequency. This figure also shows that $\varepsilon'$ depends on reactant concentration and hence on particle size.

![Graph showing variation of $\varepsilon'$ with temperature for different reactant concentrations of $\text{Ag}_3\text{P}0_4$ at 10kHz frequency.]

The high value of $\varepsilon'$ in nanophase $\text{Ag}_3\text{P}0_4$ is attributed to space charge polarisation, rotation direction polarisation and ion jump polarisation due to hopping of mobile charge carriers. It is found that $\varepsilon'$ increases with increase in reactant concentration and hence with particle size.

6.3.2.2 Dielectric loss

The dielectric loss is ‘$\tan\delta$’ as given by equation 6.2 of this chapter. The phase shift ‘$\delta$’ corresponding to a time lag between an applied voltage and induced current causes loss currents and energy dissipation in a.c. circuits which do not require charge carrier migration. For practical applications of dielectric materials low loss dielectrics are needed. Before discussing dielectric loss, one more term called ‘dielectric relaxation’ has to be considered. The self adjustment of a thermodynamic system with time...
towards a new equilibrium state by the influence of electric field is called dielectric relaxation. Energy losses in dielectrics result from three primary losses, (a) ion migration losses constituted of d.c. conductivity losses, ion jump and dipole relaxation losses (b) ion vibration and deformation losses (c) electron polarization losses. Of these, electron polarization losses are attributed to optical region and ion vibration and deformation losses to IR region. In general ion jump relaxation between two equivalent ion positions is responsible for the largest part of the dielectric loss for crystals and glasses in moderate frequencies.

Fig. 6.8 shows the variation of loss tangent with frequency. Two peaks are observed. For 0.015M $\text{Ag}_3\text{PO}_4$, the peaks are around 10kHz and 1MHz and shifts to low frequencies when the reactant concentration is changed to 0.005M having smaller particle size. The peaks arise due to relaxation time for charge transport which cause energy loss and is maximum at these two peak frequencies. The peak around 10kHz may be due to relaxation in space charge polarization and the peak at 1MHz is due to ion jump and dipole relaxation losses. In the case of nanophase $\text{Ag}_3\text{PO}_4$ sample, the mobile $\text{Ag}^+$ ions may be responsible for re-orientational and translational hopping motions based on jump relaxation model. If the relaxation time for an ion jump is $\tau$, maximum energy loss occurs for a frequency equal to the jump frequency $1/\tau$. Therefore the ion jump frequency corresponding to the frequency of a.c. applied field is about $10^6$Hz (fig. 6.8). It is reported that the region of $10^4$-$10^6$Hz is important for dielectric applications. Nanophase $\text{Ag}_3\text{PO}_4$ is found to be a dielectric relaxor material from the above discussions.
Fig. 6.8: Variation of loss tangent with logarithm of frequency for $\text{Ag}_3\text{PO}_4$

Fig. 6.9 and 6.10 show the variation of loss tangent with temperature and are found to be identical with fig. 6.6 and 6.7. Variation of $\varepsilon'$ with temperature is given by fig. 6.6 and 6.7. 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. Fig. 6.9 shows tangent loss peaks at lower frequencies and at higher temperatures similar to $\varepsilon'$ vs T graphs and same explanations are valid here also. From fig. 6.10 it was observed that loss tangent is minimum for 0.005M sample having smallest particle size and energy loss depends on particle size in the case of $\text{Ag}_3\text{PO}_4$ nanoparticles.
Fig. 6.9: Variation of loss tangent with temperature of 0.01M Ag₃PO₄ for different frequencies

Fig. 6.10: Variation of loss tangent with temperature for different molarity samples of Ag₃PO₄
In the case of Ni-Zn ferrites\textsuperscript{50} the abnormal dielectric behaviour for $\tan \delta$ curves where dielectric relaxation processes (peaks) were observed at higher temperature. The peaks were found to be shifted to higher frequency as the temperature increases just like nanophase $\text{Ag}_3\text{PO}_4$. The same behaviour of $\tan \delta$ with frequency was observed in Ni-Mg\textsuperscript{51}, Li-Ni\textsuperscript{52}, Mg-Al\textsuperscript{53}, Co-Zn\textsuperscript{54} and Li-Zn\textsuperscript{55} ferrites. The dielectric behaviour in ferrites was related mainly to the collective contribution of both types of electric charge carriers, electrons and holes to dielectric polarization.

6.3.2.3 AC Conductivity

The study of the frequency and temperature dependence of a.c. conductivity in ionic crystals and glasses has been reported by many authors.\textsuperscript{27,28,51-53} The temperature dependence of the a.c. conductivity points to the existence of various relaxational contributions characterised by different activation energies. There are some reports about the ionic conductivity studies of silver phosphate glasses\textsuperscript{27-29,54} and the a.c. conductivity was attributed to the hopping motion of $\text{Ag}^+$ ions between neighbouring sites. In silver halides conduction is mainly caused by $\text{Ag}^+$ ions upto very high temperatures and is taking place through Frenkel defects.\textsuperscript{10,55} A.C. conductivity depends on frequency and temperature. In the present study a.c. conductivity of the samples was calculated using the equation:

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta$$

where $f$ is the frequency of the applied ac field, $\varepsilon_0$ the permittivity of free space, $\tan \delta$ the dielectric loss and $\varepsilon'$ is the real part of the measured complex dielectric constant. The temperature dependence of a.c. conductivity is given by the equation.\textsuperscript{54,55}

$$\sigma = \sigma_0 \exp(-Ea/K_b T)$$
where \( \sigma_0 \) is a constant, \( T \) the absolute temperature in Kelvin, \( K_b \) the Boltzmann constant and \( E_a \) is the energy required for the formation and drift of the cations (Ag\(^+\)) called activation energy.

Fig 6.11 shows the variation of a.c. conductivity with frequency at room temperature for 0.005M and 0.015M Ag\(_3\)PO\(_4\) samples. The a.c. conductivity of the samples of Ag\(_3\)PO\(_4\) was found to be strongly dependent on the frequency of the applied field. It has been reported that a dispersion in the conductivity is a direct evidence for the hopping motions of charge carriers in neighbouring lattice imperfections.\(^{10,29,56}\) Dispersion in conductivity usually takes place when the carriers are not free to move throughout the sample. At low frequencies, conductivity is found to be very small and around 10kHz there is a very small flat peak supporting space charge polarisation and around 1MHz there is a prominent peak supporting hopping motions of mobile Ag\(^+\) ions and dielectric relaxation process as explained in the above two sections. From fig. 6.11, it is observed that conductivity is higher for larger particle (0.015M reactant concentration Ag\(_3\)PO\(_4\)). Impedance spectroscopic study at room temperature also proved that conductivity is mainly through grains and is maximum for 0.015M sample.

Fig. 6.11: Variation of a.c. conductivity with frequency for nanophase Ag\(_3\)PO\(_4\)
Temperature dependence of a.c. conductivity of nanophase Ag$_3$PO$_4$ for three reactant concentrations at 10kHz and 10MHz frequency is shown in fig 6.12 (Arrhenius plot). The temperature variation of a.c. conductivity $\sigma$ can be written as\textsuperscript{54} $\sigma T = \sigma_0 \exp(-E_a/K_b T)$, where $E_a = $ a.c. activation energy, $\sigma_0 =$ the pre-exponential factor. Experimental data was compared with straight line fit and the values of pre-exponential factor $\sigma_0$ and activation energy $E_a$ calculated from the slope of the straight line are given in table 6.2. The molecular environments in which the molecular motion take place and the number of charge carriers cause the pre-exponential factor.\textsuperscript{54} This factor is important in nanoparticles which is a defect structure and the conductivity depends on this factor too.\textsuperscript{14,54,57} From table 6.2, it can be found that activation energy depends on pre-exponential factor.

![Fig. 6.12: Arrhenius plot for the a.c. conductivity](image-url)
Table 6.2: Variation of activation energy and pre-exponential factor with reactant concentration

<table>
<thead>
<tr>
<th>Reactant concentration (M)</th>
<th>Frequency 1 MHz</th>
<th>Frequency 10 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation energy (eV)</td>
<td>Pre-exponential factor (ohm⁻¹m⁻¹K)</td>
</tr>
<tr>
<td>0.015</td>
<td>0.0842</td>
<td>2.568</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0886</td>
<td>2.587</td>
</tr>
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<td>0.005</td>
<td>0.0992</td>
<td>2.783</td>
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</tbody>
</table>

Space charge effects play an important role in controlling the electrical properties of very small crystals since the grain boundaries contain a large number of defects compared to its bulk materials. From fig. 6.12 we can observe that a.c. conductivity is frequency dependent as well as temperature dependent. Also for a given frequency, conductivity is found to be minimum for low molarity sample (0.005M). The conductivity minimum for lower concentration sample may be due to smaller size of the grains compared to other two samples. It is reported that conductivity is minimum in smaller grains due to the confined passage of the conducting species within the grains due to its smallness.15 Arrhenius plot shows that the slope change observed at higher temperature (172°C) may be attributed to the sudden release of space charges, which get accumulated at the grain boundaries.37,58,59 In this region, there is a decrease in activation energy, where space charge polarisation effect is dominant and d.c. conductivity effect starts.58,59 There are different reports attributing different causes to the change of activation energy, such as trapping of oxygen vacancies, defect interactions, formation of vacancy clusters, space charge layers etc. at lower temperatures.15 In the case of 0.015M sample having large particle size, there is no decrease in activation energy at higher temperature. But for 0.01M and 0.005M samples there is slight decrease in
activation energy at higher temperature. This may be due to the dissociation of the vacancy clusters and defects (space charge polarisation) and this polarisation effect is found to be small in larger particles (0.015M). From table 6.2, we can observe that $E_a$ and $\sigma_0$ change with frequency and is slightly lower in high frequency samples compared with low frequency. Since nanophase Ag$_3$PO$_4$ is a frequency dependent dielectric material, activation energy and pre-exponential factor may slightly vary with frequency. Reactant concentration also affects the value of $E_a$ and $\sigma_0$ which may depend on the particle size.

6.4 Conclusion

Using impedance spectroscopy, grain, grain boundary and electrode contributions to electrical conductivity were separated out in the case of nanophase Ag$_3$PO$_4$. The dielectric anomaly observed in the case of nanophase Ag$_3$PO$_4$ at high temperatures and low frequencies is due to space charge polarisation, orientation polarisation and ion jump polarisation effects. Grain boundary plays a prominent role in the dielectric behaviour of nanophase Ag$_3$PO$_4$. The reactant concentration, which plays a role in determining the grain size, has a considerable role in the electrical properties of nanophase Ag$_3$PO$_4$.

6.5 References

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