Chapter 5
ELECTRICAL PROPERTIES OF NANOCRYSTALLINE AIPO₄

5.1. Introduction

The enhanced electrical properties of nanocrystalline materials exhibiting unusual properties play a vital role in the development of new materials.¹-⁴ The electronic, optical, catalytic and electrical properties of nanostructured materials are many times superior to their bulk form and depend strongly on size, shape, composition and preparation conditions.⁵ The large surface to volume ratio and the variations in electronic structure have dramatic effects on transport and catalytic properties. The major portion of atoms located at surfaces or interfaces greatly influence the transport of ions and electrons through solids. In addition short-range rearrangement or redistribution of ions and electrons may cause electrical or chemical polarization. This effect is more dominant in nanophase dielectric materials. Each interface will polarize in its unique way when the system is subjected to an applied electric field.⁶ Studies on the effect of temperature and frequency on the dielectric behavior and a.c. electrical conductivity offer valuable information about the conduction phenomenon in nanostructured materials.⁷ Dielectric behavior can effectively be used to study the electrical properties of grain boundaries, since majority of atoms of nanomaterials reside at grain boundaries.⁸,⁹ Impedance spectroscopic studies give valuable information about the grain and grain boundary characteristics of nanophase materials. The origin of resistance or capacitance, its dispersion with small signal frequencies and the role of defects be obtained from these studies.¹⁰

In determining the electrical properties of nanocrystalline materials, the grain boundaries and grain interfaces play important roles.¹¹-¹³ Grain boundaries of nanophase materials are in a disordered state with large defect densities, which can act as traps for charge carriers from adjoining grains.¹⁴-¹⁷ The dielectric properties of materials are mainly due to contributions from electronic, ionic, dipolar and space charge polarizations.⁶,¹⁸ Among these, the most important contribution for
polycrystalline materials in bulk form is the electronic polarization, present in the optical range of frequencies. The next contribution is from ionic polarization, which arises due to the relative displacement of positive and negative ions. Dipolar or orientation polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied. Space charge polarization or interfacial polarization arises from accumulation of charge carriers at structural interfaces. These mobile charges are impeded by interfaces, since they are trapped in the material and are not supplied or discharged at an electrode. Space charges resulting from these phenomena appear as an increase in capacitance as far as the exterior circuit is concerned.

For the electrical characterization of materials including solid electrolytes, ceramics and nanocrystals, impedance spectroscopy is accepted as an important tool. Impedance spectra usually include features that are directly related to the grain boundary structure of particles. The impedance spectroscopic analysis of nanophase ZnO has been reported and the spectrum was interpreted on the basis of resistive grain boundaries and conductive grain cores. Puin and Heitjans studied the frequency dependent ionic conductivity of nanocrystalline CaF₂ through impedance spectroscopy. Electrical properties of nano-CeO₂ have also been reported through impedance spectroscopy.

In this chapter, the variation of dielectric constant, dielectric loss and a.c. electrical conductivity of n- AlPO₄ samples of different grain sizes are studied as a function of sample temperature and frequency of the applied electric field. The enhancement of the dielectric properties due to nanocrystallization and with reduction in grain size of the sample are analyzed in terms of existing theories and references of previous works in this field. The impedance spectroscopic analysis of the sample is carried out and the grain boundary parameters of the sample are deduced.

5.2. Experimental

Nano-sized aluminium phosphate (AlPO₄) in three different grain sizes was prepared from the thermolysis of new polymer matrix based precursor solutions.
The resulting powders are nano-sized, and are of high purity. Details of the preparation\textsuperscript{28} are given in the synthesis part of section 2.2. In the present study, stoichiometric amounts of the reactants were taken such that the concentration of the reactants were 1.0 mol L\textsuperscript{-1}, 0.5 mol L\textsuperscript{-1} and 0.1 mol L\textsuperscript{-1} to produce nanosized AlPO\textsubscript{4} samples of average grain sizes 16.34 nm, 13.59 nm and 12.04 nm respectively, (samples A1, A2 & A3). In order to determine the crystal structure of nanocrystalline AlPO\textsubscript{4}, the calculated \textit{d} values are compared with the standard ICDD-PDF data of cubic AlPO\textsubscript{4}. All the samples are found to be of cubic structure. The nanoparticles were consolidated into pellets of diameter 13 mm and thickness 1-2 mm by applying a pressure of about 0.4 GPa. Both faces of the pellets were coated with colloidal silver. Conducting leads were attached to both faces of the pellets and the samples were then 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°C. The capacitance ($C_p$), the modulus of complex impedance ($|Z|$) and phase angle ($\theta$) of the samples were measured using a Hewlett-Packard 4192A impedance analyzer over the frequency range 100 Hz - 3 MHz and over the temperature range 300K to 373K.

5.3. Results and Discussion

5.3(i) Dielectric constant

The real and imaginary parts of the dielectric constant $\varepsilon'$ and $\varepsilon''$ of the given samples were calculated from the measured values of capacitance $C_p$ and dielectric loss using the formulae

$$\varepsilon' = C_p \frac{d}{\varepsilon_0 A}$$  \hspace{1cm} (5.1)

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} (5.2)

where $d$ is the thickness, $A$ is the cross sectional area of the given sample, $\varepsilon_0$ is the permittivity of free space and $\tan \delta$ is dielectric loss factor.

The variation of dielectric constant for nano AlPO\textsubscript{4} samples of different grain sizes with frequency of the applied field is presented in Fig.5.1 - Fig.5.3. The
dielectric constants of all the samples are high at low frequencies that decrease rapidly with the applied frequency at all temperatures. The dielectric constant of sample A3 at 323 K decreases from a value of 273 at 100 Hz to 8 at 3 MHz. For samples A2 and A1, the corresponding variations are from 192 to 8 and from 110 to 5 respectively. The variation of dielectric constant with grain size of nano-AlPO_4 is shown in Fig.5.4. It can be seen that the dielectric constant ($\varepsilon'$) at 323 K and at 100 Hz decreases from 273 to 108 when the particle size increases from 12 nm to 16 nm. Similar variations are observed for higher frequencies, but at very high frequencies no variation of $\varepsilon'$ with grain size is observed.

The variations of dielectric constant with temperature for nano-AlPO_4 of different grain sizes are shown in Fig.5.5 to Fig.5.7. It is seen that the dielectric constant at 300 K is very small which suddenly increases and attains the maximum

![Graph](image)

Fig. 5.1. Variation of dielectric constant of n-AlPO_4 sample A3 with frequency
Fig. 5.2. Variation of dielectric constant of n-AlPO₄ sample A2 with frequency

Fig. 5.3. Variation of dielectric constant of n-AlPO₄ sample A1 with frequency
Fig. 5.4. Variation of dielectric constant ($\epsilon'$) with grain size of nano-AlPO$_4$ at 323K.

Fig. 5.5. Variation of dielectric constant ($\epsilon'$) with temperature of sample A3.
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Fig. 5.6. Variation of dielectric constant ($\varepsilon'$) with temperature of sample A2

Fig. 5.7. Variation of dielectric constant ($\varepsilon'$) with temperature of sample A1
value at 323 K and then decreases as temperature increases. This effect is more prominent at low frequencies as shown in the figures. For high frequencies the dielectric constants of all the samples are much lower and does not vary appreciably with temperature. The maximum value of the dielectric constant of AlPO₄ sample A3 decreased from 120 at 1 KHz to 8 at 3 MHz. In the case of sample A2, the corresponding variation is from 65 to 8 and for sample A1, it is from 47 to 5 respectively.

Valuable information about various aspects has been brought out from the measurement of dielectric properties of nanostructured materials. Large dielectric constant at low frequencies were reported for different materials by many authors. Biju and Khadar studied the dielectric relaxation mechanism by considering nanostructured NiO as a carrier dominated dielectric with high density of hopping charge carriers. Cochrane and Fletcher studied the ionic conductivity in silver iodide and reported a very high dielectric constant at the low frequency region. Ponpandian and Narayanasamy studied the electrical conductivity and dielectric properties of nanocrystalline ZnFe₂O₃ of various grain sizes through impedance analysis. Their results clearly indicate the presence of dielectric relaxation in these materials. Joshy and Abdul Khadar investigated the grain boundary properties of nano-ZnO and ZnO-Al₂O₃ nanocomposites. They reported the conductivity due to grain boundaries is higher than that due to grains. This is attributed to the trapping of electrons by traps present in grain boundaries. Abdulla and Yusuf studied the frequency dependence of dielectric constants of some Mg-Zn ferrites and they observed very large value of ε' at low frequencies. The dielectric properties of nanophase Ag₂HgI₄ and Ag₂HgI₄-Al₂O₃ nanocomposites were investigated by Sankara Narayanan Potty and Abdul Khadar and the observed changes in the dielectric properties were attributed to the grain boundary properties of nanophase materials. The enhanced electrical conductivity of nanophase AgI and changes in the dielectric properties of nanophase ZnS, BaTiO₃ and CdS in comparison with their bulk have also been reported.

A large volume percentage of nanocrystalline materials consist of grain or interface boundaries. These boundaries contain defects such as dangling bonds,
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vacancies, vacancy clusters etc. These defects can cause a positive or negative space charge distribution at interfaces. The space charges can move on the application of an external electric field and when they are trapped by the defects, lot of dipole moments are formed. This is space charge polarization. Hence the space charge effect will be a prominent factor, which decides the dielectric properties in materials with small particle sizes. 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. When an electric field is applied, the ion and vacancy can exchange positions by a simple jump of the cation to a neighboring position. The charge displacement occurs by an atom jump rather than movement about an equilibrium position. Space charges resulting from these phenomena appear as an increase in capacitance, which leads to an increase in the dielectric constant, as far as the exterior circuit is concerned. Thus the high values of the dielectric constant in the present 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. The large d.c. conductivity observed in fast ion conductors is interpreted as due to random hopping of mobile ions from site to site. In nanocrystalline materials, increased d.c. conductivity can be expected due to hopping by the presence of high density of trap sites. Also, at low frequencies the dielectric loss is inversely proportional to frequency, which indicates large d.c. conductivity. As frequency increases beyond a particular limit, the space charges cannot sustain with the field and hence the polarization decreases, leading to a decrease in the value of ε'.

Most of the atoms in nanocrystalline materials reside in grain boundaries, which become electrically active as a result of charge trapping. The dipole moment can easily follow the changes in electric field, especially at low frequencies. Hence the contributions to dielectric constant increases through space charge polarization and rotation direction polarization, which occur mainly in interfaces. Thus the dielectric constant of nanostructured materials, should be larger than that of conventional materials. An assembly of space charge carriers in a dielectric requires enough time to line up their axes parallel to an alternating
electric field. At low frequencies, the dielectric will get the time for this. But if the frequency of the field reversal increases beyond a certain limit, the space charge carriers cannot keep up with the field and their directions lag behind the field, resulting a lowering of dielectric constant of the material.\(^{45}\) As the frequency of the alternating field continuously increases, at some stage the space charge carriers will have started to move before the field reversal, leading to a rather frequency independent dielectric constant. The observation that \(\varepsilon'\) decreases sharply with frequency and remains almost a constant at very high frequencies, should be attributed to the increased inertia\(^{46}\) of the dipoles, as described above.

The dielectric constant of nano-\(\text{AlPO}_4\) initially increases sharply with temperature to a sufficiently high value and thereafter decreases with temperature. At sufficiently high temperatures, d.c. conductivity increases exponentially as,

\[
\sigma = \sigma_0 \exp (-E/kT) \quad (5.3)
\]

The d.c. conductivity effects enhance the value of the dielectric constant.\(^{6}\) Also, at sufficiently high temperature; the dielectric loss is dominated by the conductivity of the sample resulting an increase in dielectric constant.\(^{47}\) The increased space charge polarization and conductivity effects at the beginning of the rise in temperature is the reason for the sharp increase of the dielectric constant at low frequencies. As temperature increases, the space charge and ion jump polarization are lagging behind the applied field, resulting a decrease in dielectric constant.

5.3(ii) **Dielectric Loss**

In dielectric materials, usually dielectric losses occur due to absorption current. The orientation of molecules along the direction of the applied electric field in polar dielectrics, requires a part of electric energy to overcome the forces of internal friction. Another part of electric energy is utilized for rotations of dipolar molecules and other kinds of molecular transfer from one position to another, which also involve energy losses.

The dielectric loss of a material is given as\(^{47}\)

\[
\tan \delta = \varepsilon'' / \varepsilon' = 4 \pi \sigma / \varepsilon' \omega \quad (5.4)
\]

where \(\sigma\) is the conductivity and \(\omega\) is the frequency.
The variations of dielectric loss factor \( \tan \delta \) of nano-AlPO\(_4\) samples of different grain size with frequency are shown in Fig.5.8 - Fig.5.10. It can be seen that \( \tan \delta \) decreases with increase of frequency and at higher frequencies the loss angle has almost the same value at all temperatures. For nano-AlPO\(_4\) sample A3, the dielectric loss at 323 K is 16 at 100 Hz, which decreases to 0.6 at 3 MHz. The corresponding variations for samples A2 is from 13 to 0.4 and for A1, from 10 to 0.1 respectively. The same behaviour is observed with lower values for all other temperatures except room temperature, where \( \tan \delta \) do not change with frequency.

The variations of \( \tan \delta \) for different temperatures are shown in Fig.5.11 - Fig.5.13. For all samples in the present study, \( \tan \delta \) initially increases with temperature, attains a maximum value and thereafter decreases at a slower rate. For sample A3, the value of dielectric loss at 1 KHz increases from 0.3 at 300 K to 12 at 323 K and then decreases to 0.8 at 373 K. The corresponding variations for sample A2 is from 0.3 to 10, which decreases to 0.1. For sample A1, it is from 0.1 to 8 and

![Fig.5.8. Variation of dielectric loss (\( \tan \delta \)) of n-AlPO\(_4\) sample A3 with frequency](image)
Fig. 5.9. Variation of dielectric loss ($\tan \delta$) of $n$-AlPO$_4$ sample A2 with frequency.

Fig. 5.10. Variation of dielectric loss ($\tan \delta$) of $n$-AlPO$_4$ sample A1 with frequency.
Fig. 5.11. Variation of dielectric loss ($\tan\delta$) of AlPO$_4$ sample A3 with temperature.

Fig. 5.12. Variation of dielectric loss ($\tan\delta$) of AlPO$_4$ sample A2 with temperature.
then to 0.1 respectively. The nature of variations are similar, but with reduced values for all other higher frequencies as shown in the figures.

Absorption current in nonpolar dielectrics can be attributed to the inhomogeneity in the electrical properties of dielectrics. The formation of space charges under the action of an external electric field will initiate the redistribution of charges within the volume of the dielectric. Inhomogeneity is inevitable in a technical ceramic material. Dielectrics always have, to some extent, impurities, pores filled with air, inclusions of hygroscopic water, etc. As a result, properties of the material may vary in different parts of the volume.

In nanophase materials, the grain boundaries have an amorphous or glassy structure. All the inhomogenities, defects, space charge formation etc. together produces an absorption current, which results in dielectric losses. Due to the presence of dangling bonds at the surface, the surface layers of nanoparticles will be highly reactive and there is a chance of adsorption of gases like oxygen or nitrogen. These adsorbed gases can also cause an increase in dielectric loss. Thus a nanophase ceramic acts as a lossy dielectric with high dielectric loss at low

![Figure 5.13: Variation of dielectric loss (tanδ) of AlPO₄ sample A1 with temperature](image-url)
frequencies, which decreases at higher frequencies. In nanophase materials, inhomogeneities like defects and space charge formation in the interface layers produce an absorption current resulting in a dielectric loss. Also, enhancement in d.c. conductivity will give rise to dielectric losses.\textsuperscript{18} The absences of peaks in the frequency versus dielectric loss curves of the present samples show the wide distribution of relaxation times.\textsuperscript{6}

5.3(iii) A.C. conductivity

The a.c. electrical conductivity of the samples can be calculated using the equation

\[ \sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta \]  \hspace{1cm} (5.5)

where \( f \) is the frequency, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon' \) is the real part of the measured complex dielectric constant and \( \tan \delta \) is the dielectric loss factor.

The frequency dependence of a.c. electrical conductivities (\( \sigma_{ac} \)) of nano-AlPO\textsubscript{4} samples with different grain sizes are shown in Fig.5.14- Fig.5.16. It can be seen that \( \sigma_{ac} \) increases with frequency for all samples. For nano-AlPO\textsubscript{4} sample A3, \( \sigma_{ac} \) at 323 K and at 100 Hz is \( 0.2 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1}, which increases to \( 37 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} at 3 MHz. For sample A2, at 323 K, the value varies from \( 0.1 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} to \( 23 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} when the frequency increases from 100 Hz to 3 MHz. For sample A1, the corresponding variation is from \( 0.2 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} to \( 18 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} as the frequency varies from 100 Hz to 3 MHz. The nature of frequency dependence of \( \sigma_{ac} \) is the same for all samples at all temperatures. The values of \( \sigma_{ac} \) at higher frequencies reduce as temperature increases.

The variation of \( \sigma_{ac} \) with temperature for different fixed frequencies of all the three nano samples of AlPO\textsubscript{4} are shown in Fig.5.17-Fig.5.19. The value of \( \sigma_{ac} \) at room temperature (300 K) rises to a peak value at about 323 K and then decreases slowly for all samples. For sample A3, \( \sigma_{ac} \) at 3 MHz increases from \( 12 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} at 300 K to \( 37 \times 10^{-5} \) ohm\textsuperscript{-1} cm\textsuperscript{-1} at 323 K, which decreases as temperature
Fig. 5.14. Variation of a.c. conductivity ($\sigma_{ac}$) with frequency of sample A3.

Fig. 5.15. Variation of a.c. conductivity ($\sigma_{ac}$) with frequency of sample A2.
Fig. 5.16. Variation of a.c. conductivity ($\sigma_{ac}$) with frequency of sample A1

increases and falls to $2 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 373 K. The corresponding variation for sample A2 is from $8 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 300 K to $23 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 323 K, which decreases to $9 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 373 K. For sample A1, it is from $7 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 300 K to $18 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 323 K and then to $8 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 373 K. The nature remains similar, but no much appreciable variations as frequencies are decreased.

Improved electrical conductivity has been reported for many nanophase materials. Enhanced electrical conductivity observed in nano AgI has been attributed to defect structure of nanoparticles. In nano CeO$_2$, the enhanced electrical properties are explained on the basis of interfacial defect formation. Puin and Heitjans reported frequency dependent conductivity of nano CaF$_2$ and they observed an increase of the conductivity compared to single crystalline CaF$_2$ by more than four orders of magnitude. An increased ionic conductivity was also observed for nanostructured yttria stabilized zirconia.
Fig. 5.17. Variation of a.c. conductivity ($\sigma_{ac}$) with temperature of sample A3.

Fig. 5.18. Variation of a.c. conductivity ($\sigma_{ac}$) with temperature of sample A2.
The a.c. conductivity has been attributed to losses due to bound charges. However, every material will have some free charges, and under the applied low frequency, these charges can follow the field and cause conduction current giving rise to energy losses. Hence measured a.c. conductivity $\sigma_m$ is given by

$$\sigma_m = \sigma_{dc} + \sigma_{ac}$$  \hspace{1cm} (5.6)

where $\sigma_{dc}$ is the d.c. conductivity and $\sigma_{ac}$ is the true value of the a.c. conductivity.

The enhancement of a.c. conductivity was explained by many authors on the basis of excess ion vacancies due to the high conduction of the space charge layer. The a.c. conductivities strongly depend on the particle size, the concentration and heat treatment of the sample and the premelting of the electrolytes. Also, the frequency dependent data indicated that the enhancement was due to grains rather than grain boundary or surface conduction. Many authors presented different arguments on the frequency dependence of a.c. conductivity exhibited by nanocrystalline materials in the high frequency region. They are the quantum mechanical tunneling model, and hopping barrier model. Pollak has shown that the temperature dependence of conductivity is due to multiple hopes.
The nature of frequency and temperature dependence of a.c. conductivity of the present samples, suggests an electronic hopping mechanism, exhibited by a large number of nanocrystalline materials. This hopping mechanism is compatible with the highly disordered or amorphous structure of the grain boundary layers of nanophase materials, having high densities of localized levels. The physical significance of this type of frequency dependence comes from the fact that an alternating current can affect an electron confined to two traps.61,62 The time it spends in each trap will depend on the energy difference of the two trap states. An applied a.c. field will alter this energy difference and produces a net polarization, which lags behind the field.61,62 This polarization, which is out of phase with the applied electric field, is measured as a.c. conductivity.

5.3(iv) Impedance spectroscopic analysis

The complex plane impedance analysis of a number of polycrystalline as well as nanocrystalline materials have been reported.1-5,20-24 Lee et al.1 reported the impedance spectra of nanophase ZnO (grain size 60 nm) and found only one semicircle in the impedance spectrum, which was explained as the grain boundary arc. The impedance analysis of nanophase ZnO (grain size 13 nm)5 exhibited two partially overlapping semicircles corresponding to grain and grain boundary contributions. But the impedance spectra of ZnO- Al2O3 nanocomposite5 was found to consist of only one arc, which was explained due to the fact that the conduction process through the grain cores and grain boundaries have identical time constants. Also the arcs were found to be highly depressed, which indicates a distribution of relaxation times. Chiang et al.11 reported the impedance spectroscopic analysis of nanocrystalline CeO2 and observed a low frequency arc corresponding to grains. The complex impedance spectrum of nano CaF2 was reported 2 to contain a small segment of the electrode polarization arc at low frequency and a large and depressed arc due to grain boundary at high frequency. Complex plane impedance analysis of polycrystalline BaTiO3, showed a smaller arc due to grain and a large grain boundary arc.20 The high value of impedance at grain boundary was explained
on the basis of the presence of air gaps and high electrical inhomogeneities in the
region of the neck between grains. Aoki et. al. studied the impedance of high
purity ZrO₂, stabilized with CaO, having different grain sizes. The two well-
separated semicircles found at higher frequencies were attributed to contributions
from the grain interiors and grain boundaries, and the trace of a third semicircle at
low frequencies due to the electrode interface impedance. The arc due to grains was
found to be higher than that due to grain boundaries. The impedance spectra of
polycrystalline ceria showed a small arc corresponding to grain contribution and a
large semicircle due to grain boundary contribution.

The impedance spectra of the present sample, nanocrystalline AlPO₄ of
different grain sizes at three different temperatures are shown in Fig. 5.20 -
Fig.5.22. All the plots contain depressed or distorted semicircle due to the fact that
they are made up of two partially overlapping semicircular arcs. Depressed arcs
may arise due to several relaxation times or due to a continuous distribution of
relaxation times. The two semicircles at high and low frequencies are identified as
due to grain and grain boundary phenomena respectively. Resistances due to grain
and grain boundary are given by the intercepts of the high and low frequency arcs
with the x-axis. In the present study, only the high frequency arc is prominent. The
contribution to impedance due to grain is very small compared to the grain
boundary contribution. The single arc reported in the impedance spectrum of ZnO
by Lee et al. has been interpreted as due to grain boundary contribution. The single
arc for all the samples in the present study is in agreement with this observation.
The results also reveal that the impedance of nanostructured materials depends on
both grain size and temperature of measurement. Sample A3, having grain size 12
nm (Fig.5.20), has the highest impedance. The nature of variation remains the same,
but the diameters of the semicircles gradually increase as temperature rises. Similar
variations are observed for samples A2 and A1, with higher grain sizes (13.6 nm
and 16.3 nm). In these cases, the impedance values are diminished, as shown in Fig.
5.21 and Fig.5.22.
Fig. 5.20. Impedance spectra of n-AlPO$_4$ sample A3 for different temperatures

Fig. 5.21. Impedance spectra of n-AlPO$_4$ sample A2 for different temperatures
Fig. 5.22. Impedance spectra \( n-\text{AlPO}_4 \) sample A1 for different temperatures.

Fig. 5.23. A typical impedance spectrum showing all fitting parameters.
A typical impedance spectrum showing all fitting parameters is given in Fig. 5.23. The resistance $R$ due to grain boundary is given by the intercept of the arc with the x-axis. The diameter of the arc increases as temperature increases. The contribution to the total resistance of the sample $R_{gb}$ by the grain boundary is given by the diameter of the arc, as shown in the figure. $\phi_{gb}$ is the angle of depression of the semicircle center due to the tilting of the semicircle. The mean relaxation time for the grain boundary processes, $\tau_{gb} = R_{gb} C_{gb}$, which is the inverse of the peak frequency $\omega_{gb}$ and thus the grain boundary capacitance $C_{gb}$ can be calculated. The Cole-Cole expression for the resulting complex impedance can be written as

$$Z^*(\omega_{gb}) = R_o + \frac{R - R_o}{1 + (i \omega_{gb} \tau_{gb})^{1-a_{gb}}}$$  \hspace{1cm} (5.7)$$

where $R$ and $R_o$ are respectively the intercepts with the real impedance axis at the high frequency end and low frequency end. The parameter $a_{gb}$ measures the deviation of the shape of the impedance plot from the ideal semicircular shape of the grain boundary. $a_{gb}$ is given by

$$a_{gb} = 2 \phi_{gb} / \pi$$  \hspace{1cm} (5.8)$$

The computed parameters of the various grain boundary contributions are tabulated in Table 5.1. The results show that the conductivities of each sample, due to

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>$R_{gb}$ (kΩ)</th>
<th>$\omega_{gb}$ (rad/sec)</th>
<th>$\phi_{gb}$ (deg.)</th>
<th>$C_{gb}$ (pF)</th>
<th>$\sigma_{gb}$ ($\times 10^{-5} \Omega^{-1} \text{cm}^{-1}$)</th>
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<tr>
<td>A1</td>
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<td>73</td>
<td>611</td>
<td>8</td>
<td>2.24</td>
<td>3.25</td>
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<td></td>
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<td>130</td>
<td>2680</td>
<td>10</td>
<td>2.87</td>
<td>3.67</td>
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<td></td>
<td>353 K</td>
<td>175</td>
<td>1675</td>
<td>14</td>
<td>3.41</td>
<td>3.98</td>
</tr>
<tr>
<td>A2</td>
<td>313 K</td>
<td>170</td>
<td>2108</td>
<td>28</td>
<td>2.79</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
<td>220</td>
<td>1353</td>
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<td>240</td>
<td>1050</td>
<td>15</td>
<td>3.97</td>
<td>4.87</td>
</tr>
<tr>
<td>A3</td>
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<td>180</td>
<td>1929</td>
<td>37</td>
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<td>4.41</td>
</tr>
<tr>
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<td>220</td>
<td>1103</td>
<td>34</td>
<td>4.12</td>
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</tr>
</tbody>
</table>

Table 5.1: Grain boundary parameters of nano AlPO₄ samples
grain boundaries ($\sigma_{gb}$), increase with temperature. Thus, it is confirmed that, the
presence of grain boundaries in nanocrystalline materials is responsible for the
observed variations in the conductivities nanocrystalline AlPO$_4$.

The impedance of nanocrystalline AlPO$_4$ in the present investigation was
found to arise from both grain and grain boundary contributions of which the major
component is the latter. The presence of grains and grain boundaries in nanophase
materials are very important in determining their electrical properties.$^{63,64}$ A
significant fraction of atoms in nanophase materials reside in grain boundary
environments where they occupy positions relaxed$^{65}$ from normal sites. The grain
boundary resistivity may be attributed to partial or complete blocking of charge
carriers due to the presence of defects at the grain boundaries $.^{66, 67}$ Thus the overall
impedance behavior of the three samples arises mainly from contributions due to
grain boundaries. The intergranular porosity largely alters the diameter of the grain
boundary arc in the impedance spectrum, which is a measure of the grain boundary
resistance. Since the grain boundary resistance is very large compared with grain
resistance, conductivity in the present study is attributed mainly through grains,
which is characteristic of ionic conductors. The lesser conductivity in the grain
boundaries, observed in the present study may be due to impurity phases, porosity
and the large area of grain boundary region.$^{68}$ It can be seen from the figures that
the grain conductivity (diameter of the grain boundary arc) increases as particle size
decreases.

5.4. Conclusion

The dielectric properties of nanocrystalline AlPO$_4$ having three different
grain sizes were investigated over a wide range of frequencies 100 Hz - 3 MHz and
over the temperature from 300 K to 373 K. The dielectric constants ($\varepsilon'$) of all the
samples are high at low frequencies that decrease with frequency at all
temperatures. The dielectric constant initially increases with temperature to a
sufficiently high value and thereafter decreases as temperature is further increased.
Dielectric loss ($\tan \delta$) decreases with frequency and at higher frequencies the loss
angle has the same low value at all temperatures. Also, $\tan \delta$ was found to increase
with temperature, attains a peak value and then decreases at a slower rate. The a.c.
electrical conductivity ($\sigma_{ac}$) increases with frequency for all samples. $\sigma_{ac}$ has a low value at room temperature (300 K), which suddenly rises to a peak value at 323 K and then decreases slowly for all samples. $\varepsilon'$, $\tan \delta$ and $\sigma_{ac}$ were found to depend on grain size, frequency and temperature. Grain boundary parameters of all the nano AlPO$_4$ samples are obtained through impedance spectroscopic analysis. The impedance spectra of nanocrystalline AlPO$_4$ in the present investigation show that the impedance arises from both grain and grain boundary components of which the major component is from grain boundary.

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