Electrical conduction mechanism of barium doped strontium hydroxyapatite synthesized by co – precipitation method

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Abstract. The crystalline samples of Barium (Ba) doped Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ with x = 0, 0.5 and 1 mol% were prepared by co – precipitation method. The microstructural (SEM) image shows the distribution of densely packed grains over the surface of prepared sample. The nature of cole – cole plots confirm that the conduction mechanism is governed only by the grains with no contribution of grain boundaries for all prepared samples. The resistance of grains decreases with increase in temperature and molar (mol%) concentration, which shows a negative temperature coefficient resistance (NTCR) behaviour for all prepared samples. The a.c. conductivity increases with increase in frequency which shows non – debye nature of the prepared samples.

1. Introduction

Hydroxyapatite compounds have attracted the interest of researchers due to their large band gap, semiconducting properties, electrical conduction mechanism, high optical strength and high luminescence efficiency [1]. The general formula of hydroxyapatite is X$_{10}$(YO)$_6$(OH)$_2$ where X can be substituted by any divalent and trivalent cation and Y can be substituted by halogen atom [2]. It has a flexible structure due to which different ions can be easily incorporated into the lattice.

Strontium bearing apatites are considered well known hosts with various applications in optical and electronic devices [3]. It has application in biological field as it can be incorporated in human bones [4]. It also has suitable application as nuclear waste storage materials [5]. Many investigations on bone grafting, dental implants is done through electrical conduction phenomena in hydroxyapatite. The electrical conduction analysis is done through complex impedance spectroscopy [6], which is a potential tool to get information regarding the electrical and relaxation behaviour of compounds. In addition, it also gives information regarding the grain and grain boundary effect, real and imaginary part of impedance, resistive and capacitive elements in the compounds [7].

The present paper reports the microstructural, dielectric, impedance and a.c conductivity studies of Ba doped Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$compound. The a.c impedance studies reveal that the prepared compound obeys Jonscher’s power law and appears non – debye in nature.
2. Experimental method

All the starting materials Sr(NO$_3$)$_2$.4H$_2$O, Ba(NO$_3$)$_2$.4H$_2$O and (NH$_4$)$_2$H(PO$_4$) supplied by Sigma Aldrich were taken in stoichiometric amount. The materials were dissolved in 50 ml of distilled water and kept on a heater attached magnetic stirrer with 500 rpm for 1 hour. In between NH$_2$OH was added dropwise to set the PH at 10. After 1 hour of vigorous stirring the solution was filtered. The filtered precipitant was dried in an oven at 80°C for 3 hours. The dried precipitant was ground in agate mortar and pestle for 1 hour and placed in programming furnace at 900°C for 4 hours. The calcined powders were pressed with 200 MPa pressure to form pellets. The pellets were sintered at 900°C for 1 hour as shown in figure 1.

3. Results and discussions

3.1. Morphological and Structural Analysis

The scanning electron microscopy images of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ (x = 0.5 mol%) are shown in figure 2(a) and 2(b) respectively. The SEM images show the formation of clusters of highly densified and agglomerated spheroidal grains with varying grain size which may be due to sintering of samples at high temperature (1200°C). The powder diffraction X-ray analysis of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound confirms the formation of single phase hexagonal structure with space group P63/m [8].

![Figure 1. Flow chart for synthesis of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound.](image)

![Figure 2. SEM images of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ (x = 0.5 mol%) compound (a) 6.16 KX (b) 4.33 KX.](image)
3.2. Dielectric studies
Dielectric studies were performed in the frequency range of 1000 Hz to 100000 Hz and temperature varying from 30°C to 200°C with 5°C sweep mode. The change in value of dielectric constant (ε) with applied frequency is given in figure 3. It has been noticed that ε decreases with increase in frequency which shows the ceasing effect of polarization for higher frequency [9]. At low frequency region the dipoles are oriented in the applied electric field direction, as the frequency rises the dipoles lag to oscillate in the track of applied electric field and dielectric constant decreases.

![Dielectric constant plots for different x values](image1)

**Figure 3.** Dielectric constant plots of Sr\(_{10-x}\)Ba\(_x\)(PO\(_4\))\(_6\)(OH)\(_2\) compound for different x values (a) 0 mol% (b) 0.5 mol% (c) 1 mol%.

Figure 4 shows the variation of dielectric constant with varying temperature. At low temperature the dipoles do not orient in the direction of applied field hence, dielectric constant shows a constant value. As the temperature increases the dipoles get sufficient energy to orient themselves in the direction of applied field and hence the dielectric constant increases [10].
Figure 4. Temperature dependent dielectric constant plots of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound for different x values (a) 0 mol% (b) 0.5 mol% (c) 1 mol%.

The change in the value of dielectric loss (tan$\delta$) with applied frequency is shown in figure 5. The dielectric loss value up surges with rise in temperature and as the doping concentration increases tan$\delta$ value decreases in the high frequency side [11]. It shows the hopping mechanism of charge carriers in the Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound. For x = 0 mol% and x = 0.5 mol% the dielectric loss increases with increase in frequency due to hopping of charge carriers in the direction of applied electric field. With further increase in dopant concentration to x = 1 mol% the hopping of charge carriers lag behind the frequency of applied electric field as a result dielectric loss decreases with increase in frequency [12].
Figure 5. Dielectric loss plots of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound for different x values (a) 0 mol% (b) 0.5 mol% (c) 1 mol%.

3.3 Cole – Cole Plots
The cole – cole plots for Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ is shown in figure 6. It can be seen that with rise in temperature the semi-circular arc decreases and bends towards real part of impedance (Z') which shows increase in a.c conductivity of the samples [13].

Figure 6. Cole – Cole plots of Sr$_{10-x}$Ba$_x$(PO$_4$)$_6$(OH)$_2$ compound for different x values (a) 0 mol% (b) 0.5 mol% (c) 1 mol%.
3.4 A.C Conductivity Analysis

Figure 7 shows the frequency dependent conductivity study at different temperatures for Sr\textsubscript{10-x}Ba\textsubscript{x}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} compound. It is observed that at low frequency a plateau region is observed corresponding to d.c conductivity [14]. As the frequency increases the conductivity increases which shows that the compound obeys Jonscher’s power law.

![Figure 7. A.C conductivity plots of Sr\textsubscript{10-x}Ba\textsubscript{x}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} compound for different x values (a) 0 mol\% (b) 0.5 mol\% (c) 1 mol\%.](image)

4. Conclusion

The Ba doped Sr\textsubscript{10-x}Ba\textsubscript{x}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} with x = 0 - 1 mol\% synthesized by co – precipitation technique. SEM images show the distribution of high densified grains over the surface of samples. The dielectric constant decreases with increase in frequency which shows the ceasing effect of polarization for higher frequency. Dielectric loss follows the same trend and decreases at high frequency region which shows the hopping of charge carriers of the prepared samples. Cole – Cole plots show the presence of grains effect of the samples. A.C conductivity plots obey Jonscher’s power law and appears non – debye in nature.

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