Study of electrical conduction behaviour of \(Y_{6-x}Ba_4(SiO_4)_6O_2\) oxyapatite doped with ytterbium ions

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Abstract. This paper reports the electrical conduction behaviour of Yttrium Barium Silicate Oxyapatite \(Y_{6-x}Ba_4Yb_x(SiO_4)_6O_2\), synthesized by solution combustion method where \(x\) varies from 0.01 mol% to 0.05 mol%. The scanning electron microscopy was done for morphological analysis which shows the spheroidal shaped grains with average grain size of 35μm. The dielectric behaviour of the material was studied in the frequency range of 100Hz – 100KHz and temperature varying from 50⁰C - 400⁰C. The frequency dependent dielectric constant and dielectric loss has been plotted for different temperatures. Decrease in dielectric constant and dielectric loss with increase in frequency has been observed for \(YBaSiO:Yb\) compounds.

1. Introduction

Oxyapatite materials doped with rare earth materials have attracted researchers due to the good electrical conductivities and low activation energies of oxygen ions present in the compound [1]. These materials show optical, biological and electrical applications because of their good thermal and chemical stabilities. They are used as electrolytes for solid oxide fuel cells SOFCs [1-2], through electrochemical reactions with excellent environmental compatibilities. The silicate oxyapatites also have good luminescent properties [3-4].

The general formula of silicate oxyapatite is \(A_4B_6(SiO_4)_6O_2\), where A and B are cationic sites and allow various substitutions of alkali, alkaline earth and transition elements providing structural flexibility to the compound. The movement of these cations and oxygen (anion), are responsible for the electrical conduction behaviour of oxyapatite materials [5-6]. Various electrical properties can be examined like grain and grain boundary effect using complex impedance spectroscopy [7]. Response of a. c. conductivity to frequency can also be analysed using resistor – capacitor model [8]. In lower frequency region, the value of a. c. conductivity decays due to the slow orientation of charge carriers and in high frequency region, hopping of charge carriers results in rise in a.c. conductivity.

The influence of rare earth ions on the dielectric properties of various apatite materials such as \(Sr_{10}(PO_4)_6(OH)_2\), \(Ca_{10}(PO_4)_6(OH)_2\) etc has been widely researched [9-10]. Among various rare earth ions, Ytterbium has good chemical stability and mechanical strength [11]. The \(Yb^{3+}\) ions when coated on surface forms a protective layer against corrosive properties. It has been reported that when \(Yb^{3+}\) ions are doped in \(La_9YbSi_6O_{27}\) shows enhanced dielectric constant [12] and a. c. conductivity [13]. Keeping this in view, the present study has been carried out on \(Yb^{3+}\) ions doped \(Y_{6-x}Ba_4(SiO_4)_6O_2\) oxyapatite compound.

Solution combustion method is used for synthesizing the oxyapatite compound, \(Y_{6-x}Ba_4(SiO_4)_6O_2: xYb\) with varying concentration of \(x\) ranging from 0.01 mol% to 0.05 mol%.
2. Material synthesis

Solution combustion method is one of the promising method due to cost effectiveness, simple equipment, low temperature requirement, less time consumption and also the particle size is obtained in the nano meter region. The flow chart for the synthesis of $Y_6XBa_4(SiO_4)O_2: xYb$ compound is shown in figure 1. All the reagents i.e. $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, $Yb(NO_3)_3 \cdot 5H_2O$, SiO2 and citric acid, were weighed according to the nominal composition. After weighing the chemicals were individually dissolved in 10ml of distilled water and then all the reagents were mixed together to form a solution (50 ml). The solution was placed in a magnetic stirrer with 500 rpm to facilitate thoroughly mixing of solution along with heat supply. Meanwhile, citric acid was added drop wise and at sufficient temperature combustion took place, producing a powdered sample which after subsequent mixing placed in a programmed muffle furnace for 5 hours at 1200°C for calcination and then ground into a fine powder.

Then, the fine powders were mixed with binding agent and given the form of pellet using KBr press machine and sintered at 900°C.

![Flow chart for solution combustion synthesis](image)

**Figure 1.** Flow chart for solution combustion synthesis.

3. Results and discussions

3.1 SEM

SEM micrograph for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2 \ (x = 0.05 \text{ mol%})$ compound is shown in figure 2. SEM image show the formation of spheroidal grains with higher grain connectivity. The average grain size is calculated to be 35μm.

![SEM micrograph](image)

**Figure 2.** SEM micrograph of $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2 \ (x = 0.05 \text{ mol%})$ compound.
3.2 Dielectric studies
Dielectric studies were done in the frequency range from 100 Hz to 100000 Hz at temperatures varying from 50 °C to 400 °C using HIOKI-IM3533 LCR Meter.

The dielectric constant (€) also known as permittivity is a measure of degree to which it can oppose the flow of charge. Figure 3 shows the change in value of dielectric constant with applied frequency for different values of temperature. The graph shows decreasing pattern of € with increase in frequency. This is due to the reason that at lower frequency, the orientation of molecules take place due to different polarizations i.e. electronic, ionic and space charge polarization[14] where as at higher frequency the dipoles could not orient in the direction of applied a.c. field [15].

![Figure 3. Plot of dielectric constant Vs frequency for Y_{6.0}Ba_{x}Yb_{0.05}(SiO_{4})_{6}O_{2} (x = 0.05 mol%) compound.](image)

The dielectric loss (tanδ) also shows similar variation as dielectric constant with respect to frequency, i.e. at lower frequency dielectric loss is maximum and with rise in frequency it decreases as shown in figure 4. The tanδ can be defined as the loss of energy due to heating of the material in the presence of electric field. The change in value of dielectric loss with frequency is due to the reason that the ytterbium ions in the compound creating metastable states. In the metastable state due to relaxation phenomena and time lag, the emission energy is found to be less than the absorbed energy [15]. The loss curve recorded at highest temperature is maximum.
Figure 4. Plot of dielectric loss Vs frequency for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol%) compound.

Figure 5 shows the variation of dielectric constant with temperature for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol%) compound. At lower temperature the dipoles do not follow the direction of applied field hence dielectric constant shows saturated value. However, with increase in temperature the dipoles start orienting in the direction of applied field and the value of dielectric constant increases [16]. The change in dielectric loss with respect to temperature for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol%) compound is shown in figure 6. As temperature increases dielectric loss also increases due to the rapid motion of charge carriers present in the compound [17].

Figure 5. Plot of Dielectric constant against Temperature for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol%) compound.
Figure 6. Plot of Dielectric loss against Temperature for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol$_\text{o}$) compound.

4. Cole-cole plot
The relation between the real ($Z'$) and imaginary ($Z''$) part of impedance can be studied by Complex Impedance Spectroscopy (CIS) [18]. The CIS investigation of the prepared material is done with frequency from 100 to 100000 Hz and temperature varying from 50°C - 400°C.

Figure 7. shows the Cole-Cole plot for the compound $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol$_\text{o}$). The value of $Z'$ and $Z''$ increases with rise in frequency. Cole – Cole plots govern the nature of sample whether it is Debye or Non – Debye. The synthesized compound showed Debye nature. It also tells the effect of grains and grain boundaries.

Figure 7. Imaginary part of impedance Vs real part of impedance for $Y_{6-x}Ba_xYb_x(SiO_4)_6O_2$ ($x = 0.05$ mol$_\text{o}$) compound.
5. A. C. conductivity analysis
The response of a. c. conductivity in accordance with frequency has been recorded and is depicted in the graph below (figure 8). At lower values of frequency, the variation of conductivity is almost saturated but with rise in frequency, it increases showing the conduction behaviour of Y_{6-x}Ba_xY_{x}b(SiO_4)_6O_2 (x = 0.05 mol\% ) compound. This AC conductivity rise is almost linear with frequency for all temperatures, following Johnschers’ power law which is given as, [19]

$$\sigma(\omega) = \sigma(0) + A\omega^n$$

(1)

where $\omega$ is angular frequency, $n$ is a constant taking values from 0 to 1 and $\sigma(0)$ is the frequency independent conductivity. The low frequency conductivity is due to the motion of charge carriers through the channel connecting the cationic and anionic sites present in the compound. The relation used for the calculation of a. c. conductivity is given as,

$$\sigma = \frac{2\pi f}{2\pi f^2 + 4\pi q^2} \times \frac{t}{A}$$

(2)

where $t$ is the thickness of pellet while $A$ is the area of it.

The curves recorded at low temperature regions were overlapping and to get a clear view of the response curve, the scaling has been reset and embedded in figure. 6

![Figure 8. The graph for a. c. conductivity Vs frequency for Y_{6-x}Ba_xY_{x}b(SiO_4)_6O_2 (x = 0.05 mol\%) compound](image)

6. Conclusions
Synthesis of Yttrium Barium Silicate Oxyapatite doped with Ytterbium ions has been done by solution combustion technique. SEM micrograph showed spheroidal grains with higher grain connectivity. The dielectric studies of YBaSiO: Yb compound showed inverse relation with frequency. The temperature dependent dielectric studies showed that as temperature increases dielectric parameters increases due to increase in polarization. The synthesized compound showed increase in a. c. conductivity with increase in applied frequency. The debye nature of sample has been observed from the Cole-Cole plot.

References
[1] Reina L L, Losilla E R et al. 2005 Chem. Mater. 17 596
[2] Béchade E, Julien I et al. 2008 Jour. Of the Euro. Cer. Soc. 28 2717
[3] Steigerwald D A, Bhat J C et al. 2002 Jour. of Sel. Top. in Quant. Electro. 8 310
[4] Kharton V V, Shaula A L et al. 2004 Jour. of the Electro. Soc. 151 1236
[5] Slater P R, Sansom J E H and Tolchard J R 2004 Chemi. Rec. 4 373
[6] Yao H C, Wang J S et al. 2010 Sol. Sta. Ioni. 181 41
[7] Tank K P, Sharma P et al. 2011 Crys. Res. and Tech. 46 1309
[8] Naddari T, Savariault J M et al. 2002 Jour. of Soli. Stat. Cir. 166 237
[9] Wafi R A, Jafer R et al. 2017 Cera. Interna. 43 17153
[10] Valdes J J P, Rodriguez V et al. 1995 Journ. of Mate. Res. 10 2174
[11] Ganesan M, Berube C D et al. 2002 Organometallics 21 1707
[12] Samad R, Rather M U D et al. 2018 J. Mater. Sci. Mater. Electron. 29 4226
[13] Xiang J, Liu Z G et al 2012 Electro. Act. 65 251
[14] Arends J, Royce B S H et al. 1968Phys. Lett. 27 720
[15] Rout A and Agrawal S 2020 Cer. Inter. 46 7912
[16] Rout A and Agrawal S 2021 Cer. Inter. 47 7032
[17] Schüller J, Mel’nichenko Y B et al. 1994 Phys. Rev. Lett. 73 2224
[18] Joshi M2017 Mecha. Mate. Sci. and Eng. 9 261
[19] Gittings J P, Bowen C R et al 2009 Act. Biomater. 5 743