Nano crystalline $\text{Sr}_6\text{Sb}_4\text{NbO}_{18}$ - Energy Material in Solid Oxide Fuel Cells

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Abstract. Because of the technological applications, Niobium based ceramic is one of the most research interest. Thus, there is numerous research works in recent years on their application as electronic and optical devices. Sintered oxide ceramics, having the required shape, micro structured size can be used for different electronic applications. In this paper, nano crystalline $\text{Sr}_6\text{Sb}_4\text{NbO}_{18}$ ceramic was prepared by combustion method. The sample was analysed by the X-ray diffraction, TEM, radio frequency and Impedance spectroscopic studies. The XRD pattern of as prepared $\text{Sr}_6\text{Sb}_4\text{NbO}_{18}$ sample reveals, the material has rhombohedral perovskite structure. All the peaks were broad when compared with the bulk, which indicates the reduction in the crystallite size. This is due to the micro strain and nano size in the crystallites. The crystallite size has been calculated from the XRD data, using Scherrer formula and it was obtained as 21 nm. The surface morphology of as prepared sample was studied using TEM and the particle size was found to be 19 nm. The sample was sintered at 1050°C, obtained the 98% of theoretical density. An impedance spectroscopic study of the sample carried out with a temperature range of , 200°C to 500°C shows that the ions are the main source for the conduction. The reason for the conductivity of the material might be because of the grain and grain boundary effects which can be clearly seen in the impedance plot. The impedance study confirms that the material is a possible candidate to fabricate solid oxide fuel cell.

Keywords: Nanomaterial, Dielectric studies, Impedance spectroscopy, Solid Oxide Fuel Cell

1. Introduction

In the past few decades, the electronic market has undergone great changes mainly in the communication systems with the development of new technologies. To produce materials with superior properties, the mixing of metal oxides is used as an attractive strategy. The materials with $\text{A}_n\text{B}_{6n-1}\text{O}_{3n}$ ($n = 6$) structure have gained more attraction in the recent years due to their technological application resulting from their dielectric and electrical properties. Numerous niobium based compounds have been reported with this structure, like $\text{Sr}_6\text{Nb}_2\text{O}_{18}$ [1], $\text{Sr}_6\text{Nb}_2\text{TiO}_{18}$ [2], $\text{Ba}_6\text{Nb}_2\text{TiO}_{18}$ [3], $\text{Ba}_6\text{Sr}_2\text{ZrO}_{18}$ [4], $\text{Ba}_6\text{Ti}_6\text{Sn}_2\text{Nb}_2\text{O}_{18}$ [5], and $\text{Ba}_6\text{TiN}_{18}$ [6]. Duivenboden et al. has reported the octahedral structure of $\text{Ba}_6\text{TiNb}_2\text{O}_{18}$ due to the formation of stacked hexagonal and cubic symmetries of $\text{Ba}_6$ layers [7]. Dielectric properties of various materials in the $\text{A}_n\text{B}_6\text{O}_{18}$ family in the microwave frequency region were reported by Zhang et al., Fang et al. and Drews et al. [8-10]. In this paper we have reported the sample preparation, electrical and dielectric properties of nano sized $\text{Sr}_6\text{Sb}_4\text{NbO}_{18}$ by auto ignition combustion method for the first time.

2. Experimental

In the present investigation auto ignition combustion method [11] was used to prepare the sample $\text{Sr}_6\text{Sb}_4\text{NbO}_{18}$ (SSN). The metal nitrate act as oxidizing agent and suitable fuel act as reducing agent in this method [12]. The solution containing ions of niobium, strontium, and antimony was prepared from high-purity Niobium penta chloride ($\text{NbCl}_5$, 99.9%) and nitrates of strontium, and antimony (99.99 %). To get a precursor complex, urea ($\text{NH}_2\text{CONH}_2$) was used as reducing agent and Citric acid as complexing agent. The stoichiometric amounts of the reagents were dissolved in a minimum volume of deionized water for obtaining the transparent aqueous solution. The solution was heated at 250°C within a combustion chamber, and it has undergone dehydration with the release of huge
quantity of gases and finally got auto ignited. To obtain the pure and well crystalline powders of SSN the powder obtained after the combustion was calcined at 600 °C for 30 minutes

3. Characterization

The structure of the synthesized sample SSN, was determined by analysing the X-ray diffraction pattern (Model: Philips PW1710 diffractometer). The crystallite size of SSN was also calculated from the XRD data using Debye-Scherrer formula. Using TEM (Model: TM-300, Philips), the particle size of the sample SSN was calculated. The sample in the form of cylindrical pellet was sintered at 1050 °C for 2 hours. The Complex impedance, dielectric constant ($\varepsilon_r$) and dielectric loss (tan δ) at radio frequency region were measured in sintered pellet by using LCR meter (HIOKI, model 3532, Japan).

4. Results and discussion

The XRD pattern of the sample SSN after the combustion process is shown in figure 1. Each diffraction peaks are indexed as rhombohedral perovskite structure on comparing with the data of ICDD file 32-0095, for Ba$_6$Nb$_4$ZrO$_{18}$ ceramic. All the diffraction peaks are indexed and no other secondary phases are present in it which implies that phase pure SSN nanoparticles are formed in the single-step process. From the XRD pattern it is also clear that, the formation of SSN is complete in the combustion process without any high temperature treatment. The crystallite size of the sample SSN is calculated as 21 nm using the Debye-Scherrer formula.

![Figure 1 XRD of SSN](image)

The particle size confirmation of SSN is done using TEM analysis. The TEM of as synthesized nano crystalline SSN is shown in the figure 2. In the TEM analysis, it is observed that almost polycrystalline nano powder has been formed. It has been found that most of the nanoparticles have homogeneous morphology. The agglomeration is absent in this TEM image which clearly shows the crystallinity of the sample. Figure 3 shows the particle size distribution histogram of the nano sample SSN. The particles seem to be in 14 nm to 27 nm ranges, and the average particle size is about 19 nm.
For the dielectric and impedance studies, highly dense compact form of the powder sample without any pores and air column has high significance. It has huge surface area due to its nano-size and it leads to excellent sintering behaviour. Nano sized SSN sintered at 1050 °C and obtained about 98 % of the theoretical density within the rhombohedral perovskite structure. Figure 4 shows the SEM images of SSN sample. It is clear that the sample is well sintered with no cracks on the surface due to densification.

When the temperature has increases the grain boundaries will merge and grain growth will also takes place. In the sintering, the rate of grain growth of the grains is directly proportional to its radius of curvature. The particle size is increased from nano to micro meter range during sintering as evidenced from the TEM and SEM images. The average grain size of the sintered samples is less than 2µm. Due to the auto combustion preparation method some sintering benefits are raised such as low sintering temperature, smooth and fast densification, absence of sintering aids, and low expensive sintering equipment.

The variation in the dielectric constant ($\varepsilon_r$), ac conductance (G) and loss factor (tan $\delta$) in the radio frequency range is studied for the sample SSN. At high frequency region the dielectric constant is almost stable at 35 and it increases with the decrease of dielectric constant as shown in figure 5. This is due to interfacial polarization reported by Maxwell and Wagner [13]. Within the sample, the delay in polarization has occurred and it results the decrease in $\varepsilon_r$ with the application of the electric field [14].
From the figure 6 it is clear that, at high frequency, ac conductance of the sample increases with the increase of frequency and will remain almost constant at low frequencies upto 1MHz . Therefore in communication systems, this material are useful for the capacitive applications. The variation of tan δ in radio frequency region is shown in figure 7. At higher frequencies, Dielectric loss remains constant with value as $2.60 \times 10^{-3}$ and increases with decrease in frequencies. This behaviour has reported as Koops phenomenological model [15]. Due to the low loss in the radio frequency range, the dissipation of electrical energy of the sample is low. The studies of the variation of dielectric parameters in radio frequency region substantiate the feasibility of this material in dielectric resonator and substrate applications.

Figure 8 shows the plot of the real part of impedance ($Z'$) versus logarithm of frequency at different temperatures 200-500 °C of the sample SSN. At low frequency region, the variation of $Z'$ is inversely proportional to the frequency and is in agreement with the negative temperature coefficient of resistance behaviour. This behaviour indicates that the conductivity of the oxygen ions increases with
the frequency. All the curves at different temperatures coincide at the high frequency region. The value of $Z'$ reaches a constant value which can be an indication of dc conduction.

Figure 9 shows the plot of $Z''$ as a function of frequency at the temperatures 200-500 °C. Asymmetric peaks are obtained at different temperatures with the peak maximum corresponding to the frequency $f_z$ called as peak frequency. As the temperature rises, the peak frequency $f_z$ is shifted towards the high frequency region. This leads to the non-Debye type of relaxation behavior in the system. The broadening of the peak is attributed to the spread of relaxation time.

Figure 9. The imaginary part of impedance with radio frequencies

Figure 10. Complex impedance plot (cole-cole plot)

Figure 10 shows the impedance plot known as Cole-Cole plot of the sample SSN at the temperatures 200-500 °C. The centres of the semicircle arcs in the Cole-Cole Plot at different temperatures are found to be lying below the real axis. The first semi-circle is the contribution of grain and grain
boundary effect and the plot shows the weak trace of the second semicircle is the contribution of the electrode effect. As the temperature increases, the peaks shift towards the low frequency side, which indicates a fall-off in the grain resistance. This might be due to the prominent ionic conduction at high temperatures [16].

5. Conclusions

Nano-crystalline Sr$_6$Sb$_2$NbO$_{18}$ sample is synthesized through auto ignition combustion process. The XRD analysis confirms that the sample crystallises in rhombohedral perovskite structure. The average crystallite size calculated from FWHM is 21 nm. By analysing both XRD and TEM, the formation of nano sized Sr$_6$Sb$_2$NbO$_{18}$ is confirmed. The dielectric constant ($\varepsilon_r$) and loss factor (tan $\delta$) of the sintered pellet at 1 MHz are about 35 and 2.60 x 10$^{-3}$, respectively. The behaviour of ac conductivity, dielectric loss confirms that sample can use as dielectric resonator in radio frequency communication systems. Also, the impedance spectroscopic studies shows that the sample is suitable to be used as electrolyte in SOFC.

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