Research Article

Effect of Reaction Rate and Calcination Time on CaNb_2O_6 Nanoparticles

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The properties of CaNb_2O_6 nanoparticles synthesized by coprecipitation method under controlled reaction rate and extended calcination time were studied. Analysis of the X-ray diffraction pattern shows single orthorhombic phase of the material with lattice parameters: $a = 15.0147 \text{ \AA}$, $b = 5.74148 \text{ \AA}$, and $c = 5.30296 \text{ \AA}$. The morphology and size of particles was found to be improved due to the controlled reaction rate and extended calcination time. The average sizes of the particles were estimated as 40 nm and 90 nm for sintering temperatures 650°C and 800°C , respectively. The material was found to possess dielectric constant which is inversely proportional to the frequency. Surprisingly, the material shows ferroelectric behavior, the possible origin of which is discussed here.

1. Introduction

Alkaline earth niobates $\text{A}^{2+}\text{Nb}_2\text{O}_6$ ($\text{A} = \text{Ca}$, Sr , and Ba) have been studied extensively for the electrooptic, pyroelectric, and photorefractive applications [1, 2]. Many of them crystallize in isomorphic orthorhombic columbite phase [3–5] which is characterized by AO_6 and NbO_6 independent octahedra with the A and Nb cations at the centre of the octahedra surrounded by six oxygen atoms [6]. Among the several niobates, CaNb_2O_6 finds applications in laser, holography, and hydrogen generation [7–9]. It is also used as a substrate in electronic circuits [8]. Its dielectric behavior at microwave frequencies makes it useful for low temperature cofired ceramics (LTCC) [10]. All these applications require good quality of materials.

Earlier nanopowders of CaNb_2O_6 synthesized by using coprecipitation method were irregular in shape, and size was 100 nm [11]. There was a scope of improvement in morphology and size of the material so as to make it useful for industrial applications. In present work, an attempt is made to reduce the particle size and improve the morphology of single phase CaNb_2O_6 nanoparticles. A support is taken from the recent study, which shows that the morphology and phase of

the material can be improved by controlling the reaction time [12].

Being a centrosymmetric, the columbite phase structure is nonferroelectric. However, Ravi and Navale [11] reported the ferroelectric properties of CaNb_2O_6 nanoparticles, surprisingly. We also observed similar behavior in CaNb_2O_6 nanoparticles. The possible origin of ferroelectricity may be hidden in the impurity and the oxygen deficiency as the material contains impurity [11], and oxygen vacancies formation in materials sintered at high temperature is very common [13].

2. Experimental

The CaNb_2O_6 nanoparticles were prepared by the coprecipitation technique similar to the technique as described elsewhere [11]. The reaction was carried out very slowly. Briefly, 4.032 gm of Nb_2O_5 (AR grade) was converted to NbF_5 by reacting with a minimum amount of hot HF. During reaction, the Nb_2O_5 completely dissolves in HF to form a transparent solution of NbF_5 . To this solution, solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ which was previously prepared by dissolving 2.2053 gm of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in distilled water was added. After

FIGURE 1: X-ray diffraction pattern of CaNb_2O_6 precursor powders calcined at (a) 650°C and (b) 800°C.

FIGURE 2: (a) and (b) TEM images of CaNb_2O_6 nanocrystals calcined at 650°C and 800°C, respectively, (c) and (d) HRTEM images of the material calcined at 650°C and 800°C, respectively, (e) selected area electron diffraction pattern, and (f) EDX spectrum of CaNb_2O_6 nanoparticles.

FIGURE 3: P - E hysteresis loop of CaNb_2O_6 nanoparticles.

that, the resultant solution was vigorously stirred with a magnetic stirrer for 3–4 h. While stirring, an excess quantity of concentrated HCl was added to the above solution to dissolve the calcium fluoride formed during the reaction of NbF_5 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. A mixture of ammonium oxalate and ammonium hydroxide was then added dropwise to precipitate calcium and niobium as oxalate and hydroxide, respectively. During the entire reaction, pH was maintained around 9.5 to ensure complete reaction. The precipitate obtained was filtered and washed several times with the distilled water. The washed powder was dried at 70°C in oven for 1 day and finally calcined at 650 – 800°C for 10 h.

The X-ray diffraction (XRD) data of the powder was collected by using X-ray diffractometer (D8 Advance, Bruker, Germany) employing $\text{Cu K}\alpha$ radiation, with step size of 0.02° and step time of 46.5 sec. The crystallite size of particles was estimated from the full width at half maximum by Scherrer's equation. The morphology of particles was analyzed using transmission electron microscopy (Tecnai G2 20 Ultra-Twin, FEL, The Netherlands). The constituents of the material were identified by EDS detector.

For dielectric and hysteresis studies, pellets of 12.3 mm diameter were made using standard pelleting machine. The calcined powder was mixed with a few drops of 1 wt% solution of polyvinyl alcohol and isostatically pressed into pellets under pressure of 5–6 tons for 5 min. The pellets were sintered at 925°C for 4 hours, polished, and coated with the silver paint. The ferroelectric hysteresis loop parameters were measured by using P - E hysteresis loop tracer (Automatic P - E Loop Tracer, Marine India). A homemade circuit of current voltage converter using OP-Amp was used to measure capacitance of the sample pallet.

3. Results and Discussion

3.1. Structural Studies. Figures 1(a) and 1(b) show the XRD pattern of CaNb_2O_6 calcined at 650°C and 800°C , respectively. XRD pattern of 650°C (Figure 1(a)) annealed is

confirmed as single phase compound with pattern matching to that reported in JCPDS database (JCPDS file number 71-2406). This pattern could be identified as orthorhombic columbite similar to that of reported data (JCPDS file number 71-2406). The XRD pattern of 800°C (Figure 1(b)) annealed sample is similar to that of earlier one. The peaks are more pronounced which indicates better preferred orientation. The lattice parameters were calculated and found to be as follows: $a = 15.0147 \text{ \AA}$, $b = 5.74148 \text{ \AA}$, and $c = 5.30296 \text{ \AA}$. The average grain sizes were determined by Scherrer's equation

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the average grain size, assuming particles are spherical, k is equal to 0.89, λ is the X-ray wavelength, θ is the peak angle, and β is the full width at half maximum. The average grain size of the particles calcined at 650°C was found to be 17 nm whereas it was about 40 nm for the particles calcined at 800°C . This shows the effect of temperature on grain size.

Figure 2(a) is the TEM image of CaNb_2O_6 calcined at 650°C which shows spherical morphology. The average particle size was found to be $40 \text{ nm} \pm 5 \text{ nm}$. The size was calculated by taking average of 25 particles in the photograph. The bigger size of the particle can be attributed to the condensation of assembled nanograins. However, the quality and size of the particles were improved as compared to the earlier reported study [11]. This may be due to the controlled reaction rate and extended calcination period. Slow reaction rate allows completion of the reaction and precipitation, whereas the more calcination time allows significant crystallization of the material. The TEM image of the material sintered at 800°C is shown in Figure 2(b). On comparison, it was found that the average particle size is increased to $90 \text{ nm} \pm 5 \text{ nm}$ because of higher sintering temperature, as expected. The representative HRTEM images of the crystallite at two different sintering temperatures are shown in Figures 2(c) and 2(d), respectively. From both these HRTEM images (Figures 2(c) and 2(d)) it was observed that the interplanar distance of the crystallite is about 0.37 nm, corresponding to (400) crystal planes of CaNb_2O_6 lattice. The SAED pattern of the CaNb_2O_6 nanoparticles is shown in Figure 2(e). In the SAED pattern concentric rings along with some dots are observed. This indicates that for most of the particles there is random orientation and this happens when the particle's size is very small. Figure 2(f) shows the EDX of CaNb_2O_6 nanoparticles; it clearly gives the constituents of the material. Note that the signals of C and Cu were generated from the carbon coated copper grid.

3.2. Ferroelectric and Dielectric Studies. The polarization versus electric field (P - E) hysteresis plot for the synthesized nanoparticles is shown in Figure 3. The values of the coercive field (E_c), remnant polarization (P_r), and maximum polarization were calculated from the hysteresis loop. These values are 23.34 kV/cm , $0.59 \text{ } \mu\text{C/cm}^2$, and $0.65 \text{ } \mu\text{C/cm}^2$, respectively, at an applied electric field of 27.9 kV/cm . These values are comparable to the reported values of the parameters [11].

FIGURE 4: (a)–(c) Variation of dielectric constant with temperature at 10 KHz, 1 KHz, and 100 Hz frequency and (d) variation of dielectric constant with frequency at room temperature (30°C).

As mentioned above, theoretically the material CaNb_2O_6 is nonferroelectric as the columbite structure is centrosymmetric, but experimentally the ferroelectric property is observed in the nanomaterial. This discrepancy can be attributed to the impurity dipoles. Since the impurity present in starting chemicals was about 0.89%, some sort of impurities automatically get introduced into the synthesized material. The impurity in the form of ions can occupy some octahedra sites in the lattice structure [14]. Further the pallets were sintered at 925°C, due to which some oxygen vacancies were created. If the impurity ion is found near the oxygen vacancy site, then they constitute an impurity dipole. Thus there is a possibility of presence of many impurity dipoles in the material which can make the structure slightly off-centered. When the material is poled, the dipoles arrange themselves cooperatively and show orientation in the direction of applied electric field, giving rise to ferroelectric property in the material. The explanation is well supported by the experimentally observed facts that the ferroelectric properties get induced in otherwise nonferroelectric material by the impurity dipoles [15], and the ferroelectric properties of isomorphous orthorhombic columbite structured materials such as BaNb_2O_6 and SrNb_2O_6 were already reported [16, 17].

Figures 4(a)–4(c) show the plots of dielectric constant against temperature measured at various frequencies. The

dielectric constant initially remains steady, starts falling from 95°C, and becomes stable after 135°C. This behavior is unlikely due to the phase transitions and may be related to the luminescence property [18]. After 135°C, no further change in the dielectric variation was observed. Figure 4(d) shows the variation of dielectric constant with frequency at room temperature (30°C). It is found that the dielectric constant values decrease sharply as the frequency increases.

4. Conclusion

The single phase CaNb_2O_6 nanoparticles were successfully synthesized by coprecipitation method. Reaction rate and calcination period affect the size and morphology of the nanoparticles. The average particle size was found to be improved and is about 40 nm for the material calcined at 650°C. Sintering the powder at higher temperature creates impurity dipoles which could be responsible for the ferroelectric behavior in the material.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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