Synthesis, Structural, Dielectric and Electrical Impedance Study of CaNb₂O₆ Phase Pure Material*

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Abstract: Controlling the cooling rate during calcination pure columbite like phase of $CaNb_2O_6$ is synthesized. X-ray diffraction is used to identify the phase. The phase is orthorhombic with lattice constants $a=5.772A^0$ $b=14.9897A^0$, $c=5.2375A^0$ for the sample calcined at 1200^0C and sintered at 1250^0C . Density of material is 4.36 gm/cm³ (91.8% of theoretical density). Dielectric dispersion followed the Jonscher's relation. Detailed analysis of impedance spectrum suggested that the electrical properties are strongly temperature dependent. AC impedance analysis results indicate that the relaxation mechanism of the material is temperature dependent and has dominant bulk contribution in different temperature ranges. The frequency dependent ac conductivity at different temperatures indicated that the conduction is thermally activated process. AC conduction activation energies are estimated from Arrheneus plots and conduction mechanism is discussed.

Keywords: Electro ceramics, dielectrics, microstructure, sintering, impedance analysis.

1. Introduction

Calcium niobate CaNb₂O₆ (CN) is of interest because of its potential to be a strong source of coherent light that could be useful in holography applications¹ as well as laser host material²⁻³. The dielectric properties of the columbites are to a large extent sensible to their preparation⁴⁻⁸. Moreover, the synthesis of single phase columbite is often difficult because of the formation of corundum-like crystal phases A4Nb₂O₉⁸. Microstructure of the alkali-earth metal niobate affects optical properties critically⁹. Synthesis of ceramic powder with good sinterability and compositional homogeneity is necessary. In normal solid state route compositional homogeneity is generally not achieved. Chemical methods overcome the problems; *Presented at CONIAPS XI, University of Allahabad, Feb. 20-22, 2010. however, the sinterability of the material remains an issue. Further, detailed dielectric behavior, contribution of grains and grain boundaries in dielectric relaxation are not studied. We therefore attempted the optimization of process parameters in simple solid state reaction route viz. rate of cooling and heating during calcination in order to prepare the CaNb2O6 in phase pure columbite structure keeping relatively low calcination temperature. The preparation, structural characterization, dielectric, and impedance spectroscopic analysis of CaNb2O6 are investigated and presented in the paper.

2. Experiment Procedure

CaNb₂O₆ is synthesized by taking stoichiometric amounts of CaCO₃ (Loba Chem 99.9%), Nb₂O₅ (Loba Chem 99.5%) using solid-state reaction route. The stoichiometric amounts of constituent's powders were wet mixed in acetone for 6 hours. The mixed powders were calcined at temperature (1200^{0} C) for 6 hours. Calcined powders were structurally analyzed using X-ray diffraction data using X-ray diffractometer (Rigaku, Miniflex). Fine calcined powders were pressed into cylindrical pellets of 10 mm diameter and 1-2 mm thickness under an isostatic pressure of 100 MPa. Polyvinyl alcohol (PVA) was used as a binder. The pellet were sintered at 1250^{0} C for 6 hours and cooled down to room temperature using controlled cooling rate.

The phase formation of the sintered pellet has been identified using xray diffraction (XRD, RIGAKU, Miniflex) technique with CuK α radiation. Prepared material was used for dielectric and impedance measurements for which the sintered samples were electroded with silver paste and heated at 500^oC for 1 hour before measurements were performed. The electrical impedance (Z), capacitance (C) and loss angle were measured in the frequency range (500 Hz-1MHz) at various temperatures between room temperature up to 450^oC, using a computer controlled LCR HI-TESTER (HIOKI-3532-50). Surface morphology measured by using scanning electron micrograph (SEM).

3. Result and Discussion

3.1 Structural and Micro-structural response

Figure 1 Shows XRD pattern of CaNb₂O₆ calcined at 1200° C and sintered at 1250° C. The 100% intensity peak was observed at $2\theta = 29.31$ a characteristic feature of the columbite CaNb₂O₆.



Figure 1: X-RD pattern of pure phase CaNb₂O₆ calcined at 1200⁰C



Figure 2: Surface Electron Micrograph (SEM) of the CN

The major X-ray reflection peaks observed could be fitted satisfactorily in orthorhombic columbite phase with lattice constants $a=5.772A^{0}$

b=14.9897A⁰, c = 5.2375A⁰ which almost coincide with the earlier report (JCPDS No.11-0619; a = 5.764, b = 15.09, c = 5.232). Density of material is found to be 4.36 gm/cm3 (\approx 91.8% that of theoretical density). The particle size was determined using Scherer formula. The estimated particle size is \approx 455Å. The typical SEM micrograph of CaNb₂O₆ is shown in Fig-2. The grains are homogeneously spread and disc shaped. The average grain size calculated by linear intercept method was found to be 1.2 µm.

3.2. Dielectric response

The temperature dependence of both dielectric permittivity and tangent loss (in the inset) are depicted in figure 3 at different frequencies (0.5 KHz, 1 KHz, 5 KHz, 10 KHz, and 100 KHz); the values of dielectric constant (ϵ ') increase with increase in temperature. This increase in dielectric response with temperature may be due to interfacial polarization dominating as compared to the dipolar polarization. Contribution of the reorientation of the off-centre M²⁺ and Nb⁵⁺ ions coupling with the thermally activated conduction electrons may appear due to ionization of the oxygen vacancies resulting into such peak.



Figure 3: Temperature dependence of dielectric constant (ϵ '). Inset shows the tangent loss

The thermally activated conduction electrons interacting with the dipoles of the off-centered M^{2+} and Nb^{5+} ions and contributing to the dielectric relaxation peak is reported in $Pb_{1-x}K_xNb_2O_6^{-10}$ and $MgNb_2O_6^{-11}$.

The frequency dependence of real (ε ') and imaginary (ε '') part of dielectric constant on a log-log plot at different temperatures are compared in figure 4. Up to 300^oC, real part of dielectric constant is higher than its imaginary part, and both decreases with frequency. With further increase in temperature, ε '' starts with higher value than ε ', intersecting at 1 kHz at 350^oC; intersecting frequency shifts towards higher frequency as temperature increased (5 kHz at 400^oC). Higher values of both the components of dielectric constant, as temperature rises, reveal the effect of space charge polarization and/or conducting ion motion. The relatively higher values of ε '' at low frequency suggests the free charge motion that may be related to ac conductivity relaxation, whereas the large values of ε ' at lower frequencies may be associated with hopping conduction which becomes significant above 300^oC.



Figure 4 Comparison of dispersions in ε '' and ε ' in (300^oC-450^oC) temperature range in CN.

Moreover, with increase in frequency, the ε ' and ε '' terms becomes almost parallel at higher temperatures. This type of behavior is reported in other conducting ion dielectrics¹¹ and is associated with ion hoping as the dominant mechanism of dielectric relaxation¹². Thus, the ion hoping mechanism is dominant at elevated temperatures. The frequency dependence of dielectric constant show dispersions at low frequencies that gets almost saturated at higher frequencies. The dispersions increase with increase in temperature. This is attributed to space charge accumulation effect. Such dispersions in both components of complex dielectric constant are observed commonly in ferroelectrics with appreciable ionic conductivity and are referred to as low frequency dielectric dispersion (LEDD)¹³⁻¹⁴. The complex dielectric constant as a function of the frequency ω in accordance with the Jonscher's power law¹⁵ given as

(3.1)
$$\varepsilon' = \varepsilon_{\infty} + \sin(n(T)\frac{\pi}{2})(a(T)/\varepsilon_0)(i\omega^{n(T)-1})$$

(3.2)
$$\varepsilon'' = \sigma / \varepsilon_0 \omega + \cos(n(T)\frac{\pi}{2})(a(T)/\varepsilon_0)(i\omega^{n(T)-1})$$

where the first term in equation (3.1) determines the lattice response and the second term corresponds to charge career contribution to the dielectric response. Similarly, in equation (3.2) the first term reflects the DC conduction contribution and the second term represents the charge career contribution to dielectric loss.



Figure-5: Temperature dependence of parameter n(T) and a(T) as obtained from non-linear fitting of dielectric data.

At low frequencies, the contribution due to charge career term $(\sin(n(T)\frac{\pi}{2})(a(T)/\varepsilon_0)(i\omega^{n(T)-1}))$ dominates and lattice response part ε_{∞} can be neglected. Therefore, equation (3.1) for constant n yields a straight line with slope (n-1). With increasing temperature, the range of frequencies in which charge career contribution dominates increase showing that charges have sufficient high energy to overcome the barrier and get released. A non-linear fitting for equation (3.1) and (3.2) was used to obtain the values of parameters n (T), and a(T), as depicted in figure 5.

The interaction between the charge careers contributing in the polarization process is characterized by n(T); at low temperatures, n is almost 1, showing Debye type relaxation. With increase in temperature, its value decreases showing increase in interaction and distributed relaxation at higher temperatures. The a(T) value also increases with temperature showing the strength of polarizability increasing.

3.3 Impedance response

Impedance spectroscopy may be a better tool to understand the relaxation process than the dielectric analysis especially when the contribution of grains is separated from that of grain boundaries. Figure 6 shows the variation of the imaginary part of the impedance (Z'') with frequency at different temperatures. Z'' peak starts appearing with increase in temperature $\geq 400^{\circ}$ C with asymmetric broadening.



Figure: 6 Frequency dependence of imaginary part of impedance (Z''). Inset shows the same at higher temperature.

For temperatures below 400^oC the peak was beyond the range of frequency measurement. The peak shifts towards higher frequency with increasing temperature indicating the spread of relaxation times and the existence of temperature dependent electrical relaxation phenomena. Probably, high temperature triggers grain boundary relaxation process as is also evident from the asymmetric broadening of the peaks¹⁶.



Figure: 7 Explicit impedance plots between Z' and Z" fitted with proposed model.

The Nyquist plot for different temperatures is shown in Fig-7. At lower temperatures $<400^{\circ}$ C, there is linear response in Z" indicating the insulating behavior of the material.



Figure: 8. Temperature dependence of equivalent circuit parameters (Rg,Cg,Rgb,Cgb).

Above 400^oC the linear response gradually changes to semi circular arc that could be fitted with series network R_s -(R_gC_g)-($R_{gb}C_{gb}$). The series resistance in the model is included as the Z" does not intersect at origin. This may be due to electrode roughness and porousness of the material. The arc crosses Z' axis at lower values as temperature increases, showing that the grain resistance decreases with temperature. The values of parameters R_s , R_g , C_g , R_{gb} , C_{gb} are calculated and shown in figure 8.

The value of C_g increases slowly with increase in temperature whereas the R_g show exponential decrease at higher temperatures (>200⁰C). The behavior could be associated with the grain becoming conducting. The series resistance R_s also decreases at high temperature and reached minimum at 150⁰C, reflecting that the charges trapped at the bulk electrode interface is migrated into the bulk at this region. Thus the grains boundaries start trapping free charges that is released from grains at high temperature. The value of R_{gb} decreases with increase in temperature whereas C_{gb} increases slowly with increase in temperature.

4. Conclusions

Phase pure columbite structure in $CaNb_2O_6$ is stabilized through standard solid state reaction route by using controlled cooling rate during calcination and sintering. The crystal structure is orthorhombic with unit cell parameter a=5.772A0 b=14.9897A0, c=5.2375A0. Density of material is found to be 4.36 gm/cm³, (91.8% of theoretical density). Space charge accumulation effect and free charge motion at low frequency and higher temperature are associated with dielectric response. The dielectric dispersion followed Jonscher's formalism. The values of coefficient a(T) and exponent n(T) in the Jonscher's relation show non-Debye type relaxation at high temperatures. Impedance spectroscopy is used to model the electrical properties of the material using a two RC network representing grains and grain boundary.

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