Applied Science Periodical **ISSN 0972-5504**
Volume - XXVI, No. 1, February 2024
Journal website: www.internationaljournalsiwan.com
ORCID Link: https://orcid.org/0009-0008-5249-8441
Google Scholar: https://scholar.google.com/citations?user=BRweiDcAAAAJ&hl=en
Refereed and Peer-Reviewed Quarterly Periodical

Electrical Conductivity of $A^{2+}Nb_2O_6$ (A = Mg, Ba, Ca and Sr) Type Electro-Ceramics

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(Received: January 10, 2024; Accepted: January 24, 2024;
Published Online: February 28, 2024)

Abstract:

Ceramic oxides ANb_2O_6, has been prepared by standard solid state reaction route by optimizing the calcination and sintering temperatures as well as heating / cooling rates during calcination / sintering, respectively. Electrical properties of the material were studied using impedance spectroscopy technique. Detailed analysis of impedance spectrum suggested that the electrical properties are strongly temperature dependent. The relaxation is polydispersive and conduction is mainly through grains. The frequency dependent ac conductivity at different temperatures indicated that the conduction is thermally activated process. AC conduction activation energies are estimated from Arrhenius plots and conduction mechanism is discussed.

Keywords: Electro ceramics, dielectrics, Microstructure, sintering

1. Introduction:

As the demand for new devices, high performance capability, simple processing routes and low cost manufacturing in advanced materials has grown over the past decades. The technologies for controlling the desired properties of product have become very important. The quest for optimal powder characteristics viz. controlled chemical composition, homogeneity, reactivity, particle size and shape has directed attention towards powder production techniques [1].

A group of minerals having general formula AB_2O_6 (A being Fe, Mn, Mg & B representing Nb) are referred to as columbite structures [2-3]. These materials when synthesized show various degrees of cations disorder and stabilize in Pbcn space group. The columbite-like phase of $MgNb_2O_6$ (MN) has attracted interest for many years [4-13] with current focus on its use as precursor for the synthesis of microwave dielectric material $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) [5], perovskite Pb $(Mg_{1/3}Nb_{2/3})O_3$ (PMN), a potential candidate for multilayer ceramic capacitor, transducer, electrostrictor and actuator applications [7-10]. It is also a suitable reference material for investigating the defects induced in $LiNbO_3$ substrate for waveguide fabrication [12].

A number of preparation routes are attempted for its synthesis. For example, mixed oxide route was modified by taking more reactive precursor ($MgCO_3$). $Mg(OH)_2.5H_2O$, $Mg(NO_3)_2$ or $MgCO_3$, however, it essentially stabilized in mixed phase, and pure phase is obtained only after prolonged heating [6, 8-9]. Synthesis using flux route claims to have obtained pure phase; the reported XRD however show many weak peaks that are not assigned and grains are not well developed [14]. Various chemical routes were also tried for preparing the MN. These include co precipitation method in which ultra fine particles of MN were reported to be formed at 750°C [15], oxalate co-precipitation route that gives pure MN columbite phase with grain size ranging from 100-300 nm [16]. A reaction sintering method [17] is also reported with sintering temperature of 1300°C. However, in the chemical synthesis routes, the densification of materials is not reported that is important for using the material for device purposes. Further, all these reports mainly concerned about the preparation routes and detailed dielectric behavior, electrical conduction mechanism and contribution of grains and grain boundaries in dielectric relaxation are not studied. For any device application, an understanding of these properties is very much required along with a simple processing route that gives reproducible properties and is low cost with relatively lower temperature processing. We therefore attempted to comparative study the ac electrical conductivity of ANb_2O_6 phase pure materials and presented in the paper.

2. Experimental Procedure:

2.1 Sample Preparation:

ANb_2O_6 ($MgNb_2O_6$, $SrNb_2O_6$, $CaNb_2O_6$ and $BaNb_2O_6$) are synthesized by taking stoichiometric amounts of MgO, $CaCO_3$, $SrCO_3$ and $CaCO_3$ (Merck 99.9%), Nb_2O_5 (Merck 99.5%) using solidstate reaction route. The constituent's powders were wet mixed in acetone for 12 hours. The mixed powders were calcined at different temperatures (1000°C, 1050°C, 1100°C, and 1125°C) for 6 hours in each case, the final temperature was achieved by keeping the constant heating rate. Calcined powders were structurally characterized using X-ray diffraction technique. Fine calcined powders were pressed into disc-shaped pellets at an isostatic pressure of 100 MPa. PVA binder was used. The pellets were sintered at different temperatures (1050°C, 1100°C, 1125°C, and 1150°C) for 6 hours and cooled down to room temperature using controlled cooling rate.

2.2 Characterization:

The phase formation of the sintered pellet has been identified using X-ray diffraction (XRD, RIGAKU- Miniflex) analysis with Cu $K_\alpha(\lambda=1.5405A^o)$. To determine the dielectric properties, the sintered samples were electroded with silver paste and heated at 300°C for 1 hour before measurements were performed. The ac electrical conductivity has been calculated by using impedance data.

3. Result and Discussion:

Electrical Conductivity Study:

Fig.1 (a) and (b) shows the variation of ac conductivity with frequency at different temperatures. The ac conductivity was calculated from the impedance data using the relation $\sigma_{ac} = \omega\varepsilon_0\varepsilon_r(\tan\delta)$. It is clear from the figure that the material at low frequencies exhibits dispersion. Conductivity increases with increase in temperature and frequency. The conductivity could be fitted through the expression $\sigma_{ac} = \sigma_{dc} + A\omega^n$, known as Jonscher's law [18], where A is a thermally activated quantity and n is the frequency dependent exponent.

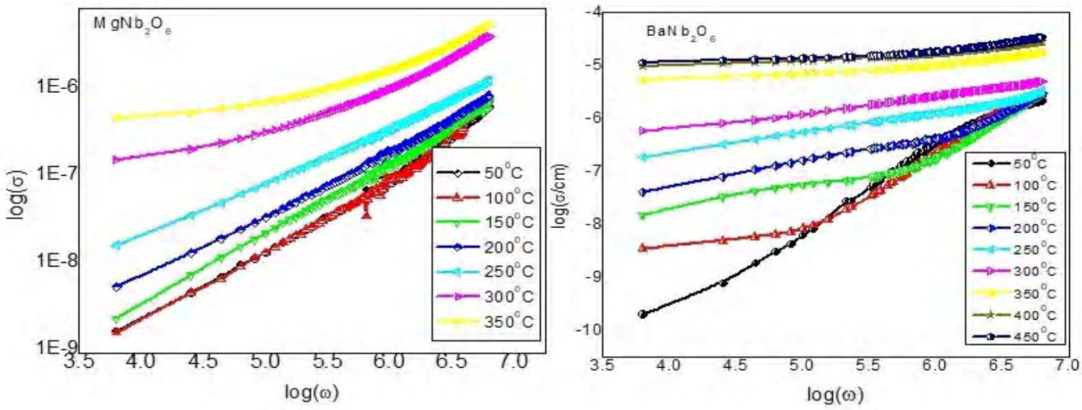

Figure 1(a): AC electrical conductivity with frequency for $MgNb_2O_6$ and $BaNb_2O_6$.

The value of $n > 1$ for lower temperature and becomes < 1 as the temperature increase. The term $A\omega^n$ represents the ac dependence and characterizes all dispersion phenomenon. According to Funke [19] the value of n might have a physical meaning; if $n<1$, charge careers takes a translational motion with a sudden hopping, when $n > 1$, would mean a localized hopping of the species (small hopping without leaving the neighborhood [20].

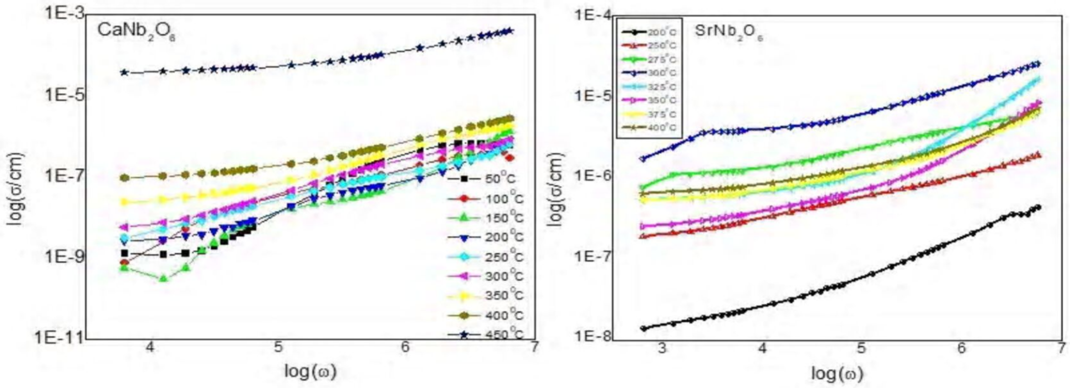

Figure 1(b): AC electrical conductivity with frequency for $CaNb_2O_6$ and $SrNb_2O_6$.

This indicates that the conduction process is a thermally activated phenomenon. According to Jonscher, the origin of the frequency dependent conductivity lies in the relaxation phenomenon arising due to mobile charge carriers. The low frequency dispersion thus is associated with ac conductivity whereas almost frequency independent (especially at higher temperatures) conductivity at high frequencies corresponds to the dc conductivity of the material. The temperature at which the grain resistance dominates over grain boundary is marked by change in slope of conductivity with frequency. The frequency at which the slope changes is known as hopping frequency, which corresponds to polaron hopping of charges species. The oxygen vacancies (V_o'') may act as polaron [21]. As the temperature increases, the hopping frequency shifts towards lower side. A strong dependence of the conductivity with frequency is observed. AC conductivity is dispersive at lower temperatures and converges towards higher temperatures. Two different slopes are clearly discernable from Fig. indicating the presence of two different conduction mechanisms in the material. The activation energy values at different frequencies have been calculated assuming the Arrhenius behavior. The small activation energy however, rules out the association of oxygen vacancies contribution in mobile ion conductivity.

4. Conclusions:

Phase pure materials ANb_2O_6 is stabilized by optimizing the calcination and sintering through standard solidstate reaction route. AC conductivity exhibits dispersion at low frequencies and follows Jonscher's power law. The charge in the exponent n in ac conductivity dispersion term ($A\omega^n$) shows that the nature of conductivity mechanics. Charges from localized hopping to free ion motion with increase in temperature and that the conduction is a thermally activated process.

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