X-ray and electrical properties of Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ ceramic

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ABSTRACT

The complex perovskite oxide barium gadolinium niobate, Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ (BGN) is synthesized by a solid-state reaction technique. The X-ray diffraction of the sample at room temperature shows a tetragonal phase. The scanning electron micrograph of the sample shows the average grain size of BGN $\sim$ 1.92 μm. The frequency-dependent dielectric dispersion of BGN is investigated in the temperature range from 303 K to 463 K and in a frequency range from 50 Hz to 1 MHz by impedance spectroscopy. The logarithmic angular frequency dependence of loss peak is found to obey an Arrhenius law with activation energy of 0.70 eV. It is observed that: (i) the dielectric constant (ε') and loss tangent (tan δ) are dependent on frequency, (ii) the temperature of dielectric constant maximum shift toward lower temperature side, (iii) The scaling behavior of dielectric loss spectra suggests that the relaxation describes the same mechanism at various temperatures. Copyright © 2011 VBRI press.

Keywords: Dielectrics; electrical properties; X-ray diffraction; scanning electron micrographs.

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Introduction

Perovskite materials with high dielectric constants have been used for technological applications such as wireless communication system, cellular phones and global positioning systems in the form of capacitors resonators and filters. High dielectric constant permits smaller capacitive components, thus enabling smaller size of electronic devices [**1**]. Complex perovskites are very promising for electroceramic applications and many researchers have shown considerable interest in the dielectric properties of these compounds. Materials having a diffuse phase transition (relaxors) have attracted the most attention due to their broad maximum in the temperature dependence of their dielectric constant [**2, 3**].The perovskite family is created by the doping of other types of cations into the stoichiometry and / or introducing anion deficiency. In the ABO_3 structure, the valences of the A (12-cordinated) and B (6-cordinated) cations are usually 2^+ and 4^+, respectively. During the intervening years, a large amount a good understanding of the many inter-related properties and phenomena associated with these materials has been achieved.

Recently, giant dielectric constant and dielectric relaxation in $A(Fe_{0.5}B_{0.5}O_3)$, (A = Ba, Sr and B = Nb, Ta) [**4-7**], $CaCuTi_4O_{12}$ [**8**], $CdCr_2S_4$ [**9**] have been pursued to understand the relaxation mechanism, which describes the dielectric relaxation i.e. charge redistribution, structural frustration or polaron redistribution, ferroelectric relaxor, and Maxwell-Wangner space charge (pseudo relaxor). The high value of dielectric constant over a very wide temperature interval is due to disorder in the distribution of B-site ions in the perovskite unit cell. This may lead to composition fluctuations and, as a consequence, to different local curie temperatures in the different regions of the ceramic. Using Fourier transform infrared spectroscopy and analyzing the reflectivity spectra, an investigation of the polar phonons of $Ba(B'_{1/2}B''_{1/2})O_3$ ceramics with B' = Nd^{3+}, Gd^{3+}, Y^{3+}, In^{3+}, Cd^{2+} or Mg^{2+} and B" = Ta^{5+}, Nb^{5+} or W^{6+} was carried by Zurmuhlen et al. to find a correlation between ionic parameters of ceramic materials and their complex permittivity at microwave frequency [**10**]. Phase transition and microwave dielectric properties in $Ca(Al_{1/2}Nb_{1/2})O_3$ and its solid solution with $CaTiO_3$ have been analyzed by Levin et al. using X-ray and neutron power diffraction, transmission electron microscope, Raman spectroscopy and dielectric measurements [**11**].

In this paper we investigate the structural and electrical impedance study of the barium gadolinium niobate, $Ba(Gd_{0.5}Nb_{0.5})O_3$ (BGN) ceramic in the temperature range from 323 K to 463 K and in the frequency range from 50 Hz to 1 MHz by means of dielectric spectroscopy. Dielectric spectroscopy allows measurement of the capacitance (C) and tangent loss (tan δ) over a frequency range at various temperatures. From the measured capacitance (C) and tangent loss (tanδ), four complex dielectric functions assumed can be computed: impedance (Z^*), permittivity (ε^*), electric modulus (M^*) and admittance (Y^*). Studying electrical data in the different functions allow different features of the materials to be recognized. Study of electrical properties, such as dielectric constant, loss tangent, AC conductivity, etc. in this oxide over wide range of frequency and temperature will help

us in assessing its insulating character for potential application.

Experimental

Materials and Methods

The solid state reaction technique was employed for the synthesis of BGN. The raw chemicals used in this study were reagent grade $BaCO_3$, Gd_2O_3, and Nb_2O_5. The mixed raw chemicals in stoichiometric ratio were calcined in alumina crucible at 1300 °C in air for 10 h and brought to room temperature under controlled cooling. The calcined sample was palletized into disc using polyvinyl alcohol as binder. Finally, the discs were sintered at optimized temperature 1100°C for 10 h. The X-ray powder diffraction pattern of the sample at room temperature and the scanning electron micrograph (inset) are shown in **Fig. 1**. All the reflection peaks of the X-ray profile were indexed and lattice parameters were determined using least-squares method with the help of standard computer program (crys fire). A good agreement between the observed and calculated interplaner spacing (d-values) suggests that the compound has a tetragonal structure at room temperature. The least-squares refined cell parameters for tetragonal unit cell are: a = 2.117 Å, c = 3.001 Å. The scanning electron micrograph of the sample was recorded by FEI Quanta 200 equipment to check proper compactness of the sample. From inset of Fig.1, the nature of the micrographs exhibits the polycrystalline texture of the material having highly distinctive and compact rectangular/cubical grain distributions (with less voids). The grain size of the pellet sample was found to be 1.92 μm. Careful examinations (scanning) of the complete surface of the sample exhibits that the grains are homogeneously distributed throughout the surface of the sample. The flat polished surface of sintered pellets were electroded with air drying silver paste and fired at 423 K for 2h before taking any electrical measurement. From the measurement, we have obtained capacitance (C) and tangent loss (tand) by using an LCR meter (Hioki) in the temperature range from 303K to 463K and in the frequency 50Hz to 1 MHz; using (C) and (tan δ), we have computed dielectric constant (ε′) and conductivity (σ) as follows:

$$\varepsilon' = \varepsilon_0 \left(C / C_0 \right) \text{------------ (1)}$$
$$\sigma = \omega \varepsilon_0 \varepsilon'' \text{------------ (2)}$$

where ε_0 is the dielectric permittivity in air, C/C_0 the ratio of capacitance measured with dielectric and without dielectric, ω the angular frequency and $\varepsilon'' = \tan \delta\, \varepsilon'$.

Results and discussion

Permittivity analysis

The relation of angular frequency, ω (= 2πν) with dielectric constant (ε′) and dielectric loss (tan δ) at various temperatures for BGN is described in **Fig. 2**. A relaxation is observed as a gradual decrease in ε′(ω) and as a broad peak in tanδ (ω). The increasing value of ε′ at frequencies below 500 Hz may arise due to space charge polarization.

This behavior is also found in other compounds of the family studied by us in their ceramic form [**12-15**]. It is evident from **Fig. 2(b)** that tan δ peaks (tan δ_{max}) shifts to higher frequency with increasing temperature and that a strong dispersion of tanδ exists in BGN [**16**].
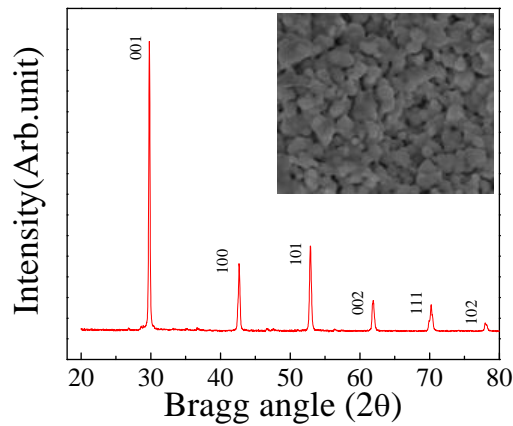
Fig. 1. XRD pattern and scanning electron micrograph (inset) of the Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ at room temperature.
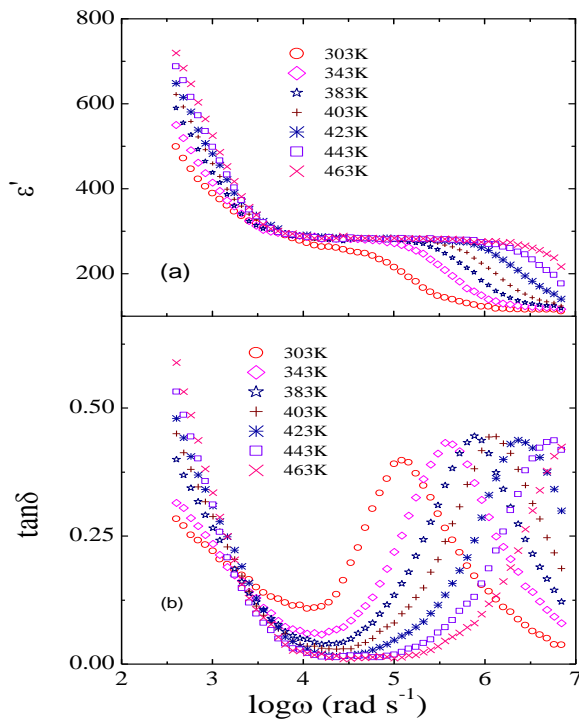

Fig. 2. Logarithmic angular frequency dependence of ε′ (a) and tanδ (b) of Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ at various temperatures.

The most probable relaxation time follows the Arrhenius law given by:

$$\omega_m = \omega_0 \exp\left[\frac{-E_a}{k_B T}\right] \quad \text{----------- (3)}$$

where ω_0 is the pre-exponential factor and E_a is the activation energy. A plot of log ω vs. 1/T is shown in **Fig. 3**, where the symbols are the experimental data points and the solid line is the least squares straight line fit to the data. The activation energy calculated from least square fit to the points is 0.70 eV. It seems clear that the width of loss peaks in **Fig. 2(b)** cannot be accounted for in terms of monodispersive relaxation, but points towards the possibility of a distribution of relaxation times.

If we plot the tanδ data in scaled coordinates, i.e. tanδ /tanδ$_m$ and log (ω/ω$_m$), where ω$_m$ corresponds to the frequency of the loss peak in the tan δ vs. log ω plots, the entire dielectric loss data can be collapsed into one master curve as shown in **Fig. 4**. The scaling behavior of tanδ clearly indicates that the relaxation follows the same mechanism at various temperatures.
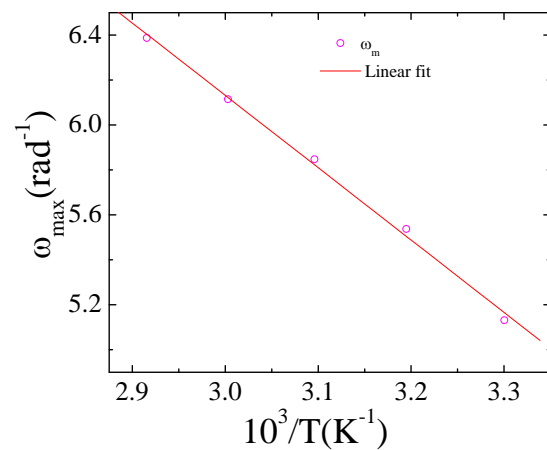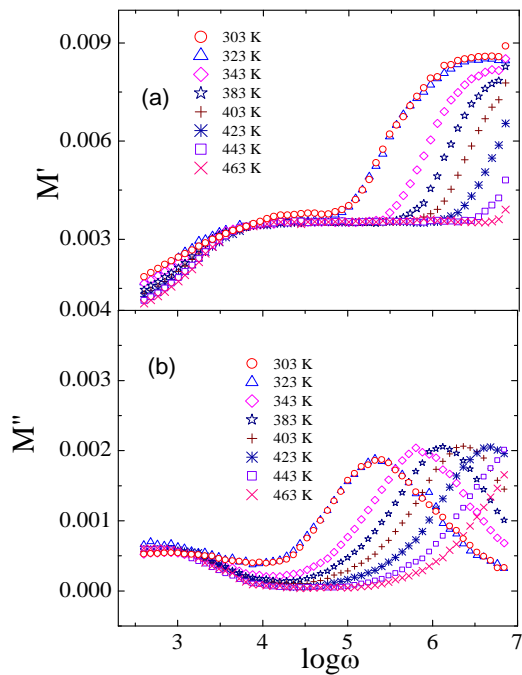

Fig. 3. The Arrhenius plot of ω$_m$ corresponding to tan δ, where symbols are the experimental points and the solid line is the least squares fit to the experimental data.
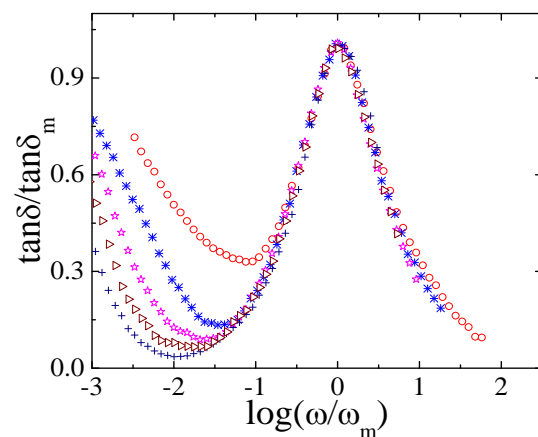
Fig. 4. Scaling behavior of tanδ at various temperatures for Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$.
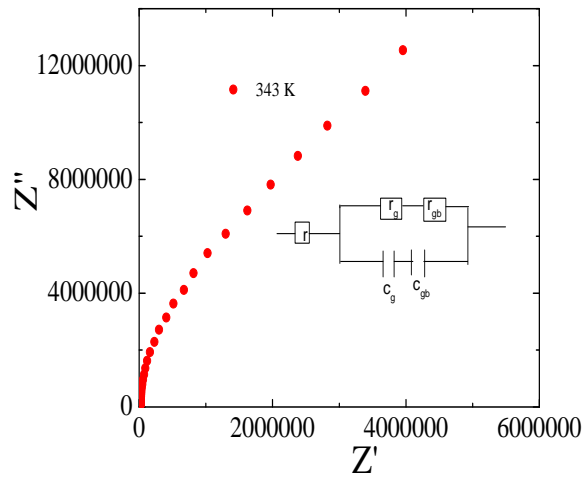
Fig. 5. Complex plane impedance plot of Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ at 343 K, and inset shows RC equivalent circuit.

Fig. 6. Logarithmic angular frequency dependence of M′ (a) and M″ (b) of Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ at various temperatures.

Modulus analysis

Complex plane impedance plots of BGN, plotting the imaginary part Z″ against the real part Z′ at temperature 343 K is shown in **Fig. 5**. For a single phase polycrystalline dielectric material having interfacial boundary layers (grain-boundary), two semicircular arcs or depressed circular arcs may be obtained in the complex plane plot, which can be explained as two parallel RC elements connected in series (inset of **Fig. 5**), one branch is

associated with the grain and other with the grain-boundary of the sample. The real (Z′) and imaginary (Z″) of total impedance of the equivalent circuit are defined as:

$$Z' = R + \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+\left(\omega R_{gb}C_{gb}\right)^2}$$

----------- (**4**)

$$Z'' = R_g\left[\frac{\omega R_g C_g}{1+(\omega R_g C_g)^2}\right] + R_{gb}\left[\frac{\omega R_{gb}C_{gb}}{1+\left(\omega R_{gb}C_{gb}\right)^2}\right]$$

----------- (**5**)

where R$_g$, C$_g$ are the grain resistance and capacitance and R$_{gb}$, C$_{gb}$ are the corresponding quantities for grain-boundary.

Modulus analysis

Complex modulus, electric modulus or inverse complex permittivity, M*, is defined by the following equation

$$M^*(\omega) = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} =$$

$$\frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} = M'(\omega) + jM''(\omega)$$

$$= M_\infty\left[1 - \int_0^\infty e^{-j\omega t}\left(\frac{d\phi(t)}{dt}\right)dt\right]$$

----------- (**6**)

where M′ is the real and M″ the imaginary electric modulus, and ε′ the real and ε″ the imaginary permittivity and $\phi(t)$ gives the time evolution of the electric field within the dielectric.

  Fig. 6 displays the angular frequency dependence of M′ (ω) and M″ (ω) for BGN as a function of temperature. M′ (ω) shows a dispersion tending towards M$_\infty$ (the asymptotic value of M′ (ω) at higher frequencies in **Fig. 6(a)**, while M″ (ω) exhibits a maximum (M″$_m$) centered at the dispersion region of M′ (ω). In **Fig. 6(b)** the position of the peak M″$_m$ shifts to higher frequencies as the temperature is increased. The frequency region below peak maximum M″ determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum M″ the carriers are confined to potential wells, being mobile on short distances.

Conductivity analysis

If we assumes that all dielectric loss in the temperature range studied are due to conductivity, the conductivity can be expressed as σ (ω) = ωε$_0$ε″, here σ is the real part of the conductivity and ε″ is the imaginary part of dielectric constant. The frequency spectra of the conductivity for

BGN at different measuring temperatures are shown in **Fig. 7**. The conductivity shows dispersion which shifts to higher frequency side with the increase of temperature. It is seen from **Fig. 7** that σ decreases with decreasing frequency and becomes independent of frequency after a certain value. Extrapolation of this part towards lower frequency will give σ_{dc}.
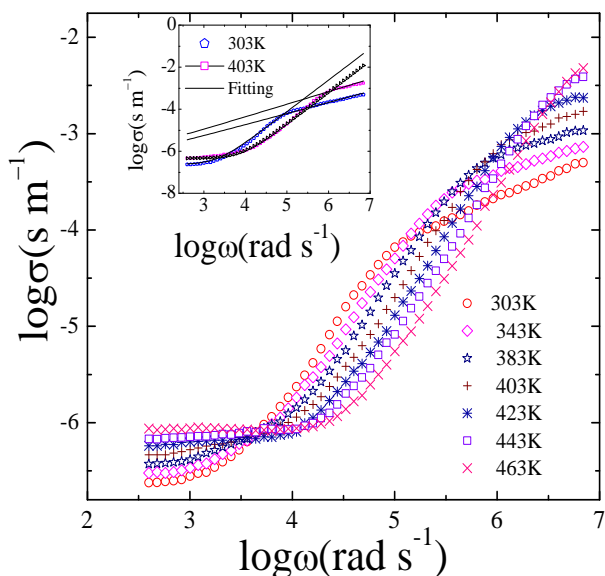
Fig. 7. Logarithmic angular frequency dependence of conductivity (σ) for Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ $_3$ at various temperatures. A fitting by power law for the same at 303 and 403 K is shown by solid lines in the inset.

The very basic fact about AC conductivity in BGN is that σ is an increasing function of frequency. The real parts of conductivity spectra can be explained by the power law define as [**17, 18**]:

$$\sigma = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_H}\right)^n\right] \quad \text{-----------} \quad (5)$$

where σ_{dc} is the DC conductivity, ω_H is the hopping frequency of the charge carriers, and n is the dimensionless frequency exponent. The experimental conductivity spectra of BGN are fitted to **Eq. (7)** with σ_{dc} as variable keeping in mind that the value of parameter n are weakly temperature dependent. The best fit of the conductivity spectra are shown in inset of **Fig. 7** by solid lines.

Conclusion

Logarithmic angular frequency dependence of dielectric constant and loss tangent of the barium gadolinium niobate, Ba(Gd$_{0.5}$Nb$_{0.5}$)O$_3$ (BGN) ceramic synthesized by a solid state reaction technique is investigated in the temperature range from 303 to 463 K. The X-ray diffraction of the sample at room temperature shows a tetragonal phase. The scanning electron micrograph of the sample shows the average grain size of BGN ~1.92 μm. The relaxation mechanism has been discussed in the framework of electric modulus. The logarithmic angular frequency dependence of the loss peak is found to obey an Arrhenius law with

activation energy of 0.70 eV. The scaling behavior of the loss tangent suggests that the relaxation mechanism describes the same mechanism at various temperatures.

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