Physica B 488 (2016) 1–7

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Dielectric and impedance spectroscopic studies of neodymium gallate

Anup Pradhan Sakhya [a,*], Alo Dutta [b], T.P. Sinha [a]

[a] Department of Physics, Bose Institute, 93/1 Acharya Prafulla Chandra Road, Kolkata 700009, India
[b] Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata 700098, India

ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
6 February 2016
Accepted 8 February 2016
Available online 9 February 2016

Keywords:
X-ray diffraction
Ceramics
Dielectric properties
Electric modulus
AC conductivity

ABSTRACT

The AC electrical properties of a polycrystalline neodymium gallate, $NdGaO_3$ (NGO), synthesized by the sol–gel method have been investigated by employing impedance spectroscopy in the frequency range from 42 Hz to 5 MHz and in the temperature range from 323 K to 593 K. The X-ray diffraction analysis shows that the compound crystallizes in the orthorhombic phase with Pbnm space group at room temperature. Two relaxation processes with different relaxation times are observed from the impedance as well as modulus spectroscopic measurements, which have been attributed to the grain and the grain boundary effects at different temperatures in NGO. The complex impedance data are analyzed by an electrical equivalent circuit consisting of a resistance and a constant phase element in parallel. It has been observed that the value of the capacitance and the resistance associated with the grain boundary is higher than those associated with the grain. The temperature dependent electrical conductivity shows the negative temperature coefficient of resistance. The frequency dependent conductivity spectra are found to follow the power law.

1. Introduction

For the preparation of a good quality high temperature superconductor (HTS) thin film, selection of a suitable substrate is imperative to accomplish a decent epitaxial growth [1]. In this perspective, perovskite oxides have been generally examined as they suffice the majority of the prerequisites for proper HTS substrates, for example, good lattice match, similar crystal structures, good surface and good microwave properties [1,2]. Among the different perovskite thin film substrates, $NdGaO_3$ (NGO) is normally utilized as a substrate for HTS thin-film deposition testimony in the light of lattice and thermal expansion match, specifically with $YBa_2Cu_3O_{7-x}$ [1]. Further, the NGO single crystal is a promising substrate material for GaN film deposition [3].

NGO crystallizes in the orthorhombic Pbnm space group (D_{2h}^{16}) at the ambient temperature with four formula units per primitive cell [4–6]. Savytskii et al. have performed the Raman-scattering experiment of NGO in the low-temperature range and found that it does not undergo any phase transition (magnetic or structural) down to 12 K [7]. Suda et al. have ascertained the phonon-dispersion curves of the NGO crystal on the basis of a rigid-ion model. They have additionally considered the temperature dependence of the Raman-active phonon spectrum in NGO and dynamic phonon range in NGO and found that the temperature dependence of the line width of the A_{1g} mode can be well described by the cubic anharmonic term in the expansion series of the crystal potential energy [8].

Rani et al. have studied the zone center frequencies of NGO utilizing a short range force constant model in the orthorhombic phase [9]. The temperature dependence of the Raman modes for $LaGaO_3$ and NGO has been measured by Sanjuan et al. from 300 to 860 K. They have observed that for the NGO crystal the softening of the mode frequencies is accompanied by the line broadening as the temperature increases, however, there exists no phase transition for the crystal up to 1816 K [10]. Reshak et al. have performed the density functional theory calculation for the centrosymmetric NGO utilizing the full potential linearized augmented plane wave method with the LDA and LDA+U exchange-correlation [11]. Bartolome et al. have studied the heat capacity of NGO in the temperature range of $0.15\ K < T < 3\ K$ and observed a sharp anomaly in the specific heat of NGO at $T_N = 0.97 \pm 0.01$ K [12]. Marti et al. [13] have studied the three-dimensional magnetic ordering of the Nd^{3+} ions in NGO by means of neutron powder diffraction and suggested a C_z configuration (Bertaut notation [14]) of the ordered Nd moments as well as a fairly isotropic g factor.

To the best of our knowledge, no systematic study has been performed to investigate the dielectric properties of this material in the low-frequency range. In this paper, the synthesis of NGO has been reported by utilizing the sol–gel technique. We have studied the complex impedance, electric modulus, and AC conductivity of

* Corresponding author.
E-mail address: npshakya31@gmail.com (A.P. Sakhya).

http://dx.doi.org/10.1016/j.physb.2016.02.017
0921-4526/

the material as a function of temperature (323–593 K) in the frequency range from 42 Hz to 5 MHz. Earlier, NGO was prepared by the high-temperature solid-state reaction technique using their corresponding pure oxides, that typically have an effect on the atomic stoichiometric ratio as a result of oxygen vacancy and the formation of undesirable phases [15]. To overcome this issue, we have utilized the sol–gel technique [16], an inexpensive route with less instrumentation, operated at an ambient temperature to synthesize phase pure NGO material. To comprehend the electrical properties of a material, comprehension of its microstructure which primarily contains grains and grain boundaries is vital. Impedance spectroscopy is a very powerful technique which can be utilized to comprehend the effects of complex microstructural features on the electrical properties of NGO. In this technique, the electrical response may be depicted in terms of impedance ($Z^*=Z'-jZ''$) and/or electric modulus ($M^*=M'+jM''$), having both real and imaginary parts [17]. The imaginary part of the impedance (Z'') plot highlights the component with the largest resistance, whereas the imaginary part of the electrical modulus (M'') plots are dominated by the component with the smallest capacitance. Thus, the consolidated utilization of impedance and modulus formalism can be utilized to get the contribution to the general electrical properties by various components [18].

It is to be mentioned that Dielectric measurements are an important means of studying the dynamical properties (capacitance, conductance, permittivity and loss factor) of a dielectric. Dielectric polarization is the displacement of charged particles under the action of the electric field so that there is a net electric dipole moment per unit volume in atoms, ions or molecules of the material. At the microscopic level, several dielectric mechanisms can contribute to dielectric behavior. It is not necessary that all of them are present in a particular material. Each polarization has its own relaxation time which may be different in different materials. In the frequency range mHz to MHz, space charge polarization and orientational polarization are effective. These contributions are important to understand the structural defects and structure in solids. From an application point of view, it is essential that the dielectric properties of a material are measured under realistic operating conditions. This means that the frequency range of measurement must be chosen to be relevant to the device application. This is particularly important for measurement of tanδ, which can be strongly dependent on frequency, especially at low frequencies. Most pyroelectric devices are operated in the frequency range from 0.1 Hz (for motion sensors) up to about 100 Hz [19]. Ceramic capacitors are mostly used because they are cheap and reliable. Its loss factor is low though it depends upon the materials in use. Ceramic capacitors are normally used in the radio frequency range and they have some audio frequency applications [20]. Hence, we have chosen this frequency range to investigate the electrical properties of NGO.

2. Experimental details

2.1. Sample preparation

NGO was synthesized by the sol–gel citrate method [21,22]. At first, reagent grade $Nd(NO_3)_3.6H_2O$ (Alfa Aesar) and $Ga(NO_3)_3.9H_2O$ (Alfa Aesar) were taken in stoichiometric proportion and separately dissolved in de-ionized water by stirring with a magnetic stirrer. The obtained clear solutions were then mixed together. Citric acid and ethylene glycol were added to this solution drop wise according to the molar ratio of {Nd^{3+}, Ga^{3+}}:{citric acid}:{ethylene glycol}=1:1:4 to form a polymeric metal cation network. The solution was stirred at 343 K using a magnetic stirrer for 4 h to get a homogeneous mixture of brown color and then dried at 393 K to obtain the gel precursor. In the next step, the gel was ground to get a fine powder. The powder was calcined at 1523 K in air for 10 h to get the powder of NGO. The calcined sample was pelletized into a disc of diameter 8 mm and thickness 1.16 mm utilizing polyvinyl alcohol as a binder. Finally, the disc was sintered at 1623 K and cooled down to room temperature by cooling at the rate of 1 K/min.

2.2. Sample characterization

The X-ray diffraction (XRD) pattern of the sample was taken at room temperature utilizing a Rigaku Miniflex-II X-ray powder diffractometer in the 2θ range of 10–120° by scanning at 0.02° per step. The Cu K_α radiation generated at 30 kV and 15 mA was used as the source. The Rietveld refinement of the XRD profile was performed utilizing the Fullprof program [23]. The background of the XRD profile is fitted by the linear interpolation while the peak shapes are described by the pseudo-Voigt function. All through the refinement, the scale factor, zero correction, background, half width parameters, lattice parameters, positional coordinates and isotropic thermal parameter (B_{iso}) of cations are varied. Occupancy parameters of all the ions are kept fixed during refinement. No correlation between the positional and thermal parameters was observed during refinement and as such it was possible to refine all the parameters together. Scanning electron micrographs of the sample was taken by FEI Quanta 200 scanning electron microscope (SEM). The bulk density of the material was measured by Archimedes principle as well as from the pellet dimensions.

For dielectric measurements, both the flat surfaces of the sintered disc were polished. Two thin gold plates were used as electrodes. The capacitance (C), impedance (Z), phase angle (φ) and conductance (G), of the sample, were measured in the frequency range from 42 Hz to 5 MHz and in the temperature range of 323 – 593 K using a computer controlled LCR-meter (HIOKI-3552) at the AC voltage of 1.0 V. The temperature was controlled by a programmable temperature controller (Eurotherm 818 P) connected with the oven. Each measured temperature was kept constant with an accuracy of $\pm$ 1 K. The complex dielectric constant ε^* ($= 1/i\omega C_o Z^*$) was obtained from the temperature dependence of the real (Z') and imaginary (Z'') components of the complex impedance Z^* ($=Z'+iZ''$), where, ω is the angular frequency ($\omega=2\pi\nu$) and $i=\sqrt{-1}$. $C_o=\varepsilon_o A/t$ is the empty cell capacitance, where ε_o is the permittivity of free space (8.854×10^{-12} F/m), t is the sample thickness, and A is the cross-sectional area of the gold electrode.

3. Results and discussion

3.1. Structural analysis

The XRD pattern of NGO is shown in Fig. 1. A decent agreement between the observed (symbols) and refined (lines) data proposes that the compound is crystallized in the orthorhombic perovskite structure with the space group *Pbnm* which is in concurrence with the past study [24]. The unit-cell parameters, atomic positions, reliability factors, bond lengths, and bond angles for the diverse constituent ions are listed in Table 1. A schematic presentation of the NGO unit cell is shown in Fig. 2, with the following distribution of ions in crystallographic positions: Nd^{3+} ions in 4c, Ga^{3+} ions in 4b and O^{2-} ions in 4c and 8d. Ga^{3+} ions are encompassed by six O^{2-} ions, constituting GaO_6 octahedra. The orientation of the corner-sharing GaO_6 octahedra in NGO can be portrayed by utilizing the tilting Glazer system $a^-a^-c^+$ [25] demonstrating that the octahedra turn along the Cartesian axes x and y in consecutive