Hindawi Publishing Corporation
Research Letters in Materials Science
Volume 2008, Article ID 746256, 5 pages
doi:10.1155/2008/746256

Research Letter

Complex Impedance Spectroscopic Properties of $Ba_3V_2O_8$ Ceramics

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Received 27 November 2007; Accepted 18 February 2008

Recommended by Stephen Danforth

The polycrystalline sample of $Ba_3V_2O_8$ was prepared by a high-temperature solid-state reaction technique. The effect of temperature on impedance parameters was studied using an impedance analyzer in a wide frequency range (10^2–10^6 Hz). The real and imaginary parts of complex impedance trace semicircles in the complex plane. The temperature-dependent plots reveal the presence of both bulk and grain boundary effects above 125°C. The bulk resistance of the material decreases with rise in temperature. This exhibits a typical negative temperature coefficient of resistance (NTCR) behavior of the material. The modulus analysis suggests a possible hopping mechanism for electrical transport processes of the material. The nature of variation of dc conductivity suggests the Arrhenius type of electrical conductivity.

1. INTRODUCTION

Dielectric oxide ceramics with high permittivity, low dielectric loss, and near zero temperature of dielectric constant are critical elements in components such as resonators, oscillators, and filters for wireless communications [1–3]. Relatively few ceramic systems are currently available with the properties needed for practical applications at various operating frequencies [4]. Recently the materials having the coupling between the ferroelectric and ferromagnetic ordering parameters received considerable attention of the researchers to study their both fundamental physics and device engineering [5]. A new perovskite-related phase with composition 3CaO:Nb_2O_5 in the system of CaO–Nb_2O_5 was reported long ago by Ibrahim et al. [6]. Recent studies of phase equilibria study [7] of the CaO–Nb_2O_5 system undertaken in air atmosphere in the higher CaO composition (70–90 mol %) showed that the 3 : 1 molar composition of system can have a small amount of $Ca_2Nb_2O_7$ as impurity phase. Three equilibrium phases, $Ca_3Nb_2O_8$, $Ca_2Nb_2O_7$, and $CaNb_2O_6$, of CaO:Nb_2O_5 systems were shown in the earliest published work [6]. Substitution of Ba (group IIA element) at the Ca sites and vanadium at the Nb of the above system can provide many solid solutions with many interesting properties for wide industrial applications. Detailed literature survey of the system exhibits that not much has been reported on the importance of the material for applications, therefore, we have extensively studied the various properties of $Ba_3V_2O_8$ compound. The work done on structural and dielectric properties of the compound have been reported elsewhere [8]. In this paper, the electrical (complex impedance) properties of $Ba_3V_2O_8$ are reported.

2. EXPERIMENTAL DETAILS

The polycrystalline sample of $Ba_3V_2O_8$ was prepared by a high-temperature solid-state reaction technique using high-purity (99.9%) ingredients $BaCO_3$ and V_2O_5: in a suitable stoichiometry. These ingredients were mixed thoroughly; first in an air atmosphere for 1 hour, and then in alcohol (i.e., methanol) for 1 hour. The homogeneous mixture of the compound was calcined in an alumina crucible at 925°C for 5 hours. The process of grinding and calcinations was repeated several times until the formation of the desired compound was confirmed (using X-ray diffraction pattern). The calcined fine powder was cold pressed into cylindrical pellets of 10 mm diameter and 1-2 mm of thickness at a pressure of 4×10^6 Nm^2 using a hydraulic press. Polyvinyl alcohol (PVA) was used as binder to reduce the brittleness of the pellets. The binder is burnt out during high-temperature

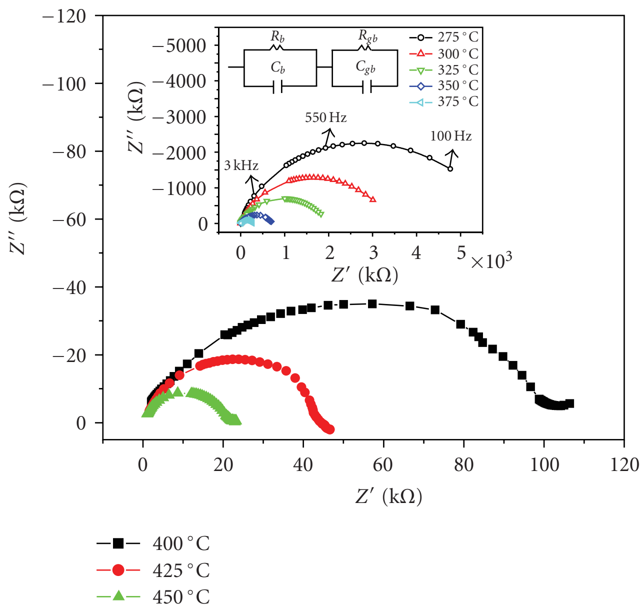


Figure 1: Complex impedance plot of $Ba_3V_2O_8$ at selected temperatures with equivalent circuit.

sintering. The pellets were sintered at an optimized temperature (975°C) and time (10 hours) in air atmosphere using an alumina crucible. In order to study the electrical/impedance properties of the compound, both the flat and parallel surfaces of the samples were polished and electroded with air-drying conducting silver paint. After electroding, the pellets were dried at 150°C for 4 hours to remove moisture (if any) and then cooled them to room temperature before taking electrical measurements. The impedance parameters were obtained using a computer-controlled impedance analyzer (HIOKI 3532 LCR HiTESTER) in a wide frequency range (10^2–10^6 Hz) at different temperatures (23–500°C).

3. RESULTS AND DISCUSSION

3.1. *Impedance studies*

The grain, grain boundary, and interface properties of ceramics are studied using the complex impedance formalisms, which include the determination of capacitance (bulk and grain boundary), relaxation frequency, and electronic conductivity. A polycrystalline material usually gives grain and grain boundary properties with different time constants leading to two successive semicircles. The electrical properties of a material are often represented in terms of some complex electrical parameters like complex permittivity ε^*, complex impedance Z^*, electric modulus M^*, and loss tangent $\tan\delta$. They are related to each other as follows:

$$Z^* = Z' - jZ'' = R_s - 1/j\omega C_s,$$
$$M^* = M' + jM'' = j\omega C_o Z^*, \qquad (1)$$
$$\varepsilon = \varepsilon' - j\varepsilon'', \qquad \tan\delta = \frac{\varepsilon''}{\varepsilon'},$$

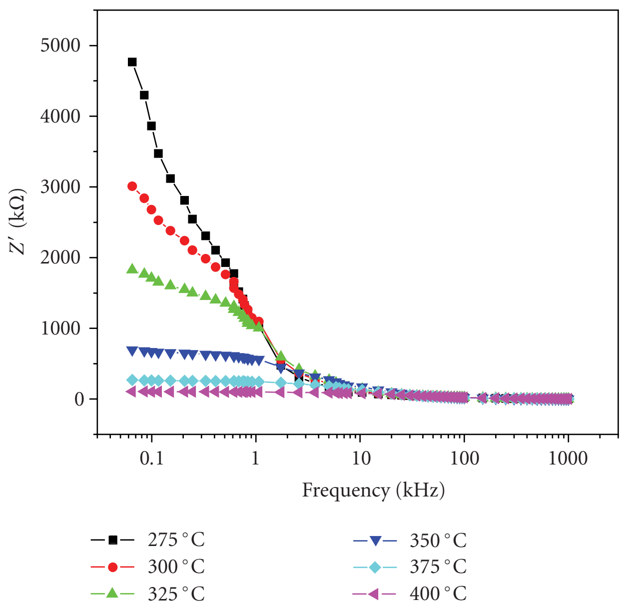
where R_s is the series resistance, $\omega = 2\pi f_r$ (f_r = resonance frequency), C_s the capacitance in series, $j = (-1)^{1/2}$ the imaginary factor, and C_o is the vacuum capacitance of the circuit elements. Above four expressions give a wide scope for graphical representation. The complex impedance of the electrode/ceramic/electrode structures can be demonstrated as the sum of the single RC circuit with parallel combination.

The plot of Z' versus Z'' (Nyquists diagram) at different temperatures (275–450°C) is shown in Figure 1. The inspection of the semicircle showed that there is a depression angle instead of a semicircle centered on the real axis. The behavior of the electrical response follows Cole-Cole formalism [9]. It is observed that at lower temperatures (shown in inset), a single semicircular arc appears. This single semicircular arc suggests the presence of grain interior (bulk) property of the material [10]. However, at higher temperatures, another arc appears, and the spectrum comprises of two semicircular arcs with their centers lying below the real axis. The high-frequency semicircle (first arc) can be attributed to the bulk (grain) properties of the material arising due to a parallel combination of bulk resistance (R_b) and bulk capacitance (C_b). The value of bulk resistance (R_b) and grain boundary resistance (R_{gb}) above 400°C has been obtained from the intercept of the semicircular arc on real axis (Z'). The electrical process taking place within the material can be modeled on the basis of brick-layer model [11]. However, with subsequent rise in temperatures, both the grain and grain-boundary phenomena appear to merge into a single arc (pattern) suggesting a substantial modification in the overall electrical behavior of the material.

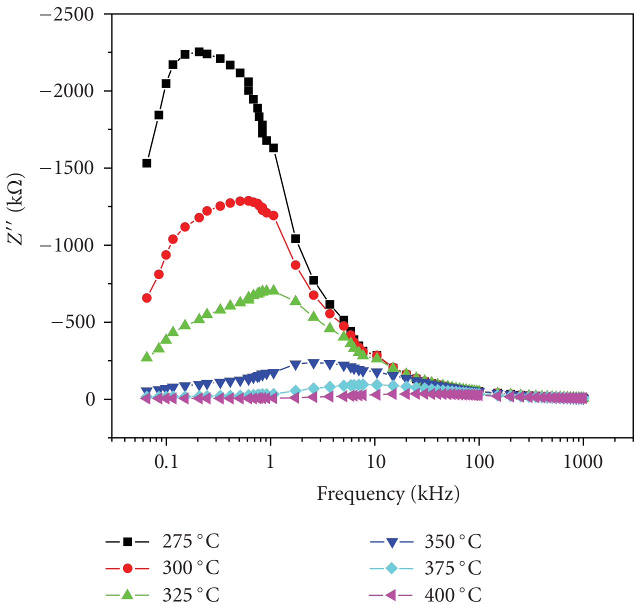
Figure 2(a) shows the variations of real part of impedance with frequency at different temperatures. This plot is suitable for evaluation of the relaxation frequency of most resistive component. The peak occurs above 300°C, and shifts to higher frequencies on increasing temperature. This exhibits the occurrence of relaxation in the system. The relaxation frequency is obtained either from the plot of Z versus frequency or semicircles (from the Nyquist plot). The peak broadening (due to increase in temperature) suggests the presence of temperature-dependent relaxation processes in the compound [12]. The relaxation process is due to the presence of immobile species at low temperature and defects at higher temperature. Figure 2(b) shows the variation of Z'' with frequency at different temperatures. The imaginary part of impedance decreases with rise in frequency. This plot exhibits that conduction is increasing with rise in temperature and frequency. The coincidence of the impedance Z values at higher frequencies at all the temperatures indicates a possible release of space charge [13].

3.2. *Modulus studies*

The complex electric modulus was calculated using the relations; $M^* = M' + jM''$, where $M' = \omega C_o Z''$, and $M'' = \omega C_o Z'$ ($\omega = 2\pi f_r$), C_o = geometrical capacitance = $\varepsilon_o A/t$ (ε_o = permittivity of free space, A = area of the electrode surface, and t = thickness). In order to confirm the ambiguity arising in connection with the presence of grain boundary effect at elevated temperatures, the impedance data has been



(a)



(b)

FIGURE 2: (a) Variation of Z' as a function of frequencies at selected temperatures. (b) Variation of Z'' as a function of frequencies at selected temperatures.

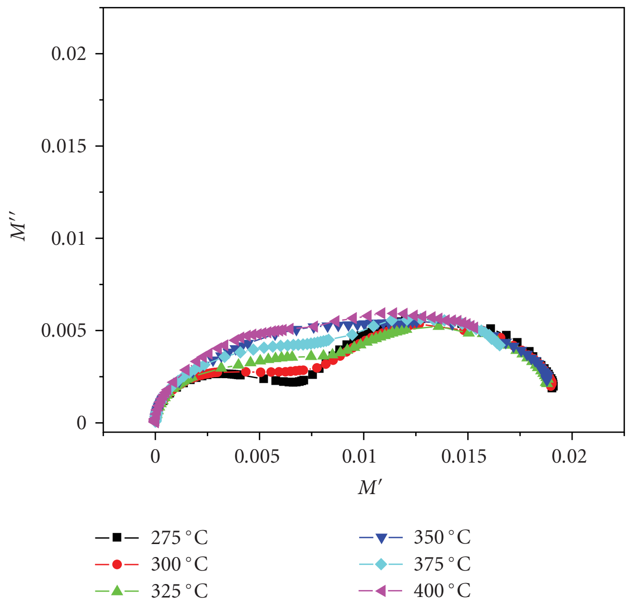


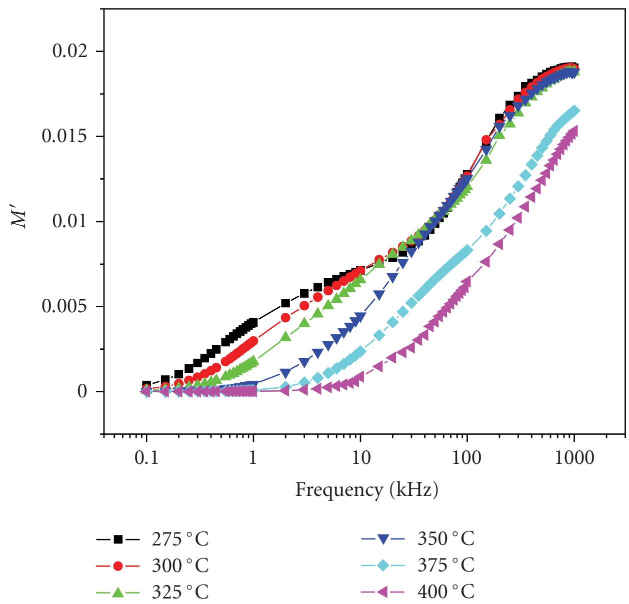
FIGURE 3: Complex modulus plot of $Ba_3V_2O_8$ at selected temperatures.

replotted in the modulus formalism at the same temperatures (Figure 3). It shows two semicircular arcs in the complex modulus plots with a small semicircle at low frequency and very large semicircular arc in the high-frequency region at all the temperatures. A relative comparison of the complex impedance spectrum and modulus spectrum of $Ba_3V_2O_8$ shows two arcs in the modulus pattern with different radius, whereas only one arc in the impedance spectrum.

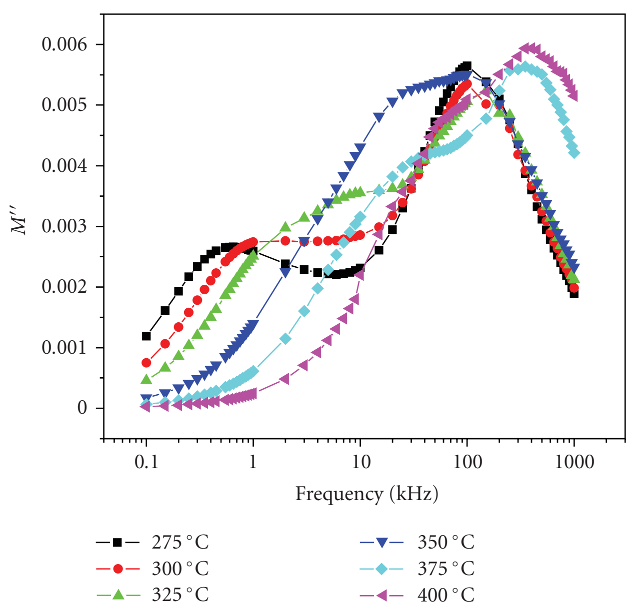
Figure 4(a) shows the variation of M' and as a function of frequency at selected temperatures. It shows a very low value (approximately zero) of M in the low-frequency region. A continuous dispersion on increasing frequency may be due to the short-range mobility of charge carriers. Figure 4(b) exhibits that the maxima of the imaginary components of modulus (M''_{max}) shift towards higher relaxation frequencies with rise in temperature. This behavior suggests that the dielectric relaxation is thermally activated in which hopping mechanism of charge a carrier dominates intrinsically. The asymmetric broadening of the peak indicates the spread of relaxation with different time constant, and hence, relaxation in the material is of non-Debye type .The magnitude of the peak increases on increasing temperature.

The electrical conductivity(s) is a thermally activated process, and obeys the Arrhenius law $\sigma = \sigma_0 \exp(-Ea/KT)$ where the symbols have their usual meanings. Figure 5(a) shows the variation of σ (bulk conductivity σ_b) against $10^3/T$. The activation energy (Ea) of $Ba_3V_2O_8$ can be calculated from the slope of a straight line (Figure 5(a)), and the corresponding value of Ea is found to be 1.28 eV. The bulk conductivity of the sample was evaluated from the complex impedance plots at different temperatures. The value of grain-boundary resistance (R) at different temperatures is also estimated from the complex impedance spectrum. In this case, dc conductivity increases with rise in temperature showing a typical characteristic of a semiconductor (i.e., negative temperature coefficient of resistance).

The peak frequency M''_{max} helps to evaluate relaxation time (τ) using a relation $\omega_{max}\tau = 1$. The variation of τ as a function of temperature (275–475°C) is shown in Figure 5(b) (inset). The variation of τ as a function of inverse of absolute temperature appears to be linear which follows the relation $\tau = \tau_0 \exp(-Ea/KT)$, where the symbols have their usual meaning. The value of activation energy is found to be 1.29 eV.



(a)

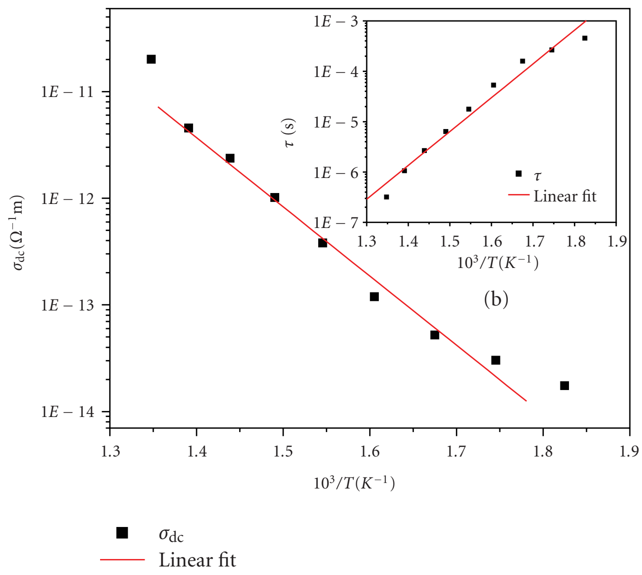


(b)

FIGURE 4: (a) Variation of M' and as a function of frequency at selected temperatures. (b) Variation of M'' and as a function of frequency at selected temperatures.

4. CONCLUSIONS

The polycrystalline sample $Ba_3V_2O_8$ of prepared by a high-temperature solid-state reaction technique. Complex impedance spectroscopy was used to characterize the electrical properties of the material. The electrical conduction in compound is due to bulk and grain-boundary effect. Both the bulk and grain boundary resistance decrease with rise in temperature indicating a typical NTCR behavior of the compound. This compound also exhibits the temperature-dependent relaxation phenomena. Electrical modulus analysis has confirmed the presence of hopping mechanism in the material. The ac conductivity shows a typical Arrhenius type of electrical conductivity. The activation energy of the compound was found to be 1.28 eV (due to grain).



(a)

FIGURE 5: (a) Variation of σ_{dc} (due to bulk) of $Ba_3V_2O_8$ with inverse of temperature. (b) Variation of relaxation time (τ) as a function of temperature calculated from the M with frequency (inset).

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