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Pseudo-relaxor behavior in 0.35La₂O₃-0.65Nb₂O₅ glass prepared by aerodynamic levitation method



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1. Introduction

Materials with high dielectric constants are essential to the miniaturization of many capacitance-based electronic devices. To achieve excellent dielectric properties, doping as the most convenient method is frequently used [1]. Recently, with the using of some new manufacturing techniques, an increasing numbers of intimately well-researched materials were reported to exhibit new excellent properties [2]. For example, the aerodynamic levitation furnace (ALF), a container-less processing technique, can suppress the heterogeneous nucleation from container wall, achieve deep under-cooling from molten materials and allow the synthesis of materials with novel properties by phase selection. Hexagonal BaTiO₃ (h-BaTiO₃) crystal synthesized by this new method was reported to show a giant permittivity over 10⁵ and a low tan δ of ~0.01 at room temperature (RT) [2–4]. The permittivity value is much larger than the value of \sim 200 for both ceramics and crystals synthesized by traditional methods [5]. This finding evidences that the ALF can be a useful method to achieve excellent dielectric properties in the well-known materials.

More recently, the La₂O₃-Nb₂O₅ (LNO) binary glasses had been successfully fabricated via the ALF technique. The glasses were corroborated to exhibit a high refractive index of \sim 2.15 with a wide

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ABSTRACT

 $0.35La_2O_3 - 0.65Nb_2O_5$ glasses were prepared by aerodynamic levitation method. The dielectric properties of the sample were investigated as a function of temperature $(30 - 700 \,^{\circ}C)$ in the frequency range from 100 Hz to 1 MHz. The glasses show a temperature and frequency-independent dielectric constant of ~40 below 200 $^{\circ}C$. A relaxor-like behavior was observed above 200 $^{\circ}C$, which was found to be composed of two relaxations with the activation energy of 1.32 eV and 1.3 eV for the low- and high-temperature relaxations, respectively. Impedance analysis reveals that the low-temperature relaxation is a conduction relaxation associated with hopping motion of oxygen ions and the high-temperature one is a Maxwell-Wagner relaxation associated with phase boundary. The relaxor-like behavior is attributed to the combining effect of both relaxations.

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transmittance window ranging from 380 to 5500 nm [6–8]. It may be potential candidate for optical application in the region from visible to IR light. According to the theoretical formula $n = \sqrt{\varepsilon_r \mu_r}$ (where *n* is the refractive index, ε_r is the relative permittivity, and μ_r is its relative permeability) [9], the optical properties are directly correlated with the dielectric properties. The amazing high refractive index implies that the material might show superior dielectric properties. However, the dielectric properties of LNO glasses have not yet been reported.

In the present work, we conducted dielectric measurements on the LNO glasses in the frequency range from 100 Hz to 1 MHz and temperature range from 30 °C to 600 °C. An apparent relaxor-like behavior appears above 200 °C, whose mechanism was discussed in details.

2. Experimental details

LNO glasses pellet used for dielectric investigation (3.5-mmdiameter) were fabricated by ALF method. Detailed synthesis processes were given elsewhere [7]. The dielectric properties were measured on a Wayne Kerr 6500B precise impedance analyzer (Wayne Kerr Electric Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside <u>the PST-2000HL</u> dielectric measuring system (Wuhan Pusite Instrument Co., Wuhan. China). The experiment temperature varying with a heating rate of 3 K/min was automatically controlled by a Stanford temperature controller (Stanford Research System Instrument, Sunnyvale, CA). Before measuring, electrodes were made by printing platinum paste on both sides of the sample and then fired at 800 °C for 2 h in order to remove the polymeric component and get good sample/electrode contact.

3. Results and discussion

Fig. 1 depicts the dielectric constant $\varepsilon'(a)$ and loss tangent tan δ (b) as a function of temperature (T) at a number of representative frequencies for the LNO glasses. It is clearly seen that the $\varepsilon'(T)$ basically behaves as a frequency-independent plateau with the dielectric constant of ~40 below 200°C. Within the same temperature range, the loss tangent shows a value less than 0.02. The permittivity found here is twice as large as LaNbO₄ prepared by the conventional methods (ε' : ~19, tan δ : ~0.05) [10,11]. Further increasing the temperature, $\varepsilon'(T)$ shows a dielectric anomaly (peak). The peak position shifts to high temperature while its intensity decreases with increasing frequency. This is the typical relaxor behavior. When the temperature is higher than 500 °C, $\varepsilon'(T)$ increases rapidly, owing to the fact that when the temperature trends to the glass-transition temperature ($T_g \approx 800 \,^{\circ}$ C), $\varepsilon'(T)$ will register a sharp peak as reported by Yu et al. in h-BaTiO₃ [2]. In the $tan\delta(T)$ curve, it behaves as a temperature-independent constant in the temperature of T < 200 °C. Whereas when the temperature is higher than 200°C, it nearly exponentially increases with temperature forming a pronounced background. The strong increasing background is frequently caused by conductivity, which will shadow any relaxations.

The possibility that the observed dielectric anomaly related to ferroelectric phase-transition can be excluded, because ferroelectricity has never been reported in none of the components. Besides, thermal analysis only revealed a glass-transition temperature close to 800 °C [7]. Dielectric anomaly unrelated to ferroelectricity has been widely reported in glass materials [12-14], and whose mechanism is still an open question. In single crystal, ceramics, and even thin film systems, this kind of anomaly is called pseudorelaxor behavior [15]. This behavior can result from negative capacitance as the investigated sample is highly leaky at high temperatures [16]. Our recent work pointed out that the anomaly is composed of two close relaxations with the low-temperature one being the dipolar relaxation and the high-temperature one being the Maxwell-Wagner (MW) relaxation. Both relaxations are related to the hopping motion of oxygen vacancies [17,18]. The absence of negative capacitance effect in the present sample indicates that the two-relaxation model might account for the observed dielectric anomaly.

In order to obtain more information about the dielectric relaxation, the background must be eliminated. We, therefore, applied the electric modulus, which is known as a powerful approach to reveal the relaxation obscured by the background [19,20]. Fig. 2 (a) displays the temperature dependence of the imaginary part of the electric modulus. At a first glance, it seems that M''(T) contains only one thermally activated relaxation. But a careful examination revealed that there exists a weak hump in the low-temperature side of the M''(T) peak. This is further confirmed by the normalized plot as shown in Fig. 2(b), therein, the normalized electric modulus peak (M''/M''_{max}) recorded at 1 kHz was plotted as a function of the reduced temperature (T/T_P) with $M''_{\rm max}$ and $T_{\rm p}$ being the peak intensity and position, respectively. Theoretically, the peak for a thermally activated relaxation is dominated by the relaxation time (τ) , which is frequently described by the Arrhenius relation, Vogel-Fulcher relation, or a complicated relaxation-time distribution function [21]. The relaxation peak is physically the same as the atomic absorption line, which links the lower and higher energy levels. In condensed mater, the level expands forming energy band; the absorption line thus becomes a peak. No matter what relation is used, the relaxation peak should be symmetric in shape. It was found that the half value of the full width at half maximum (FWHM) of the low temperature side is 0.135, which is larger than the 0.12 of the high temperature side. This feature convincingly evidences that one or more relaxation peaks exist in the low temperature side. For a thermally activated relaxation, the higher frequency it appears in the frequency spectrum, the lower temperature it occurs in the temperature spectrum (and vice versa). It is naturally expected that the normalized frequency peak should predicate an additional peak in the high-frequency side. To clarify this inference, we performed detailed dielectric measurements in the frequency domain. Fig. 2 (c) shows the spectroscopic plots of M''(f) at a series of temperatures. Likewise, a pronounced M''(f) peak following the thermally activated behavior can be seen. The normalized electric modulus peak (M''/M''_{max}) recorded at 500 °C was plotted as a function of the logarithmic scale of the normalized frequency $(f/f_{\rm P})$, with $f_{\rm p}$ being the peak position in the frequency domain. As expected, the half value of the FWHM of the high-frequency side (0.79) is larger than that of the low-frequency side (0.67), confirming the multiple relaxation processes in the sample. Impedance analysis, which will be discussed late, reveals that there are two relaxation processes in the sample. For convenience, the two relaxations were named as R1 and R2 in the order of ascending temperature (descending frequency). Relaxation parameter analysis is favorable for better understanding the relaxation mechanism. In doing so, the accurate peak positions for both relaxations are needed. Therefore, the M''(f) curves were fitted by using two Gaussian peaks. As an illustration, the



Fig. 1. Temperature dependence of ε' (a) and tan δ (b) at selected frequencies for the LNO glass.



Fig. 2. (a) and (c): Temperature and Frequency dependence of the imaginary part of the electric modulus for the LNO. (b) and (d): The normalized modulus vs. the reduced temperature and frequency (in log scale). (e): A representative example showing the comparison between the experimental data (open circles) measured at 500 °C and fitting result (solid curve) as well as the resulting peaks (dashed curves). (f): The Arrhenius plots of LNO for the two relaxation.

comparison between the experimental data (open circles) of M''(f) measured at 500 °C and the fitting curve (solid line) as well as the resulting peaks (dashed lines) were presented in Fig. 2 (e). The fitting curve matches well with the experimental data, indicating perfect fitting result was achieved. Then, the relaxation parameters can be deduced in terms of the Arrhenius law:

$$f = f_0 \exp(-E_a/k_B T) \tag{1}$$

where f_0 is the pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann's constant. Fig. 2 (f) plots the peak frequency f_p obtained from the fitting results versus the reciprocal of the measuring temperature for R1 and R2. The values of E_a and f_0 were calculated, respectively, to be 1.32 eV and 4.3×10^{13} Hz for R1, 1.3 eV and 2.5×10^{12} Hz for R2. The activation energy with the value of ~1.0 was widely reported to be closely related to the diffusion of oxygen vacancies [22,23]. Oxygen vacancies (also called F or color centers) are the ubiquitous point defects in oxides, which are induced due to the loss of lattice oxygen ions during the high-temperature sintering process, nonstoichiometry, acceptor doping, etc. At high enough temperatures, the vacancies become mobile carriers. Oxygen atoms can move via the nearby vacancies and can contribute to both conduction and polarization in terms of hopping motion [24]. The activation energy for both relaxations is somewhat higher than 1.0 eV. This is because that the electromigration of oxygen vacancies leads to tested sample actually acting as an ionic conductor. The relaxations in which were widely reported to show a non-Debye behavior due to strong interaction between the conductive species and their surrounding medium [25]. This interaction in glasses was believed to be significantly stronger than that in crystals and ceramics. The measured



Fig. 3. The impedance spectrum data measured at 460 and 600 °C is presented in terms of Z' vs. Zn/f. The inset in Fig. 3 is the impedance spectrum for the sample varying with increasing dc bias at 600 °C.

activation energy (E_a) for the non-Debye relaxation as predicated by the coupling theory [26] is lower than the real value of activation energy (E_a^*). Relationship between the two parameters can be found in our previous paper [27].

The above results strongly support that the two-relaxation model is the cause of the observed dielectric anomaly. In this model, the low-temperature is a dipolar relaxation and the hightemperature one is a MW relaxation. In order to clarify the natures of the two relaxations, we performed impedance analysis. Fig. 3 exhibits the impedance spectra measured at 460 and 600 °C. The spectrum was plotted in terms of Z' vs. Z''/f, which is a sophisticated method to clarify the dielectric contributions from grain, grain boundary, and sample-electrode contact [28]. In this kind of representation, three sectional straight lines can be usually obtained with the sequential regions from low to high frequencies corresponding, respectively, to the dielectric responses from the contact, grain boundary, and bulk grain. It is clearly seen that the curve measured at 460°C consists of two linear segments with different slopes. The low-frequency segment is the main part of the spectrum, while the high-frequency segment occurs at the vicinity of the high-frequency limit of our equipment. Compared with the result shown in Fig. 2 (e), the low-frequency segment is associated with the relaxation R2 and the high-frequency segment is related to the relaxation R1. Further increasing the measuring temperature, both R1 and R2 should move to higher frequencies. From the spectrum recorded at 600 °C, we can see that the absence of R1segment indicating that it moves out of the measuring frequency window. As a consequence, the R2-segment becomes the predominant part of the spectrum. Additionally, a short horizontal segment appears. This segment is believed to be the dielectric contribution of sample-electrode contact [28], which is active in the high-temperature and low-frequency ranges. Therefore, the R2-segment is clarified to be related to the interfacial contribution and R1-segment is attributed to the bulk contribution. For the present sample, the interfacial dielectric relaxation, i.e., the MW relaxation can result from the phase boundary between the Nb₂O₅ and La₂O₃ phases. The three-dimensional atomic configuration model for the Nb-rich La₂O₃ – Nb₂O₅ reported by Masuno et al. [30] further evidenced this boundary. Thus, R2 is a MW relaxation due to phase boundary. The nature of MW relaxation is further convinced by impedance analysis. The inset of Fig. 3 shows the complex impedance plots measured at 600 °C under different dc biases. It is seen that the plot can be depressed by the dc bias convincing the MW relaxation nature [29].

Now, we turn our attention to the nature of R1. Masuno et al. [30] and Inoue et al. [31] reported that, compared with the conventional optical glasses, the Nb-rich $La_2O_3 - Nb_2O_5$ glasses prepared by ALF method showed unusually high oxygen packing density and significant electronic polarizabilities of oxygen ions. The high refractive index is predominantly governed by electrons around the oxide ions [32]. This leads to significant ion conductivity in LNO. It is well-known that the ac conductivity $\sigma(\omega)$ for ionically conducting glasses in wide temperature and frequency ranges can be described by the universal dielectric response (UDR) model [33]. To verify this viewpoint, Fig. 4 (a) displays the ac conductivity as a function of frequency at various temperatures. It is seen that the each curve shows a frequencyindependent plateau (dc plateau) in the low frequency range followed by a rapid increase at high frequencies. According to the UDR model, the ac conductivity $\sigma(\omega)$ can be described by [33]

$$\sigma = \sigma_{\rm dc} + A\omega^{\rm s} \tag{2}$$

where σ_{dc} is the dc conductivity, *A* and *s* (0 < s ≤ 0) are temperature-dependent constants. It is found that the experimental conductivity data of LNO can be well fitted by Eq. (2). As a representation, the best fit to the conductivity spectrum recorded at 380 °C is shown in Fig. 4 (b). The parameter *s* for each temperature obtained by the curve fitting is illustrated in the inset of Fig. 4 (b). The power value of *s* is almost independent of temperature with the value of ~0.5 in the tested temperature range. The *s* value agrees well with the theoretical value reported in the range from 0.5 to 0.7 [34]. Similar temperature-independent behavior of *s* had also been reported in Na₂O-3SiO₂ glasses [35,36] and MgTiO₃ [37].

The dc conductivity σ_{dc} can be directly extracted from the plateau value. The dc conductivity shown in Fig. 4 (c) is found to



Fig. 4. (a): Frequency dependence of ac conductivity for LNO at selected temperature. (b): A representative nonlinear fitting result using the UDR model to the experimental data (open circles) recorded at 380 °C. (c): The Arrhenius plots for dc conductivity. (d): Summerfield scaling for conductivity spectra at different temperatures of LNO. The inset in Fig. 3 (b) is variation of the frequency exponent *s* as a function of temperature.

obey the Arrhenius law:

$$\sigma_{\rm dc} = \sigma_0 \exp(E_{\rm dc}/k_{\rm B}T) \tag{3}$$

where σ_0 is the pre-exponent constant and E_{dc} is the activation energy of conduction. Linear fit yields $E_{dc} = 1.27 \text{ eV}$. This value agrees well with the activation energy of R1 obtained from M''(f), indicating that the relaxation is linked with the conductivity. Actually, the ε'' can be obtained from the power law: [33]

$$\varepsilon''(\omega) = [\sigma(\omega) - \sigma(0)]/(\varepsilon_0 \omega) = (A/\varepsilon_0)\omega^{-(1-s)}$$
(4)

where ε_0 is the vacuum permittivity. With the help of Cole-Davidson formula, we can get the complex dielectric permittivity: [33]

$$\epsilon * (\omega) \propto (1 + i\omega\tau)^{-\beta} \quad (0 < \beta < 1)$$
⁽⁵⁾

which gives rise to a peak in $\varepsilon''(\omega)$. Since the electric modulus is defined as $M^* = 1/\varepsilon^*$, the peak caused by the same mechanism will occur in M''(f) as shown in Fig. 2(c). Therefore, we can come to the conclusion that R1 is a conduction relaxation associated with hoping motion of oxygen ions.

Fig. 4 (d) displays the Summerfield scaling plot at selected temperatures for LNO with the σ_{dc} and T as the scaling parameters [38]. The conductivity data measured at different temperatures merge into a master curve indicating that the dynamic processes occurring at different temperatures almost share the same transport mechanism.

4. Conclusions

In conclusion, a relaxor-like behavior was observed above $200 \degree C$ in the $0.35La_2O_3 - 0.65Nb_2O_5$ glasses prepared by aerodynamic levitation method. By means of electric modulus, impedance analysis, and ac conductivity, the relaxor-like behavior was found to be composed of two relaxations. The low-temperature relaxation is a conduction relaxation resulting from the hopping motion of oxygen ions and the high-temperature relaxation is a Maxwell-Wagner relaxation associated with phase boundary. The relaxor-like behavior results from the combination of the conduction relaxation and the Maxwell-Wagner relaxation.

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