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Ferroelectric phase transition in $Pb_3R_3Ti_5Nb_5O_{30}$ (R = Eu and Gd) ceramics

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Some ferroelectrics compounds of the tungsten-bronze (TB) structure family have attracted much more attention of researchers because of their wide device applications based on their pyroelectric, piezoelectric, ferroelectric and nonlinear optical properties [1–7]. The TB-structure has a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$ where A-type cations (mono to divalent) can be substituted for any or all three different types of interstitial A_1, A_2 and C while B-types cations (tri to pentavalent) can be substituted for octahedral site B_1 and B_2 [8]. It was observed that some compounds of this family, such as (Ba, Sr, Pb)$RTi_3Nb_7O_{30}$ (R = rare earth ions) [9–11], $Pb_{5-x}La_{1+x}Ti_{3+x}Nb_{7-x}O_{30}$ ($x = 0, 1, 2$) [12], $Ba_3Sm_3Ti_5Nb_5O_{30}$ [13] showed a diffuse phase transition. A detailed literature survey shows that there is no report on the titled compounds which belong to TB-structure family, therefore we have systematically studied the structural, dielectric and electrical properties of the compounds $Pb_3R_3Ti_5Nb_5O_{30}$ (R = Eu, Gd) for a better understanding of physics and chemistry of the materials for possible applications.

The polycrystalline samples of $Pb_3R_3Ti_5Nb_5O_{30}$ (R = Eu, Gd; hereafter abbreviated as R(Eu) and R(Gd)) were prepared from high purity raw materials; PbO (99+%, M/s. Aldrich Chemical Co., USA), Eu_2O_3 and Gd_2O_3 (99.9%, M/s. Indian Rare Earth Ltd., India), TiO_2 (99%, M/s s.d. Fine Chem. Pvt. Ltd., India) and Nb_2O_5 (99.9%, M/s Loba Chemie Pvt. Ltd., India) using a high-temperature solid-state reaction technique. All these ingredients taken in stoichiometry were thoroughly mixed in an agate mortar for about 2 h. The mixed powder of the compounds was then calcined at 1100 °C in an alumina crucible for 15 h. The process of grinding and calcination was repeated until the formations of the desired compounds were confirmed. The quality and formation of the compounds was checked by an X-ray diffraction (XRD) technique. The XRD patterns of the titled compounds were recorded at room temperature using an X-ray powder diffractometer (Philips PW1817) with Cuk_α radiation ($\lambda = 1.5418$ Å) in a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 80^\circ$) at a scanning rate of 2 deg./min. The fine and homogeneous powders of the above compounds were uniaxially pressed into cylindrical pellets (10 mm diameter and 1–2 mm thickness) at a pressure of 6×10^6 N/m^2 by a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The pellets were then sintered for 15 h at 1150 °C in air atmosphere. The binder was burnt out during the sintering process. After that the surfaces of sintered pellets were polished with fine emery paper in order to make both the faces flat and parallel and electroded with high purity air-drying silver paste, and then dried at 150 °C for 4 h, to remove moisture before taking any electrical measurements. The surface micrographs of gold sputtered sintered pellets were taken by Jeol JSM-5800 scanning electron microscope (SEM) at room temperature. The dielectric constant (ε) and tangent loss (tan δ) of the titled compounds were obtained as a function of frequency (1 to 70 kHz) at different temperature (25 to 375 °C) using Hioki 3532 LCR Hitester along with a laboratory-made sample holder and a heating arrangement. The dc resistivity/conductivity of all the compounds was measured as a function of temperature (room temperature to 300 °C) at a constant electric field of 330 V/cm with the help of a Keithley-617 programmable electrometer. A laboratory-fabricated 2-terminal sample holder, furnace and a chromel-alumel thermocouple were used for all the experiments. Accuracy of the temperature measurement was found to be about ±2 °C.

Fig. 1 shows the sharp and single diffraction peaks of XRD pattern of the powder of the compounds recorded

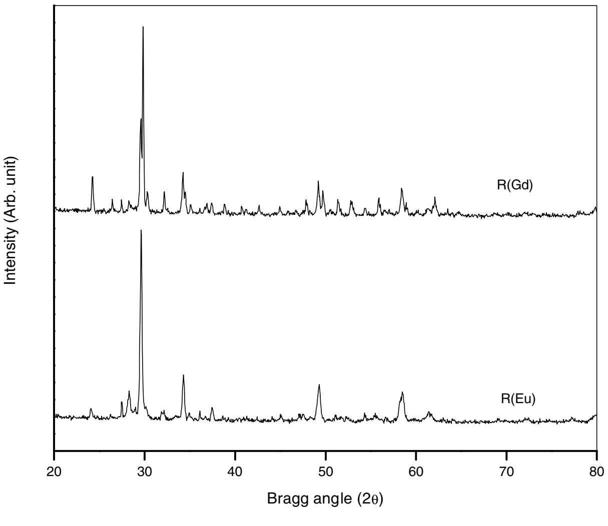

Figure 1 Comparison of XRD pattern of the compounds R(Eu) and R(Gd).

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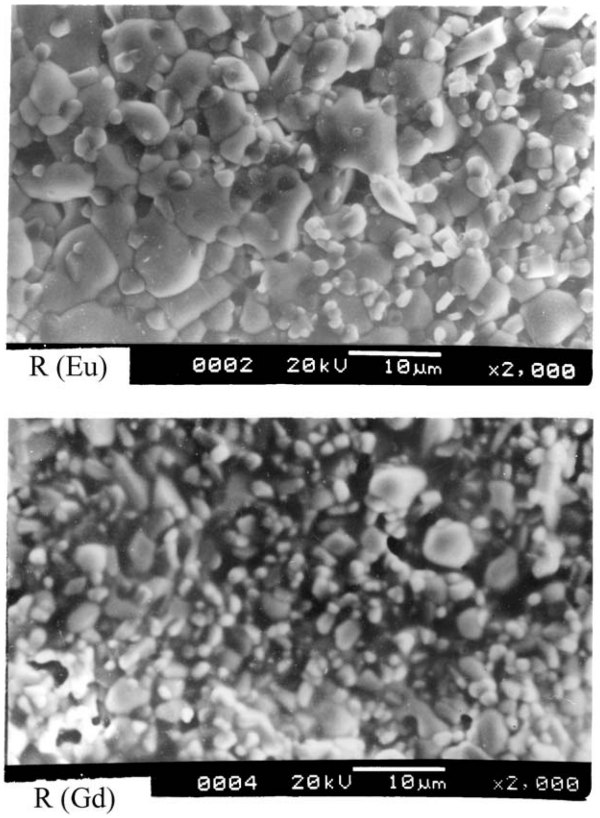

Figure 2 SEM photographs of compounds *R*(Eu) and *R*(Gd).

at room temperature (25 °C). The XRD pattern indicates the formation of single-phase compounds. All the reflection peaks of both the compounds were indexed in different crystal systems and unit cell configurations using a computer program package POWD [14]. Finally, an orthorhombic crystal system and its cell parameters were selected for which $\Sigma\Delta d = \Sigma(d_{obs} - d_{cal})$ was found to be minimum. The least-squared refined cell parameters of *R*(Eu) and *R*(Gd) were found to be: $a = 10.0714$ Å, $b = 11.8333$ Å, $c = 13.9181$ Å and $a = 10.0203$ Å, $b = 12.0000$ Å, $c = 13.9199$ Å respectively, with an estimated error of ±0.002 Å. The average crystallite size (P) of the titled compounds was calculated from a few reflection peaks widely spread in 2θ (Bragg angles) range using Scherrer's equation $P_{hkl} = K\lambda/\beta_{1/2}\cos\theta$ [15], where $K = 0.89$, $\lambda = 1.5418$ Å, $\beta_{1/2}$ = half peak-width. The average crystallite sizes of the compounds *R*(Eu) and *R*(Gd) were found to be 23 and 28 nm respectively. Fig. 2 show the microstructures of the sintered pellet samples. It was found from the SEM photographs that the grains are homogeneously and uniformly distributed over the entire surface of the samples.

Room temperature (25 °C) variation of dielectric constant (ε) and loss tangent (tan δ) of the compounds *R*(Eu) and *R*(Gd) with frequency (1–70 kHz) are shown in Fig. 3. It can be seen from Fig. 3 that the dielectric constant (ε) and loss tangent (tan δ) of both the compound decrease very slowly with increase in frequency, which suggests that interfaces and dipoles play an important role at low frequency. This is normal behavior of this type of compound.

Fig. 4 shows the variation of dielectric constant (ε) and loss tangent (tan δ) of the compounds *R*(Eu) and *R*(Gd) with temperature at 10 kHz. It has been observed that compounds *R*(Eu) and *R*(Gd) undergo a ferroelectric-paraelectric phase transition at 293 and 142 °C respectively. The maximum value of dielectric constant (ε) for *R*(Eu) and *R*(Gd) are 117 and 86 respectively. It was also observed from Fig. 5 that loss tangent (tan δ) changes very slowly with temperature up to 230 °C, after that it increases very significantly with temperature. The increase in tan δ at high temperature of both the compounds may be due to transport of ions at higher thermal energy. An anomaly in tan δ was also observed in *R*(Eu) compound, this may be due to the fact that dipole losses are more dominant in this compound.

The degree of disorder or diffusivity (γ) in the *R*(Eu) and *R*(Gd) compounds was calculated using

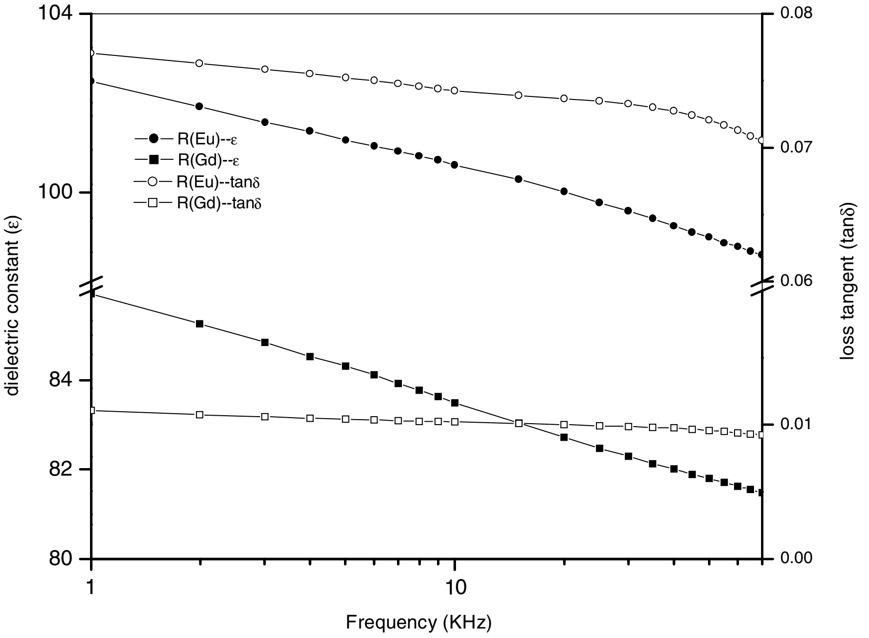

Figure 3 Variation of ε and tan δ in compounds *R*(Eu) and *R*(Gd) as a function of frequency.

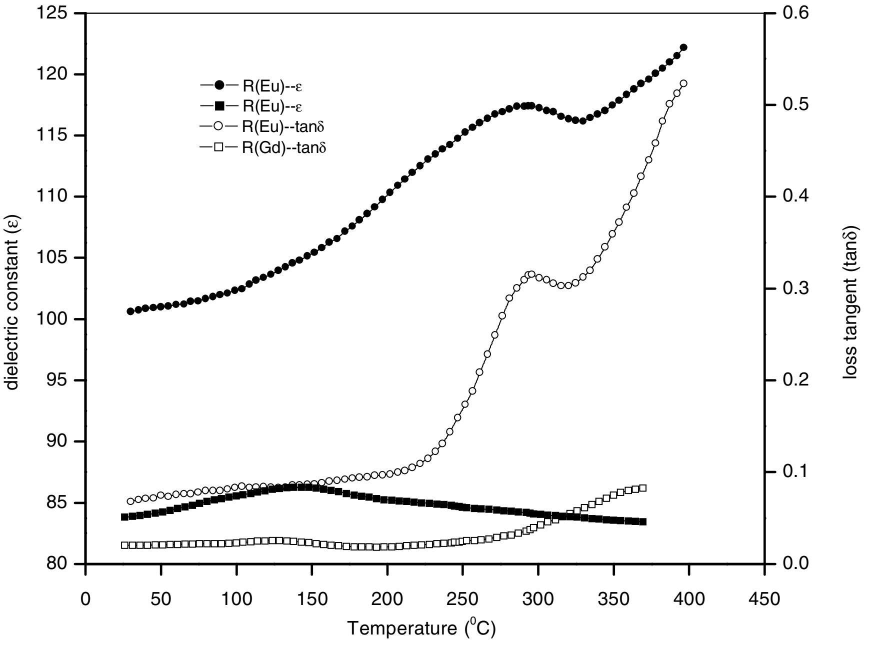

Figure 4 Variation of ε and tan δ in compounds *R*(Eu) and *R*(Gd) with temperature at 10 kHz.

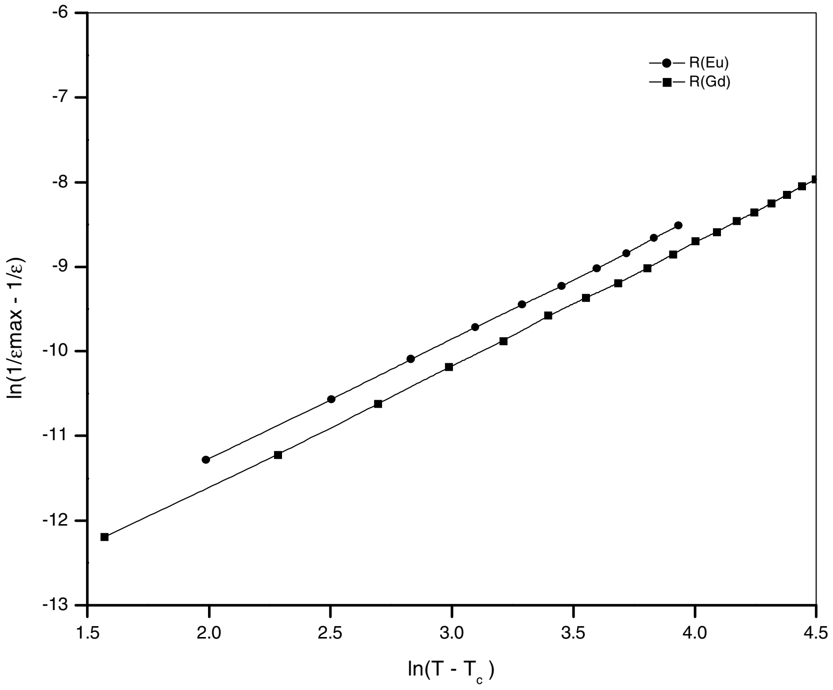

Figure 5 Variation of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ with $\ln(T - T_c)$ of *R*(Eu) and *R*(Gd) compounds at 10 kHz.

an empirical relation $\ln(1/\ \varepsilon - 1/\varepsilon_{\max}) = \ln K + \gamma \ln (T - T_c)$ [16], where $\varepsilon_{\max}$ is the maximum value of ε at T_c and K is an arbitrary constant. The value of γ for both the compounds at 10 kHz obtained from the slope of the curve, ln $(1/\varepsilon - 1/\varepsilon_{\max})$ Vs ln $(T - T_c)$ (Fig. 5), the value of γ for the compounds *R*(Eu) and *R*(Gd) was found to be 1.4 and 1.5 respectively, the value of $\gamma = 1$ obeying the Curie Weiss law and $\gamma = 2$ for completely disordered system. The intermediate γ value of the titled compounds indicated that compounds exhibits some characteristics of diffuse-phase transition.

The temperature variation of conductivity ($\ln\sigma_{dc}$) with inverse of absolute temperature ($10^3/T$) is shown in Fig. 6. It follows the Arrhenius relation $\sigma = \sigma_o \exp(-E_a/k_B T)$; where k_B Boltzmann constant, E_a activation energy, σ_o the conductivity at absolute zero temperature. It was observed that as the conductivity of *R*(Eu) increases very slowly up to 220 °C after that it increases very significantly showing that the compound has negative temperature coefficient at high temperature, but for the compound *R*(Gd), conductivity increases with temperature. From the slope of the curves, the activation energy for both the compounds was calculated. The value of the activation energy was found to be 0.9 eV and 0.4 eV for the compounds *R*(Eu) and *R*(Gd) respectively.

Finally, it is concluded that the compounds $Pb_3R_3Ti_5Nb_5O_{30}$ (R = Eu and Gd) have orthorhombic structure at room temperature. These compounds show a diffuse-type ferroelectric phase transition with

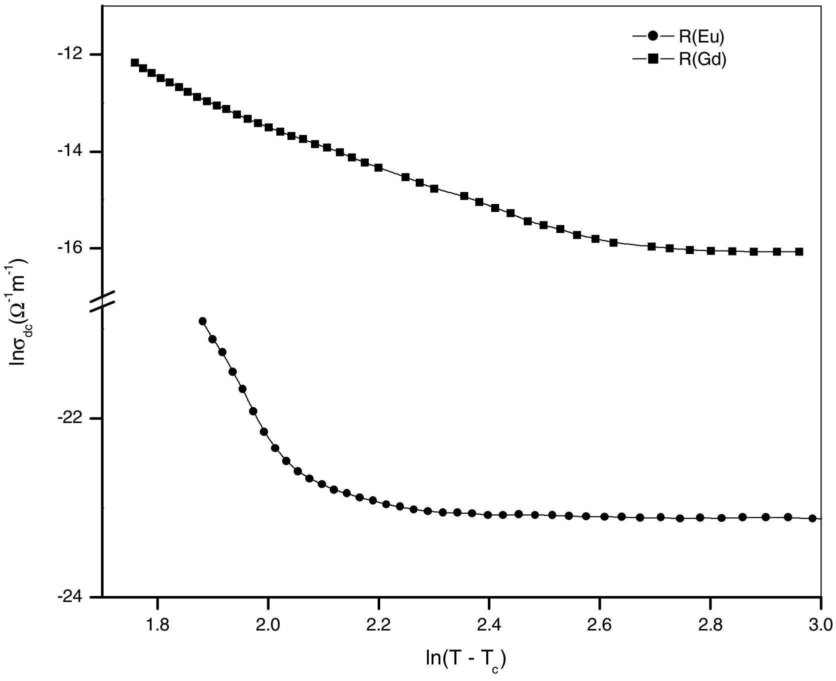

Figure 6 Variation of dc electrical conductivity ($\ln\sigma_{dc}$) of *R*(Eu) and *R*(Gd) compounds with the inverse of absolute temperature ($10^3/T$).

transition temperature well above the room temperature. We also observed low activation energy and decreasing resistance with rise in temperature, which indicate the intrinsic semiconductor character of the materials.

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