Electric responses of \( \text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18} \) (R = La, Nd, Sm, Gd, Dy) ceramics

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Single-phase orthorhombic tungsten bronze ceramics of \( \text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18} \) (R = La, Nd, Sm, Gd, Dy) are prepared via high temperature solid-state reaction method. The values of cell parameters phase transition temperature and activation energy are found to depend on rare earth ion content. These materials have low dielectric constant, low loss and high resistivity. The samples showed dielectric relaxation which are found to be of non Debye type. The nature of variation of resistivity with temperature and Nyquist plots suggested the NTCR character. The ac conductivity is found to obey the universal power law and supports the correlated barrier hopping of the carriers as conduction mechanism.

**Keywords:** Phase transition; Transition temperature; X-ray diffraction; Orthorhombic; dc resistivity.

Ferroelectric ceramics have been widely used in various electrical/electronic devices since past few decades. In recent years, considerable interest has been developed to improve the performance characteristics of TB-materials suitable for practical applications \(^1\)\(^-\)\(^5\). A number of ferroelectric compounds having TB structure such as \((\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6\) \(^6\)\(^-\)\(^7\), \((\text{Pb},\text{Ba})\text{Nb}_2\text{O}_6\) \(^8\), rare-earth doped \((\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6\), \(\text{Pb}_2\text{Bi}_4\text{Ti}_2\text{O}_{18}\) \(^9\), \((\text{Pb},\text{K})\text{LiTa}_{10}\text{O}_{31}\), \(\text{Ba}_2\text{NaNb}_2\text{O}_{15}\) \(^10\), \(\text{Ba}_2\text{Na}_3\text{RNb}_{10}\text{O}_{30}\) (R = rare-earth ions) \(^11\), \(\text{Ba}_5\text{RTi}_3\text{Nb}_3\text{O}_{30}\) (R = Dy, Sm) \(^11\), \(\text{Ba}_5\text{RTi}_3\text{Nb}_3\text{O}_{30}\) (R = Nd, Eu, Gd) \(^11\), \(\text{Ba}_3\text{R}_2\text{Ti}_6\text{Nb}_{30}\) (R = Y, Sm, Dy) \(^11\) and \(\text{Ba}_2\text{Nd}(\text{Ti},\text{Zr})\text{Nb}_{30}\) \(^11\) have been extensively investigated for intended applications. These multi-component systems are very sensitive to the additives and show variety of phase transitions. Continuous efforts are being made to investigate \(\text{Pb}_2\text{A}_3\text{RTi}_5\text{O}_{18} \) (A \(\equiv\) Sb or Bi; R \(\equiv\) rare-earth ions) compounds with desired characteristics both from theoretical and application point of view \(^1\)\(^-\)\(^2\)\(^4\). Accordingly in the present work, structural, dielectric, impedance, ac conductivity and dc resistivity studies of \(\text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18} \) (R \(\equiv\) La, Nd, Sm, Gd, Dy) ceramics prepared using the solid-state ceramic route are carried out.

**Experimental Procedure**

Polycrystalline samples of \(\text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18} \) (R \(\equiv\) La, Nd, Sm, Gd, Dy) were prepared by normal powder ceramic method. The chemical reactions, taking place are

\[
2\text{PbO} + \frac{3}{2}\text{Sb}_2\text{O}_3 + \frac{1}{2}\text{R}_2\text{O}_3 + 5\text{TiO}_2 \xrightarrow[\Delta]{\text{\text{\_}}} \text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18}
\]

To synthesize these ceramics, AR grade (99.9%+ pure) chemicals (\(\text{PbO}\), \(\text{Sb}_2\text{O}_3\), \(\text{La}_2\text{O}_3/\text{Nd}_2\text{O}_3/\text{Sm}_2\text{O}_3/\text{Gd}_2\text{O}_3/\text{Dy}_2\text{O}_3/\text{Ti}_2\text{O}_3\)) were taken in stoichiometric ratios. The initial powder was ground and heated at 1050°C for 10 h in air. Two percent extra \(\text{PbO}\) was added to compensate lead loss. The calcined powder was then grounded and put in form of disk (9 mm diameter). The optimized sintering conditions were 1070°C for 6 h. Completion of the reaction and the formation of the desired compounds were checked by X-ray diffraction. X-ray diffraction data were acquired on the powder samples using CuK\(_\alpha\) radiation. The data were collected over the range 20°-80°, with a scan rate of 2°/min.

In order to measure the electrical properties of the compounds, silver paint was applied on both the large faces of the samples to serve as electrode. Electrical impedance (Z), phase angle (\(\theta\)), capacitance and loss were measured as a function of frequency (0.1 kHz-1 MHz) at different temperatures using a computer controlled LCR Hi-Tester (HIOKI 3532-50), Japan. DC resistivity was measured using Keithley-617 electrometer. To overcome the effect of moisture, if any, on electrical properties, the samples were pre-
heated to 150°C and then cooled to room temperature prior to conducting the measurements.

**Results and Discussion**

Figure 1 shows the XRD patterns of Pb$_2$Sb$_3$RTi$_5$O$_{18}$ (R ≡ La, Nd, Sm, Gd and Dy) ceramics at room temperature. The sharp and single XRD peaks of all the samples suggest the formation of single-phase compounds. All the peaks of the XRD-pattern were indexed and cell parameters were determined with a standard computer program ‘POWD’ using their experimental $d$-values. Finally, unit cells of orthorhombic system were selected.

The criteria adopted for evaluating the rightness, reliability of the indexing and the structure of Pb$_2$Sb$_3$RTi$_5$O$_{18}$ (R ≡ La, Nd, Sm, Gd, Dy) for which $\sum (d_{obs} - d_{calc})$ was found to be minimum. Figure 2 shows the variation of lattice parameters with content of rare earth ions.

It is observed that the values of $a$, $b$, $c$ as well as unit cell volume increases with the content of rare earth ions from La through Dy. However, the crystal structure remains the same even after substitution of different rare-earth ions except a smaller change in $2\theta$-values and relative intensity of the observed reflections.

Figure 3 shows the variation of dielectric constant and dielectric loss at room temperature and the phase transition temperature ($T_c$) with rare earth content.

It can be seen that $T_c$ shifts to higher temperature side (from 54°C for Pb$_2$Sb$_3$LaTi$_5$O$_{18}$ to 301°C for Pb$_2$Sb$_3$DyTi$_5$O$_{18}$) with the content of rare earth ions except for Pb$_2$Sb$_3$SmTi$_5$O$_{18}$ (39°C). Also, the dielectric loss was found to be maximum in Pb$_2$Sb$_3$SmTi$_5$O$_{18}$ ($= 0.177$). All the compounds were found to have low dielectric constant (~$10^2$) and loss tangent (~$10^{-2}$) values at room temperature. Further, the capacitors are considered to be an important element in electrical/electronic circuits, performing various functions, e.g., blocking, coupling and decoupling, ac-dc separation, filtering, power factor correction and energy storage. If $V$ is the working voltage, $E (= V/t)$ is the applied electric field, which must be lower than the breakdown strength of the...
dielectric material $E_b$ by a factor $k$. The volume efficiency of the capacitor is then defined as:

$$\eta = C / A t = \varepsilon \varepsilon_0 / t^2$$

... (1)

Therefore the maximum permissible energy density for a capacitor can be $C V^2 / 2 A t = \varepsilon \varepsilon_0 F_b^2 / 2 k^2$. The figure of merit for dielectrics can therefore, be defined as:

$$F_e = \varepsilon / F_b^2$$

... (2)

Inset Fig. 3 shows the variation of $F_e$ with rare earth content. The value of $F_e$ was found to be maximum ($5.72 \times 10^7$) in $\text{Pb}_2\text{Sb}_3\text{GdTi}_5\text{O}_{18}$.

Figure 4 shows the complex impedance spectrum for all the compounds at different temperatures. It is observed that with the increase in temperature the slope of the lines decreases and they curve towards real ($Z'$) axis, indicating the increase in conductivity of the samples. This indicates the NTCR character of the samples. It can also be observed that the peak maxima of the plots decrease and the frequency for the maximum shifts to higher values with the increase
in temperature. The Debye/non-Debye type nature of dielectric relaxation could be judged through complex impedance plots. For a Debye type relaxation, one expects a semicircular plot with its centre located on the $Z'$-axis whereas, for the non-Debye type relaxation, the centre lies below this axis. It can be noticed that the complex impedance plots are not represented by full semicircles, rather the semicircular arcs are depressed and their centers lie below the real ($Z'$), which suggests that the relaxation to be of non-Debye type in all the cases. This may be due to the presence of distributed elements in the material-electrode system.

The ac electrical conductivity data for all the compounds were obtained in accordance with the relation: $\sigma(\omega) = l / AT'$, where $l$ and $A$ are respectively the thickness and area of the specimen. The log-log plot of electrical conductivity versus frequency at different temperatures (Fig. 5) show strong dependence on frequency as well as temperature.

They obey universal power law: $\sigma(\omega) = \sigma(0) + K\omega^s$, with $0 \leq s \leq 1$ and $\omega$ is angular frequency of applied ac field and $K = \pi N^2 e^2 / 6k_B T (2\alpha)$, $e$ is the electronic charge, $T$-temperature, $\alpha$-polarizability of a pair of sites, and $N$- number of sites per unit volume among which hopping takes place. Such variation is associated with displacement of carriers which move within the sample by discrete hops of length $R$ between randomly distributed localized sites. We find the value of $s$ to decrease with the increasing temperature in all the cases. The model based on correlated hopping of electrons over barrier predicts a decrease in the value of the index $s$ with the increase in temperature and so found to be consistent with the experimental results. Thus, the correlated hopping of electrons may be the dominating mechanism in these systems.
indicates that the conduction process is a thermally activated process.

Figure 6 shows the variation of \(\log \rho_{dc} \) with \(10^3/T\) for \(\text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18}\) (\(R = \text{La, Nd, Sm, Gd, Dy}\)). The nature of variation is almost linear over a wide temperature range, indicating the ohmic nature of contact and obeys the Arrhenius relationship: 
\[
\rho_{dc} = \rho_0 \exp(E_a/kT),
\]
where \(E_a\) is the activation energy of conduction, \(k\) is the Boltzmann constant and \(T\) is the absolute temperature.

The nature of variation shows the negative temperature coefficient of resistance (NTCR) behaviour in all the ceramics. The decrease in resistivity with temperature may be considered on the basis that within the bulk, the oxygen vacancies due to the loss of oxygen are usually created during sintering and the charge compensation follows the Kröger and Vink equation\(^{27}\):

\[
O_o \rightarrow \frac{1}{2}O_2 \uparrow + V_{o}^* + 2e^- \quad \text{which may leave behind free electrons making them } n\text{-type. The values of activation energy for all the samples were obtained by least squares fitting of the data at higher temperature region and variation of which is shown in insert of Fig. 6. We find that the value of } E_a \text{ to decrease with the increase in unit cell volume (i.e. through } \text{Pb}_2\text{Sb}_3\text{LaTi}_5\text{O}_{18} \text{ to } \text{Pb}_2\text{Sb}_3\text{DyTi}_5\text{O}_{18}). \text{The conduction in the higher temperature region is supposed to be dominated by oxygen vacancies, which are considered mostly due to the mobile charges in } \text{BO}_6\text{-octahedra ferroelectrics that play an important role in conduction process.}

Conclusions

It is concluded that \(\text{Pb}_2\text{Sb}_3\text{RTi}_5\text{O}_{18} \quad (R = \text{La, Nd, Sm, Gd, Dy})\) have orthorhombic structure at room temperature. The values of cell parameters and phase transition temperature increase while the value of activation energy decreases as the content of rare earth ions changes from La through Dy. Also, these materials have low dielectric constant, low loss and high resistivity. The low loss \((\sim 10^{-2})\) of this kind can be advantageous when improved directivity is required. The nature of variation of resistivity with temperature and Nyquist plots suggested NTCR behaviour. The ac conductivity is found to obey the universal power law and the correlated barrier hopping (CBH) may be the dominating mechanism for carrier conduction in the system.

References