Abstract

Ferroelectric materials have occupied a significant position in the field of material research in the recent years because of their huge applications in various electronic, electro-optic, computer and communication devices. The properties of these materials are sensitive to the type and amount of substitutions as well as on preparation methodology. Hence it has become possible to synthesize a large number of ferroelectric materials of different structural family with improved physical properties like electro-optic, elato-optic, pyroelectric and piezoelectric. Among different structural groups tungsten-bronze (TB) structure covers a large number of ferroelectric materials. The TB structure consists of a complex array of distorted BO_6 octahedral, sharing corners in such a way that a wide variety of cations (i.e., of different atomic size and valences) can be substituted at three different type of interstices A, B and C of a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$, where A-type cations (mono/divalent) can be accommodated in different type of interstitial A_1, A_2 and C, and B-type cations (tri/pentavalent) are substituted at octahedral sites B_1 and B_2. Generally, the smallest interstice C is empty, so the general formula for the filled tungsten-bronze structure is $A_6B_{10}O_{30}$. The presence of many interstices provides a scope of wide variety of cation substitution and hence to synthesize a large number of TB structure compounds. Although there exists a large number of ferroelectric in TB family, interest has been developed in electro-optic uses of niobates, for example barium-sodium niobate (BNN) and its related compounds. Although some of the compounds of this family have already been studied in the past, there is no such systematic work has been reported on $Pb_5RTi_3Nb_7O_{30}$ (R = La, Nd, Sm, Eu, Gd and Dy), $Pb_4R_2Ti_4Nb_6O_{30}$, $Pb_3R_3Ti_5Nb_5O_{30}$ and $Pb_5RTi_{3-x}Zr_xNb_7O_{30}$ family. In view of the above, we have carried out structural and electrical properties of the above families for better understanding of the phase

transition mechanism as well as complex impedance spectroscopy analysis in the materials.

The polycrystalline samples of the proposed compounds were prepared by a high temperature solid-state reaction technique using high purity oxides. The preliminary structural information (i.e. crystal system, cell parameter, particle size etc.) were obtained from room temperature X-ray diffractogram taken over a wide range of Bragg angles 2θ ($20^0 \leq 2\theta \leq 80^0$) using Cuk_α radiation (λ=1.5418 Å). All the reflection of the compounds was indexed and the lattice parameters were determined from observed d values and finally the lattice parameters were refined using least-squares method. It was found that all the prepared compounds have orthorhombic crystal structure at room temperature. The average crystallite/particle size (P) of the compounds was calculated from some strong and medium reflection peaks widely spread in 2θ (Bragg angles) range using Scherrer's equation. The average value of particle size was found to be in range of 20 to 44 nm. The surface morphology of proposed compounds was studied by scanning electron microscopy (SEM). The microstructures of the sintered pellets show that the grains are distributed more or less uniformly throughout the surface of the samples. The average grain size of the particle was found to between 1.67-5.83 μm.

The dielectric constant and loss of all the compounds were obtained both as a function of frequency and temperature. The dielectric constant and loss were found to be decreased with increasing frequency, which was the normal behavior of ferroelectrics materials. From the studies of dielectric constant and loss as a function of temperature at 10 kHz we found that the dielectric anomaly (i.e., the phase transition) occurred above the room temperature in most of the compounds. Diffusivity (γ) parameters of all the compounds were estimated and value of γ was found in between 1 and 2.

We have employed impedance spectroscopy (CIS) technique to study complex impedance formalism, complex electric modulus formalism, and complex permittivity formalism and relaxation process of the materials under present study. It was found that

the contribution to the impedance is only from grain and grain boundaries; the effect of material-electrode interface is insignificant. The relaxation process is polydispersive and non-Debye type in nature. The general feature of impedance pattern (a) decrease in bulk resistance with the rise in temperature and (b) negative temperature coefficient of resistance (NTCR) behavior indicates semiconducting nature of the studied materials. It was also found from CIS study that transition temperature did not change with frequency, which indicates non-relaxor behavior of the studied materials.

The ac conductivity of the compounds was measure as a function of frequency (100 Hz-1 MHz) and temperature upto 450 ^{0}C using Hioki LCR HiTESTER. The electrical conductivity studies show that materials are polydispersive in nature. The dc conductivity of the studied materials was found in the range of 10^{-4} to 10^{-9} Scm^{-1}.

Measurement of Polarization was carried out using an oscilloscope connected to the modified Sawyer and Tower circuit. The polarization values of the studied compounds are found to be very small as compare to the other ferroelectric materials like PZT and PLZT. The maximum value of the pyroelectric coefficient of the studied compounds was found to be approximately 50 $nC/cm^2.^0C$. Room temperature piezoelectric properties (piezoelectric strain coefficient d_{33}) are measured for a few poled samples using Pennebaker Model 8000 Piezo d_{33} Tester at 110 Hz. The values of piezoelectric coefficient (d_{33}) are found to be very small as compared to PZT, PLZT materials.