ABSTRACT

With the growing interest and suitability for device applications, a large number of ferroelectric ceramics have been developed in the wide variety of Oxide ferroelectrics, synthesized in the form of single compositions. crystal, thin film, and ceramic are now widely used in computer memory and display devices, electro-optic modulators, pyroelectric and gas sensors, transducers, hydrophones and other electronic applications. Among all the ferroelectric oxides, oxides with perovskite structure of the general formula ABO_3 (A = mono or divalent, B = tri-, tetra-, penta- and hexavalent ions) have extensively been studied for the last five decades in the search of new compounds for the device applications. It has been found that a wide variety of compositions of perovskite ferroelectrics can be obtained by making suitable substitutions at A and/or B sites in the above general formula. Lead based complex molybdate and tungstate compounds belong to ferroelectric family with slightly distorted perovskite structure and have interesting physical properties.

The main objectives of the present study are: (i) Preparation of alkalirare-earth doped complex lead molybdate and tungstate perovskite ferroelectrics using high-temperature solid-state reaction techniques, (ii) study of preliminary crystal structure of the above mixed compounds for the better understanding of the phase transition in them, (iii) study of electrical properties (i.e., dielectric constant and loss, ac conductivity, dc resistivity, polarization reversal) and (iv) study of pyroelectric coefficient.

In the present study the following compounds have been synthesized and characterised.

Gr. A. Modified PbMoO₃ compounds:

(a) $Pb(Li_{1/4} R_{1/4} Mo_{1/2})O_3$ and (b) $Pb_{1-x}X_x(Li_{1/4} La_{1/4} Mo_{1/2})O_3$ Gr. B. Modified PbWO₃ compounds:

(a) $Pb(A_{1/4} R_{1/4} W_{1/2})O_3$ and (b) $Pb_{1-x}X_x(Li_{1/4} La_{-1/4} W_{1/2})O_3$ Where, R = La, Nd, Sm, Eu, Gd, Dy, Y; X = Ca, Sr, Ba; A = Li, Na, K and x = 0.00, 0.03; 0.07, 0.10.

The polycrystalline samples of Gr.A and Gr.B compounds were synthesized by conventional solid-state reaction technique using high

purity ingredient oxides and carbonates. The room temperature structural studies of Gr.A and Gr.B compounds were undertaken using X-ray powder diffraction technique (XRD) over a wide range of Bragg angle 2θ ($20^0 \le 2\theta$ $\leq 100^{\circ}$ for FeK_a and $15^{\circ} \leq 2\theta \leq 75^{\circ}$ for CuK_a). The sharp and single peaks of XRD patterns showed the quality and formation of the desired compounds. All the reflection peaks of the compounds were indexed and the lattice parameters were determined from observed d-values. Finally, the lattice parameters were refined using least-squares method. The preliminary X-ray analysis indicated that all the compounds had orthorhombic unit cell at room temperature. The cell parameters of all the compounds were different for different alkali and rare-earth dopants. It was also observed that the cell parameters and unit cell volume were slightly increased with increase of the ionic radius of alkali dopants for a particular rare-earth ion substitution. However, the cell parameters were found to be almost independent on the atomic numbers of the substituted rare-earth ions. This was due to closeness of the ionic radii of the consecutive rare-earth ions. With the increase in concentration of Ca. Sr and Ba at Pb-site, the cell parameters were found to be slightly larger both in lithium-lanthanum doped lead molybdate and tungstate compounds without changing their basic crystal structure. The average linear particle size of all the samples was calculated from some strong and medium intensity reflections of XRD profiles using Scherrer's equation and was found to be in the range of 250Å to 400Å.

The surface morphology of some of the proposed compounds was studied by SEM and grains were found to be uniformly distributed in the samples. The average grain size was found to be about $3\mu m$. The elemental analysis of some of the above mentioned compounds were carried out with EDAX (Energy Dispersive Analysis of X-ray) attached to SEM which indicated the presence of desired elements in the compounds. The elements with low atomic number (i.e., less than 16) could not be detected.

The density of all the ceramic compounds was measured by Archimedes' principle and was found to be between 6 gm/cc to 7 gm/cc.

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The dielectric constant and loss of all the compounds were obtained both as function of frequency (200 Hz to 10 kHz) and temperature (123 K to 600 K) using GR 1620 AP capacitance measuring assembly. In most of the cases, the dielectric constant and loss were found decreasing with increasing frequency which is a normal behaviour of most of the ferroelectric materials. From the studies of the variation of dielectric constant and loss as a function of temperature at 10 kHz, it was found that the dielectric anomaly of Gr.A and Gr.B compounds were above and below the room temperature respectively. However, diffuse phase transition or broadening in dielectric peak was found in most of the complex compounds. The degree of diffusness of dielectric peak was examined in each compound and the value of diffusivity was found in between 1 and 2.

The ac conductivity of the above compounds was calculated from the dielectric data and using the formula : $\sigma = \varepsilon_0 \varepsilon \omega$ tand where $\omega =$ angular frequency, ε_0 = dielectric constant of free space and tand = tangent loss. The activation energy E_a of the compounds calculated from the well known Arhenius relation $\sigma = \sigma_0 \exp(-E_a/K_BT)$, $K_B =$ Boltzmann constant and was found to be between 0.02 eV and 1.00 eV.

The dc volume resistivity (ρ) of all the samples was obtained by using KEITHLEY 617 programmable electrometer both as function of biasing electric field (0 - 80 Volts/cm) and temperature (300 - 600 K). The value of resistivity was found to be decreased with increase in temperature in all the above compounds which indicated that the compounds under study had negative temperature co-efficient of resistance (NTCR).

Measurement of polarization was carried out with the help of laboratory made modified Sawyer and Tower (ST) circuit. Polarization was found to be decreased with increasing temperature and ultimately it became zero. The transition temperature of the compounds obtained from dielectric and polarization studies was found approximately the same.

The pyroelectric co-efficient P^{T} , defined as the temperature derivative of polarization, was calculated from the hysteresis loop for most of the compounds. The variation of P^{T} with temperature also showed an anomaly exactly at the transition temperature observed earlier.