Synthesis and Characterisation of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ Ferroelectrics

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Abstract **- Polycrystalline samples of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0, 0.03, 0.07 and 0.1] compounds of perovskite family were prepared by solid-state reaction technique. The formation of the compounds was checked by x-ray diffraction technique. All the compounds were found to have orthorhombic crystal structure at room temperature. All the compounds showed ferro – paraelectric phase transition. Substitution of Ca, Sr. Ba at Pb – site considerably affects the electrical conductivity (ac and dc) of the mother compound, i.e., $Pb(Li_{0.25}La_{0.25}Mo_{0.5})O_3$.**

Keywords **– Solid-state reaction, Ferroelectric properties, AC and DC conductivity**

I.INTRODUCTION

Ferroelectric materials belong to different structural families. Ferroelectrics with perovskite structure having general formula ABO_3 (A→ mono or divalent cation, B → tri, tetra, penta or hexavalent cation) find wide range of applications in solid state devices, such as transducer, computer memory and display, pyroelectric detector etc. [1-3]. Among all the perovskites studied so far, some Pb-based compounds, viz., $PbTiO_3$, $Pb(ZrTi)O_3$ and $(PbLa)(ZrTi)O_3$ etc. have interesting ferro-, piezo- and pyroelectric properties. A wide variety of multi-component substitutions can be made both at A- and B-sites of perovskites in order to enhance their dielectric and electrical properties [4]. Studies on lead – alkali – rare earth tungstate and molybdate compounds [5 - 11] showed diffuse - type ferro - paraelectric phase transition. The effects of substitution of group IIA elements (e.g., Ca, Sr and Ba) at Pb-site of the parent compounds [6, 7] on structural and ferroelectric properties are studied [12 - 17]. Here the structural, dielectric and electrical properties of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0, 0.03, 0.07 and 0.1] ceramics are reported.

II. MATERIALS & METHODS

The proposed compounds were prepared from the pure oxides and carbonates: PbO (99.99%, M/s. Aldrich Chemical Co., USA), $CaCO_3$ (AR Grade, M/s. Loba Chemie Industrial Company, India), Li_2CO_3 (99%, M/s. S. D. Fine Chemicals Pvt. Ltd., india), La_2O_3 (99.99%, M/s. Indian Rare-earth Ltd.), MoO_3 (99.9% , M/s. John Baker Inc., USA). Conventional high-temperature solid-state reaction technique was used to synthesise the compounds. The stoichiometrically weighed constituents for a particular composition were thoroughly mixed in agate mortar for 4 hours in wet (ethanol) medium. The mixed powders were then calcined in alumina crucibles at 900 K for 20 hours in air. The initially calcined powders were ground once again and finally recalcined at 930 K in the same atmosphere for 10 hours. The completion of reaction was checked by X-ray diffraction technique (XRD). The XRD pattern of calcined powder was obtained by using X-ray powder diffractometer (Philips PW 1710, Holland) with CuK_α radiation (λ= 1.5418 Å) in the Bragg angle range 15^o - 65^o at a scanning rate of 2^o min^{-1}. The fine homogeneous recalcined powders were cold pressed into cylindrical pellets (discs) at a pressure ~ 6×10^6 Pa. An organic solution (Polyvinyl Alcohol – PVA) was used as binder to reduce the brittleness of the pellets. These pellets were sintered at 960 K for 5 hours in air. The organic binder was burnt out during high temperature sintering. The diameter of the green samples was reduced by 0.5% after sintering. The thickness of the pellets was 1-3 mm. The samples were cooled down to room temperature by rapid cooling process. The sintered pellets were polished with fine emery paper to make both the surfaces flat and parallel. The pellets were electroded with high purity silver paste for electrical measurements. The dielectric parameters (ε and $\tan\delta$) were measured both as a function of frequency (200 Hz – 10 kHz) and temperature (300 - 500 K) using GR 1620 AP capacitance measuring assembly along with a laboratory-made three-terminal sample holder and heating arrangements. The ac conductivity [$\sigma_m(\omega)$] was calculated from the dielectric data. Measurement of polarization was carried out using a modified Sawyer – Tower circuit [18] with a dual trace oscilloscope at an ac field 4.5 kV/cm with a frequency of 50 Hz. The dc conductivity (σ_{dc}) of all the compounds were measured as a function temperature (300 – 673 K) at constant electric field using KEITHLEY 617 Programmable Electrometer along with laboratory-made sample holder and heating arrangements. All the samples were kept at 400 K for 12 h before each experiment and silica gel was kept inside the sample holder to eliminate moisture effect.

TABLE I
Cell parameters of the $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

A	x	a (Å)	b (Å)	c (Å)
Ca	0.00	6.9260	8.7228	16.7228
	0.03	6.9324	8.7341	16.4102
	0.07	6.9324	8.7450	16.4205
	0.10	6.9330	8.7481	16.4317
Sr	0.00	6.9260	8.7228	16.7228
	0.03	6.9324	8.7363	16.5234
	0.07	6.9324	8.7370	16.5240
	0.10	6.9324	8.7380	16.5250
Ba	0.00	6.9260	8.7228	16.7228
	0.03	6.9324	8.7366	16.5241
	0.07	6.9324	8.7370	16.5245
	0.10	6.9324	8.7380	16.5250

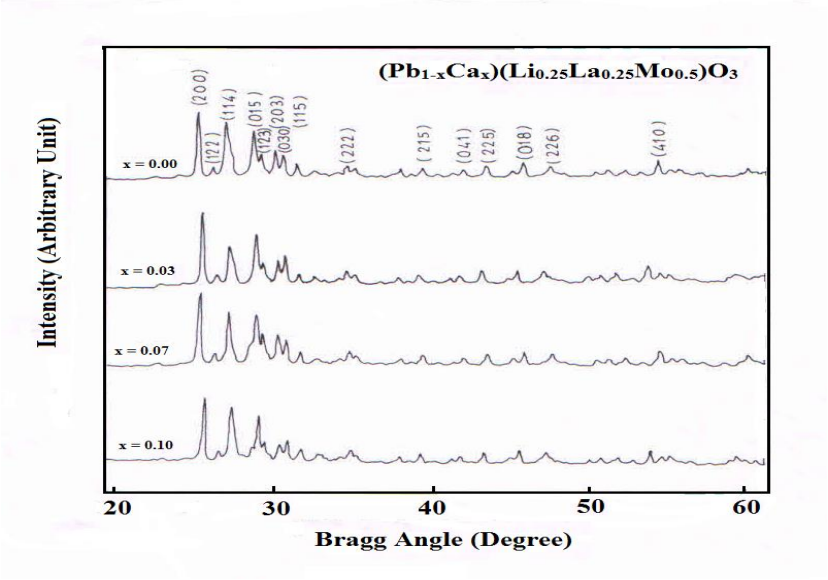

Fig.1. Room temperature XRD pattern of $(Pb_{1-x}Ca_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

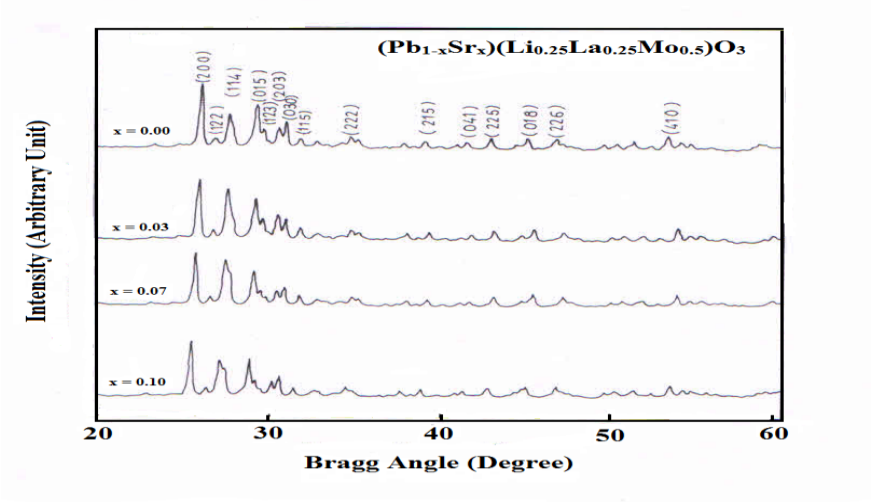

Fig.2. Room temperature XRD pattern of $(Pb_{1-x}Sr_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

III. RESULTS & DISCUSSION

A. STRUCTURAL PROPERTY

The prominent XRD peaks were indexed using a standard computer program 'POWD'. The lattice parameters were determined and refined by least square method. Figs 1, 2 and 3 show the room temperature XRD patterns of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0, 0.03, 0.07 and 0.1] compounds. All the compounds have orthorhombic structure at room temperature (~300 K). Table I shows the cell parameters of all the compounds. All the XRD peaks remain at same position as that of the mother compound, i.e., $Pb(Li_{0.25}La_{0.25}Mo_{0.5})O_3$, suggest that the substitution of group IIA cations upto 10 mole% at Pb-site does not affect the basic crystal structure. However, slight change in cell parameters occurs due to the change in occupancy of Pb cations. But no specific trend in the cell parameter change is found.

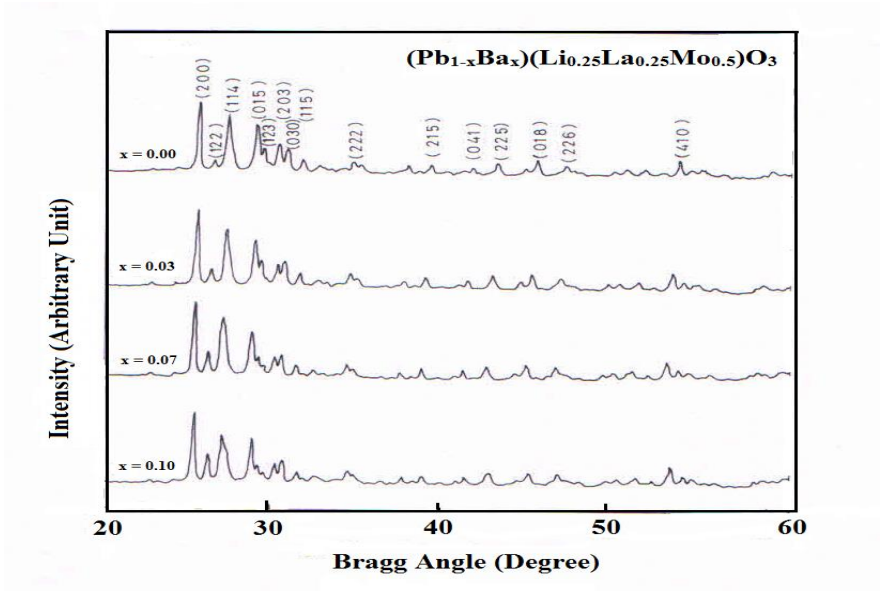

Fig.3. Room temperature XRD pattern of $(Pb_{1-x}Ba_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

B. DIELECTRIC PROPERTY

The dielectric parameters (ε and tanδ) of the $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds were studied as function of temperature (300-500 K) at 10 kHz. The mother compound, i.e., $Pb(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ has ferro - paraelectric phase transition at 372 K [7]. This type of behaviour is found in all the daughter compounds upto 10 mole% substitutions [Table II]. All the daughter compounds have ferro - paraelectric transition temperature (T_c) higher than that of mother compound, i.e., $Pb(Li_{0.25}La_{0.25}Mo_{0.5})O_3$. In all the daughter compounds, T_c decreases from 3 - 10 mole% substitutions. But the tungatate counterpart of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0, 0.03, 0.07 and 0.1] compounds did not behave in the similar way [12 – 14]. The mother compound, i.e., $Pb(Li_{0.25}La_{0.25}W_{0.5})O_3$ has ferro - paraelectric phase transition at 257 K [6]. This type of behaviour is found in the daughter compounds upto 3 mole% substitutions. But above this, all the daughter compounds do not have any dielectric anomaly in the studied temperature range .The diffuseness of phase transition (γ) in $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0 and 0.03] compounds was calculated [Table II]. The phase transition becomes more diffuse in the daughter compounds.

TABLE II
Some dielectric data of the $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

A	x	ε at 300 K	tanδ at 300 K	T_c (K)	ε at T_c	γ	Polarization ($\mu C/cm^2$) at 300 K
Ca	0.00	24	0.300	372	54	1.37	0.11
	0.03	16	0.067	393	1700	1.75	0.07
	0.07	17	0.033	386	2100	1.78	0.06
	0.10	17	0.667	383	2400	1.80	0.06
Sr	0.00	24	0.300	372	54	1.37	0.11
	0.03	20	0.225	396	1050	1.87	0.07
	0.07	17	0.050	393	1400	1.80	0.06
	0.10	15	0.875	386	2275	1.83	0.06
Ba	0.00	24	0.300	372	54	1.37	0.11
	0.03	17	0.075	384	1100	1.87	0.07
	0.07	14	0.025	378	1800	1.81	0.05
	0.10	13	0.925	376	2800	1.91	0.05

C. AC & DC CONDUCTIVITY

Measurement of the response when a sinusoidal potential difference is applied across a sample is a useful method for electrical characterisation. A great deal can be learnt from frequency and temperature dependence of the resulting impedance. In an ideal insulator, there are no free charges and ac conductivity is related to only to the bound charges or charges hopping between well defined sites, without contributing anything to long range motion or dc conductivity. However, in real materials, there are also some free charges, which give rise to dc conductivity without contributing anything to dielectric polarisation. Hence, the measured ac conductivity, $\sigma_m(\omega)$, will have the contribution from both ac and dc conduction. The values of ac and dc conductivity at 300 and 500 K are shown in Table III. Both ac and dc conductivity increase with temperature. The rate of increase is not same in all the compositions. Addition of thermal energy creates new mobile charge carriers which along with existing charge carriers increase the conductivity of the compounds. The rate of increase in ac conductivity with temperature is much slower in the tungstate counterparts of $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ [A → Ca, Sr, Ba; x= 0.0, 0.03, 0.07 and 0.1] compounds.

TABLE III
Comparison of $\sigma_m(\omega)$ and σ_{dc} $[(ohm.cm)^{-1}]$ of the $(Pb_{1-x}A_x)(Li_{0.25}La_{0.25}Mo_{0.5})O_3$ compounds

A	x	$\sigma_m(\omega)$ at 300K	$\sigma_m(\omega)$at 500K	σ_{dc} at 300K	σ_{dc} at 500K
Ca	0.00	1.8×10^{-8}	1.2×10^{-5}	8.3×10^{-11}	5.6×10^{-9}
	0.03	5.3×10^{-9}	7.8×10^{-6}	1.1×10^{-9}	6.8×10^{-9}
	0.07	1.3×10^{-9}	4.3×10^{-5}	3.8×10^{-10}	5.2×10^{-10}
	0.10	2.3×10^{-7}	1.4×10^{-4}	1.4×10^{-9}	2.3×10^{-7}
Sr	0.00	1.8×10^{-8}	1.2×10^{-5}	8.3×10^{-11}	5.6×10^{-9}
	0.03	2.5×10^{-8}	1.5×10^{-5}	4.1×10^{-10}	3.4×10^{-8}
	0.07	3.3×10^{-9}	2.3×10^{-5}	1.5×10^{-10}	1.5×10^{-8}
	0.10	4.9×10^{-7}	1.3×10^{-5}	6.1×10^{-8}	1.2×10^{-8}
Ba	0.00	1.8×10^{-8}	1.2×10^{-5}	8.3×10^{-11}	5.6×10^{-9}
	0.03	4.9×10^{-9}	4.2×10^{-7}	5.6×10^{-11}	3.4×10^{-9}
	0.07	4.6×10^{-10}	2.5×10^{-5}	2.1×10^{-11}	7.4×10^{-9}
	0.10	3.8×10^{-7}	2.2×10^{-5}	6.1×10^{-11}	5.6×10^{-9}

V. CONCLUSION

All the studied compounds have orthorhombic crystal structure at room temperature (~ 300 K). All studied compounds have undergone ferro – paraelectric phase transition. The substitution of Ca, Sr and Ba considerably affect the electrical conductivity (ac and dc) of the mother compound $Pb(Li_{0.25}La_{0.25}Mo_{0.5})O_3$.

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