Dielectric properties of the system $\text{Pb}_{2-x}\text{La}_x\text{Li}_{0.5}\text{O}_{6+\delta}$

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Abstract. The dielectric properties of the ceramic pyrochlore structured system $\text{Pb}_{2-x}\text{La}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_{6+\delta}$ has been studied as a function of concentration x and frequency at room temperature 25°C . The results have been analysed for relaxation process and conduction mechanism.

Keywords. Dielectric properties; ceramics; lanthanum doping; pyrochlore structured system.

1. Introduction

The general formula $\text{A}_2\text{B}_2\text{O}_6\text{X}$ where A and B are cations, X is O, OH or F stands for the pyrochlore group having the structure of the mineral $\text{CaNaNb}_2\text{O}_6\text{F}$ studied by Bystrom (1944). Cadmium niobate ($\text{Cd}_2\text{Nb}_2\text{O}_7$) and lead niobate ($\text{Pb}_2\text{Nb}_2\text{O}_7$) belong to this group. In some cases the site X may be vacant or partly vacant as in $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ and $\text{Pb}_2\text{Nb}_2\text{O}_6$ respectively. $\text{Cd}_2\text{Nb}_2\text{O}_7$ has been reported to show ferroelectric nature by Cook and Jaffe (1952). Venevtsev (1970) reported that the composition $\text{Pb}_{1.9}\text{Ba}_{0.1}\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_6$ is possibly ferroelectric. The electrical resistivity and the dielectric properties of the system $\text{Pb}_{2-x}\text{Ba}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_6$ were studied by Khare and Rajan (1977, 1978) and Rajan and Khare (1980). The thermoelectric properties of the system $\text{Pb}_{2-x}\text{La}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_{6+\delta}$ have been studied earlier (Phadnis *et al* 1982). The present paper reports the same system for material characterisation.

2. Material preparation

The specimens were prepared by reaction between the mixtures of PbO (BDH 98%) LR, $\text{La}_2\text{CO}_3 \cdot 8\text{H}_2\text{O}$ (Fluka 99.9%) AR, Nb_2O_5 (Fluka $\geq 99.9\%$) AR and Li_2CO_3 (BDH 98%) LR. The compounds were mixed thoroughly in a mortar and presintered at 800°C for 4-5 hr. The presintered mixture was ground to a fine powder and pressed into circular pellets at 50 kbar and were finally sintered at $900\text{--}1000^\circ\text{C}$ for 12 hr. The concentrations x of lanthanum and the dimensions of the samples were similar to the earlier report of Phadnis *et al* (1982) and are given in table 1.

3. Method and measurements

X-ray diffractometer patterns of the samples of various concentrations were identical, indicating qualitatively the presence of one phase only. The strong peaks gave the

Table 1. Physical dimensions of samples.

Sample No.	x	Weight % La	Diameter (d) mm	Thickness (t) mm	C_{air} μf calculated
0	0.00	0.00	11.68	2.47	0.30
I	0.05	1.54	7.55	3.19	0.12
II	0.10	3.01	7.56	3.41	0.11
III	0.15	4.44	7.42	1.44	0.27
IV	0.20	5.80	7.56	2.37	0.17

following values for the unit cell in the cubic system: $a_0 = 10.53 \pm 0.01 \text{ \AA}$ $Z = 8$ molecular units, calculated density $\rho = 7.3 - 7.4$ space group $F\bar{D}3M$. The strong peaks were assigned to (222), (440) and (622) planes. The measured value gave the apparent specific gravity as 6.6, due to the porosity of the ceramics. These unit cell parameters agree with earlier data (Anon 1974).

The capacitor electrodes system was a compact three-terminal type. Short lengths of fine teflon coated connecting wires were used as leads to the capacitor. The capacitance with dielectric C_d was measured with a Hewlett Packard 4275A multifrequency model with digital readout. The frequencies were in the range 10 kHz to 10 MHz in steps. The capacitance of the air gap C_a was calculated from sample dimensions. The measurements were earlier tried with a two terminal electrode system, but the results using the three terminal type, with proper shielding to avoid stray capacitances were more reliable.

The real part of the dielectric permittivity ϵ' and the loss $\tan \delta$ were obtained experimentally, while the imaginary part was evaluated using the relation $\epsilon''/\epsilon' = \tan \delta$.

4. Results and discussion

Table 1 shows the physical dimensions of the circular pellet samples, the weight percentage of lanthanum and the calculated capacitance of equivalent air gap. Table 2 gives the experimental $\tan \delta$ and the approximate calculated values of AC resistivity ρ in ohm-meters, for various frequency ranges. Figures 1 and 2 indicate respectively the graphs of ϵ' and ϵ'' vs concentration x of lanthanum. Figures 3 and 4 show respectively the plot of ϵ' and ϵ'' vs $\ln f$ for varying x . Figure 5 shows the semilog plot of $\ln \rho$ vs concentration x , for different frequencies.

The thermoelectric studies by Phadnis *et al* (1982) revealed that the samples are semiconductors. The majority carriers are n -type for $x = 0$ and 0.05 while the p -type predominates for $x = 0.10, 0.15$ and 0.20. It is observed that ϵ' and ϵ'' values reach a maximum at approximately $x = 0.075$ when the nature changes from n to p -type. The frequency variation of ϵ'' does not show a step and $\tan \delta$ do not show any maximum in the frequency range 10 kHz to 10 MHz which indicates the absence of well-defined relaxation processes. Thus the construction of a cole-cole diagram would not yield further information. The conduction mechanism is

Table 2. Frequency vs loss factor and a.c. resistivity (calculated).

Frequency kHz	x = 0		x = 0.05		x = 0.1		x = 0.15		x = 0.2	
	tan δ	$\rho \times 10^{-6}$	tan δ	$\rho \times 10^{-6}$	tan δ	$\rho \times 10^{-6}$	tan δ	$\rho \times 10^{-6}$	tan δ	$\rho \times 10^{-6}$
10	0.082	3.0	0.044	0.59	0.032	0.75	0.042	1.3	0.023	1.6
30	0.033	2.9	0.036	0.22	0.024	0.30	0.034	0.5	0.014	0.9
50	0.023	2.5	0.032	0.15	0.022	0.22	0.031	0.33	0.011	0.6
100	0.014	2.0	0.026	0.10	0.018	0.14	0.027	0.18	0.008	0.42
300	0.006	1.5	0.017	0.03	0.012	0.06	0.022	0.07	0.006	0.27
500	0.005	1.2	0.013	0.04	0.010	0.05	0.019	0.05	0.004	0.01
1000	0.003	0.9	0.009	0.03	0.007	0.04	0.015	0.04	0.003	0.01
3000	0.005	0.6	0.007	0.01	0.006	0.02	0.010	0.02	0.004	0.05
5000	0.000	3.6	0.004	0.01	0.003	0.02	0.005	0.02	0.001	0.06
10000	-	-	0.002	0.02	0.001	0.05	0.001	0.09	-	-

Figure 2. ϵ'' vs concentration x . Figure 1. ϵ' vs concentration x .

Figure 3. ϵ' vs $\ln$ frequency.

Figure 4. ϵ'' vs $\ln$ frequency.

the only process, going to low values at high frequencies. The magnitude of ϵ' shows an increase from $x = 0$ to $x = 0.1$ for n type electronic conduction. For $x = 0.15$, the whole conduction mechanism proceeds with decrease in ϵ' . For $x = 0.2$, the concentration of p -type carriers increase with increased conduction. The contribution

Figure 5. $\ln$ resistivity (a.c. calculated) vs concentration x .

to the n -type carriers are attributed to the La^{3+} substitution in the Pb^{2+} site for low concentrations of lanthanum. It is, however, interesting to note that for higher concentrations, it results in net p -type carriers. The n -type carriers are assumed to be present in the sample due to surface state phenomena occurring during sintering process, as discussed by Heywang (1964). It is surmised that some recombination occurs with the actual carrier concentration of La^{3+} being smaller than $x = 0.075$.

Bogoroditsky *et al* (1979) suggest the formula for the active or real part of AC resistivity as $\rho = 1/w\epsilon_0 \epsilon' \tan \delta$ where $w = 2\pi f$ the angular frequency, ϵ_0 = permittivity of free space, ϵ' = the dielectric permittivity and $\tan \delta$ = loss factor. Substituting for ϵ_0 and expressing frequency f in hertz $\rho = 1.8 \times 10^{10}/\epsilon' \tan \delta$. The formula is valid for volume conduction when there is dielectric loss due to leakage current. The variation of $\ln \rho$ as a function of concentration (x) for different frequencies show that the slope of n and p -types are opposite in nature. Minimum resistivity occurs at about $x = 0.075$, when maximum conduction occurs. The results indicate that the dielectric properties are closely related to the type of charge carriers, the concentration of impurity atoms, and the frequency of the applied electric field.

The samples may be characterised as medium permittivity ones and perhaps weakly ferroelectric. Further work is necessary to establish the ferroelectric nature.

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