Dielectric properties of the system $\text{Pb}_{2-x}\text{Nd}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_{6+\delta}$

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MS received 3 June 1985; revised 14 October 1985

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

Keywords. Dielectric properties; ceramics; neodymium doping; pyrochlore-structured system.

1. Introduction

The system $\text{A}_2\text{B}_2\text{O}_6\text{X}$, 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 $\text{Cd}_2\text{Nb}_2\text{O}_7$ has been reported to show ferroelectric nature by Cook and Jaffe (1952). In some cases the site X may be vacant or partly vacant as in $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$. Venetsev (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). The thermoelectric properties of the system $\text{Pb}_{2-x}\text{La}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_6$ have been studied by Phadnis *et al* (1982) and the dielectric properties of the same system by Phadnis *et al* (1983). The present paper reports the dielectric properties as a part of the material characterization of the system $\text{Pb}_{2-x}\text{Nd}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_6$.

2. Material preparation

The specimens were prepared by reaction between the mixtures of PbO (BDH) LR, Nd_2O_3 (Indian Rare Earths), Nb_2O_5 (Fluka) AR and Li_2CO_3 (BDH) 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 0.5 kbar and were finally sintered at $1000\text{--}1100^\circ\text{C}$ for 12 hr.

3. Method and measurements

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

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following values for the unit cell in the cubic system $a_0 = 10.53 \pm 0.01$ Å. $Z = 8$ molecular units, calculated density = 7.3–7.4 space group Fd3m agreeing with published data (Anon 1974) for other pyrochlore-structured systems. The strong peaks were assigned to (222), (440) and (622) planes. The measured value gave the apparent specific gravity 6.6, due to the porosity of the ceramics.

The capacitor 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 read-out. The frequency range was from 10 kHz to 10 MHz in steps. The capacitance of the air gap c_a was calculated from sample dimensions. The c_d was measured as a function of temperature with a capacitance meter (E12-I Russian make) working on the principle of the heterodyne beat. The samples were coated with conducting silver paint (Ladd Co., USA) to increase the ohmic contact. The temperature was measured by copper-constantan thermocouple.

The real part of the dielectric permittivity ϵ' and the loss $\tan \delta$ were obtained experimentally while the imaginary part was evaluated using the relations $\epsilon''/\epsilon' = \tan \delta$. The a.c. conductivity was calculated by the formula $1/\sigma = \rho = 1.8 \times 10^{10}/f\epsilon' \tan \delta$ as shown by Bogoroditsky *et al* (1979).

4. Results and discussion

Table 1 shows the physical dimension of the circular pellet samples, the weight percentage of neodymium and the calculated capacitance of equivalent air gap. A 10 mm die was used in making the pellet. The sintering produced varying contractions for different concentrations, giving changed macroscopic densities. Table 2 gives the experimental $\tan \delta$ and the approximate calculated values of a.c. resistivity in ohm-meters, for various frequency ranges. Figure 1 shows the plot of ϵ' vs $\ln f$ for varying x . Figure 2 shows the variation of ϵ' vs temperature for varying x .

The thermoelectric properties of the system studied by Phadnis *et al* (1985) revealed that concentration $x = 0.0, 0.001, 0.01$ and 0.05 show n type behaviour, whereas $x = 0.15$ and 0.2 show p -type. Similar results were observed earlier on the system $\text{Pb}_{2-x}\text{La}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_{6+\delta}$ (Phadnis *et al* 1982). The frequency variation of ϵ'' does not show a step and $\tan \delta$ does not show any maximum in the frequency range 10 kHz to 10 MHz indicating the absence of well-defined relaxation processes. The conduction mechanism is the only process, going to low values at high frequencies. The temperature

Table 1. Physical dimensions of the samples $\text{Pb}_{2-x}\text{Nd}_x\text{Li}_{0.5}\text{Nb}_{1.5}\text{O}_{6+\delta}$

Sample No.	x	Weight % Nd	Diameter (d) mm	Thickness (t) mm	C_{air} pf calculated
0	0.00	0	11.68	2.47	0.30
I	0.001	0.033	9.33	1.84	0.33
II	0.010	0.327	8.86	1.66	0.33
III	0.050	1.63	8.98	2.24	0.25
IV	0.150	4.88	9.05	2.77	0.21
V	0.200	6.39	9.19	1.97	0.30

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

Frequency (kHz)	x = 0		x = 0.001		x = 0.01		x = 0.05		x = 0.15	
	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	0.081	3.0	0.718	0.072	0.432	0.082	0.559	0.110	0.948	0.052
30	0.033	2.9	0.523	0.045	0.310	0.046	0.391	0.067	0.608	0.036
50	0.023	2.5	0.441	0.036	0.260	0.036	0.322	0.053	0.487	0.031
100	0.014	2.0	0.344	0.026	0.205	0.014	0.244	0.039	0.456	0.023
300	0.006	1.5	0.230	0.015	0.139	0.016	0.157	0.022	0.215	0.015
500	0.005	1.2	0.191	0.011	0.117	0.009	0.128	0.017	0.170	0.012
1000	0.003	0.9	0.147	0.008	0.092	0.006	0.097	0.012	0.124	0.008
3000	0.005	0.6	0.093	0.004	0.062	0.003	0.061	0.006	0.073	0.005
5000	0.000	3.6	0.067	0.003	0.047	0.002	0.043	0.005	0.051	0.004
10000	—	—	0.006	0.019	0.010	0.006	—	—	0.0031	—

Figure 1. ϵ' vs $\ln f$ (sample with conducting point).

Figure 2. ϵ' vs temperature.

variation of ϵ' vs temperature shows a peak near room temperature for all concentrations. However, the peak broadens with increasing x and $\epsilon'_{\max}$ occurs at different temperatures. The ϵ' values decrease slowly in the range 100–300°C for lower concentrations, whereas there is an increase for $x = 0.15$ and 0.20. The following conclusions are surmised.

- (i) A positive temperature coefficient (PTC) effect is present for lower concentrations which show *n*-type behaviour.
- (ii) Cation vacancies are formed for lower concentrations whereas oxygen anion vacancies are preferred at higher concentrations.
- (iii) The conduction mechanism is predominantly electron-hole type with low activation energies.
- (iv) Non-stoichiometry plays considerable part in the conduction mechanisms.
- (v) Point defects in the lattice are responsible for the complex behaviour of the temperature variation of ϵ' .
- (vi) The $\tan \delta$ values are dependent on the electrodes, being fairly high for samples coated with conducting point than those of unpainted samples. Both bulk conduction and surface conduction are envisaged.
- (vii) Differences in the grain size and losses at the grain boundaries perhaps account for the temperature variation differences.
- (viii) Surface state phenomena suggested by Heywang (1964) occurs on sintering at high temperatures.

Acknowledgement

The authors thank Prof. C M Srivastava for facilities.

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