Thermoelectric properties of the ceramic system
$Pb_{2-x}\ La_x\ Li_{0.5}\ Nb_{1.5}\ O_{6+\delta}$

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Abstract. The Seebeck voltage of the ceramic solid solutions of the system $Pb_{2-x}\ La_x\ Li_{0.5}\ Nb_{1.5}\ O_{6+\delta}$ has been studied as a function of temperature and concentration of lanthanum. The thermoelectric power was strongly dependent on the temperature and doping amount of lanthanum.

1. Introduction

The general formula ABO_6X stands for the pyrochlore group having the structure type of the mineral $CaNaNb_2O_6F$ studied first by Bystrom (1944). Here A and B are cations, X is O, OH or F. Cadmium niobate ($Cd_2Nb_2O_7$) and lead niobate ($Pb_2Nb_2O_7$) belong to this group. In some cases the site X may be vacant or partly vacant as in $Pb_{1.5}Nb_2O_{0.5}$ (Cook and Juffe 1953). Lead metaniobate has been reported to be ferroelectric (Goodman 1953). $Cd_2Nb_2O_7$ has been reported to show ferroelectric nature by Cook and Jaffe (1952). The composition $Pb_{1.9}Ba_{0.1}Li_{0.5}Nb_{1.5}O_6$ has been reported to be possibly ferroelectric by Venevtsev (1970). The electrical resistivity and the dielectric properties of the system $Pb_{2-x}Ba_xLi_{0.5}Nb_{1.5}O_6$ were studied by Khare and Rajan (1977, 1978) and Rajan and Khare (1980). The present work forms part of the preparation and characterisation of this pyrochlore structure group.

2. Materials preparation

The solid solutions were prepared by the solid state reaction between the mixtures of PbO, $La_2(CO_3)_3 \cdot 8H_2O$, Li_2CO_3 and Nb_2O_5. The chemicals used in the sample preparation were PbO (BDH 98%) LR $La_2(CO_3)_3 \cdot 8H_2O$ (Fluka 99·9%) AR, Nb_2O_5 (Fluka $\geqslant$ 99·9%) AR and Li_2CO_3 (BDH 98%) LR. The samples were prepared as follows. The pure compounds were first mixed thoroughly with a binder in a mortar and presintered at 800° C for 4-5 hr. The presintered mixture was ground to fine powder and pressed in the form of thin circular pellets at a

pressure of 50 kbar. They were finally sintered at 900–1000° C for 12 hr. The samples were circular pellets 8 mm in diameter and 1·5 to 3 mm in thickness.

The concentrations of lanthanum were $x = 0·00$, $0·05$, $0·10$, $0·15$ and $0·20$ giving weight percentages respectively as 0, 1·54, 3·01, 4·4 and 5·8% respectively. It is surmised that some concentrations may be in the region of heavy dopings.

3. Method and measurements

X-ray diffractometer patterns of the samples of various concentrations showed identical peaks indicating qualitatively the presence of one phase only. The strong peaks gave the lattice parameter $a_0 = 10·53 \pm 0·01$ Å, compared to the value $a_0 = 10·32$ Å reported by Bystrom (1944). The calculated densities for the different concentrations (x), varied from 7·3–7·4 for 8 molecular units in the cubic system. The measured value gave the apparent specific gravity only about 6·6, due to the porosity of the ceramics. The peaks were assigned to (222), (440) and (622) planes agreeing with published powder data (Selected powder diffraction data 1974). The space group was F_D3_M. The a_0 values for different materials vary from 10·32–10·43 Å.

The thermoelectric power was measured for different temperature gradients ΔT and with increasing values. The thermo emf voltage across the specimen was measured by a very sensitive panel type microvoltmeter (Levell Type TM 10 England). The temperature gradient was measured by a copper-constantan thermocouple. The thermoelectric power was measured as a function of concentration and temperature in the range 30–100° C by the conventional arrangement.

4. Results and discussion

Figures 1 and 2 show the thermoelectric power *versus* $10^3/T$ behaviour for the samples with lanthanum concentration $x = 0·0$, $0·05$ and $x = 0·10$, $0·15$, $0·20$ respectively. The concentrations $x = 0·00$ and $x = 0·05$ show n-type behaviour whereas $x = 0·10$, $0·15$ and $0·2$ show holes to be the majority carriers. While the n-type behaviour appears normal, compared to the data quoted by Madelung (1964), the behaviour of the three higher concentrations is different. The following conclusions are surmised : (i) lanthanum ion with an ionic radius 1·15 Å prefers a substitutional site of Pb^{2+} with an ionic radius of 0·84 Å. (ii) The system $Pb_{2-x}La_xLi_{0}·N_{-1}·O_3$ is deficient in electrons at low concentrations; but Heywang (1964), shows that chemical conditions at the grain surfaces of the ceramics may have an important bearing on the surface states. During the heating and preparation of the samples, conditions similar to doping occur. The recombination of the holes (available by La^{3+} substitution) with negative carriers leaves a very small negative thermoelectric power for $x = 0·05$. For higher concentrations, excess p-type carriers give positive thermoelectric power. (iii) The decrease in thermoelectric power with increase of temperature for higher concentrations may be due to conduction process by both types of carriers. The contribution by lithium ion movement partly as interstitial is also surmised. (iv) In the case
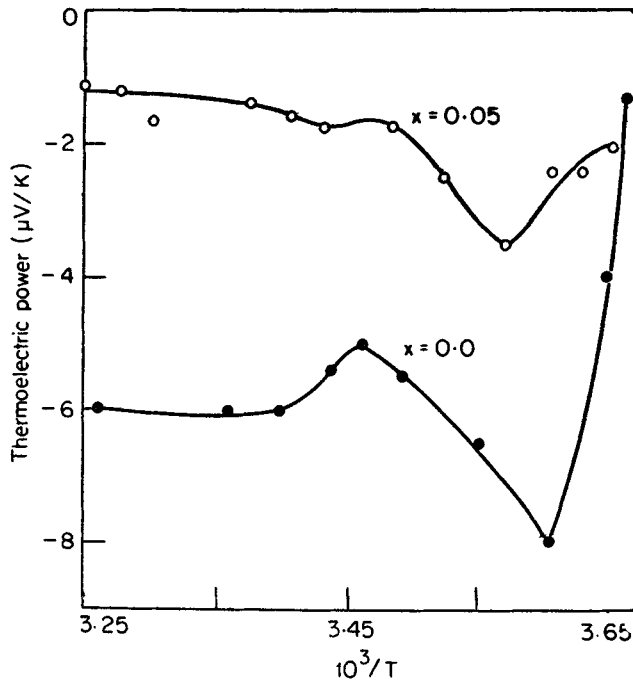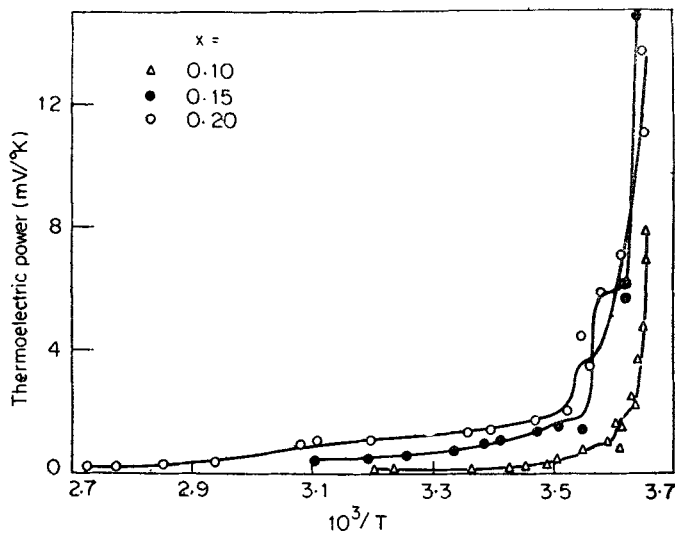
Figure 1. Thermoelectric power (μV/°K) vs $10^3/T$.

Figure 2. Thermoelectric power (mV/°K) vs $10^3/T$.

of heavy doping of lanthanum, there seems to be a critical doping concentration, beyond which the dopant ions are in close proximity. Mott (1968) shows that under critical doping conditions, temperature effects if any, vanishes. The behaviour for $x = 0 \cdot 15$ and $0 \cdot 20$ overlaps probably due to critical doping. Proceeding from $x = 0 \cdot 0$ to $0 \cdot 05$ and onwards, the bahaviour changes perceptably till $x = 0 \cdot 15$ is reached beyond which no more change is noticed.

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