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Electrical Resistivity of Ca,Ba-Doped Lead Molybdate Ceramics

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Polycrystalline samples of $Pb_{1-x}R_xMoO_4$ (x = 0.00; 0.05; 0.10; 0.15 and R = Ca, Ba) were prepared using solid-state reaction technique. Detailed studies of dc resistivity as function of biasing electric field (0.5 to 9.2 kV/m) and temperature (304–573 K) indicate that the compounds have non-ferroelectric properties but contain space charge polarization at high temperatures.

INTRODUCTION

In the last few decades, oxides with ferro, piezo, and pyroelectric properties of different structural families have extensively been studied for possible device application[1–4]. It has been found that some Pb-based pure/mixed oxides such as lead tungstate[5], samarium molybdate[6] etc. have many interesting ferroelectric and related properties. Lead molybdate compound (m.p. 1133 ± 3 K) is a member of scheelite structural family with the space group symmetry of $14_1/a$ and is suitable for laser application[7]. Recently, it has received much attention as a low temperature scintillator crystal for nuclear instrumental application[8] and widely used as acousto-optic high deflectors and modulators[9]. It has high figure of merit, low optical loss in the region 420 nm to 3900 nm and good mechanical impedance for acoustic matching. Though, some work on structural and electrical properties of a few members of the family has been done in the past[10–12]. We have concentrated our attention mostly on Ca,Ba-doped lead molybdate ceramics having chemical formula $Pb_{1-x}R_xMoO_4$ (x = 0.00; 0.05; 0.10; 0.15 and R = Ca, Ba) in regard to their electrical resistivity and applications. In this paper we report the electrical resistivity of Ca,Ba-doped lead molybdate ceramics.

EXPERIMENTAL

Polycrystalline samples of $Pb_{1-x}R_xMoO_4$ (x = 0.00; 0.05; 0.10; 0.15; R = Ca, Ba) have been prepared from high purity PbO (99.9%, Aldrich Chemical, USA); MoO_3 (99.5% pure, M/s BDH Ltd); $CaCO_3$ and $BaCO_3$ (99.5% pure M/s LOBA Chemical Industrial Co.) using conventional solid-state reaction technique in a proper stoichiometry. These oxides and the carbonate were thoroughly mixed

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in an agate mortar for 3 h and calcined at 1003 K for 16 h in a pure alumina crucible. The mixing and calcination were repeated at 1023 K for 18 h. The calcined powders were reground to make a homogenous power. The powders were pressed in the from of pellets (10 mm diameter and 1-2 mm thickness) using a stainless steel die-punch at an isostatic pressure of 6.3×10^7 kg/m^2. The pellets were then sintered at 1043 K for 12 h in an alumina crucible. The formation and the quality of the compounds were checked with X-ray diffraction (XRD) technique. The structural and detailed studies of dielectric properties of the compounds have been reported elewhere[12].

To measure the electrical properties of these compounds, the pellet samples were electroded with silver paint. The dc electrical resistivity of the samples was measured both as a function of biasing electric field (0.5 to 9.2 kV/m) at room temperature and temperature (RT to 573 K) at constant electric field (5.9 Kv/m) using a Keithley 617 programmable electrometer, a laboratory made sample holder and a furnance.

RESULTS AND DISCUSSION

The variations of the dc resistivity (ρ) with increase in applied electric field at room temperature [RT = 304 K] of all the $Pb_{1-x}R_xMoO_4$ compounds are shown in Figs 1 and 2. It is found that resistivity of all compounds decreases with the increase of the biasing electric field, which can be explained in the following

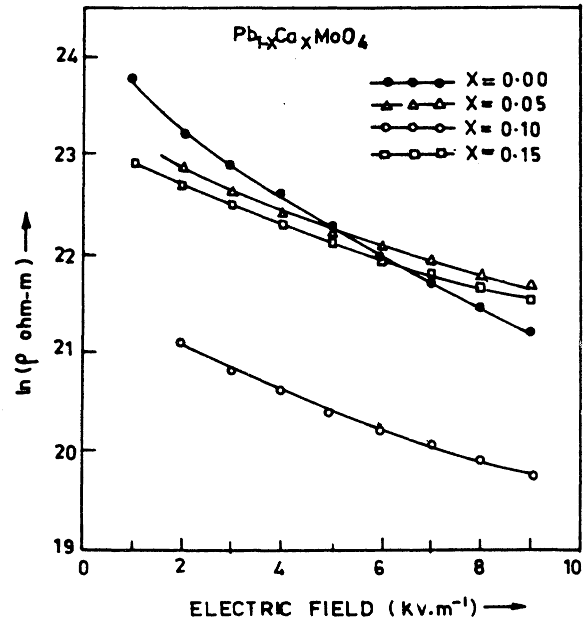

Fig 1. Variation of ln ρ_{dc} of $Pb_{1-x}Ca_xMoO_4$ as a function of electric field at room temperature.

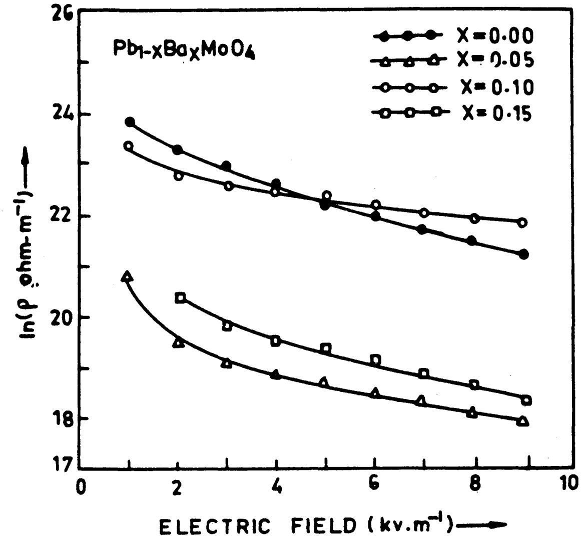

Fig 2. Variation of ln ρ_{dc} of $Pb_{1-x}Ba_xMoO_4$ as a function of electric field at room temperature.

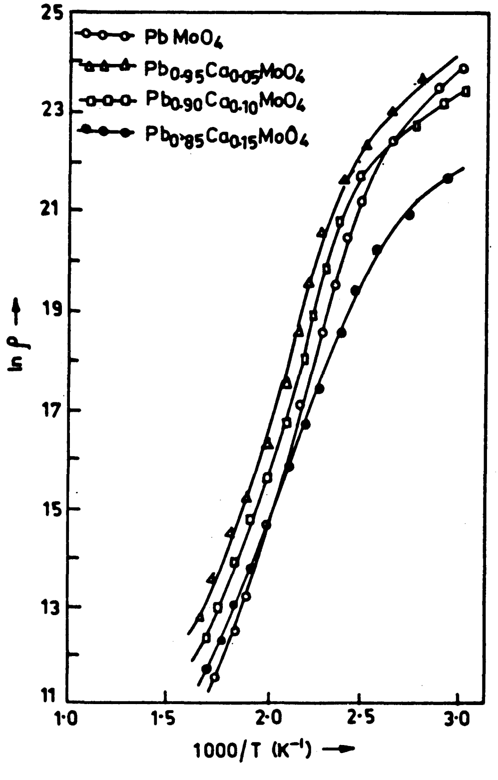

Fig 3. Variation of ln ρ_{dc} of $Pb_{1-x}Ca_xMoO_4$ as a function of inverse of absolute temperature at constant field 5.9 kV/m.

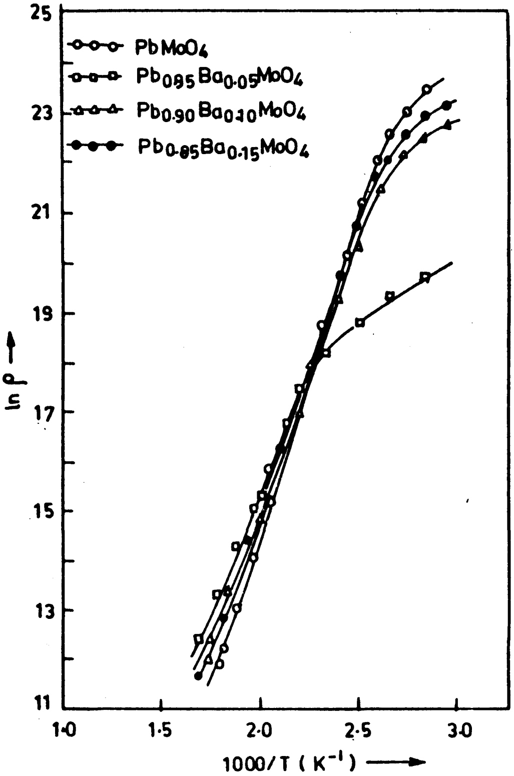

Fig 4. Variation of ln ρ_{dc} of $Pb_{1-x}Ba_xMoO_4$ as a function of inverse of absolute temperature at constant field 5.9 kV/m.

way. The ceramic samples have cracks/pores. The occurrence of some ionization of gases present is also possible in the cracks/pores, and when ionization of gases increases, the conductivity of the ceramic samples increases. Further, it may be possible that the electrode materials eject same electrons which are accelerated through the sample and collide with other ions or atoms and ionization takes place[13]. Therefore conductivy increases as the biasing field increases. Fig. 3 and 4 give variation of resistivity (in ρ_{dc}) with the inverse absolute temperature for all compositions of Ca and Ba-doped compounds at constant biasing electric field. It has been found that all the compounds show that resistivity decreases with increasing temperature, which may be due to the creation of free electrons due to thermal energy[14]. Above 448 K, the value of the resistivity and its temperature variation of ceramics containing various amounts of concentration of Ca and Ba ions doped in Pb site are almost equal in nature to those of pure ceramics. Precise measurement of the resistivity of all compounds is difficult near room temperature, because of very large resistivity. Such variation of resistivity with temperature indicates that the compounds has non-ferroelectric property but contains specific charge polarization at high temperature.

Conclusion

There is no change in the basic structure of lead molybdate with substitution of Ca or Ba at the lead site. Three different effects take place by addition of impurities:

(i) The temperature variation of the resistivity of ceramic cantaining impurities (Ca or Ba) is similer to that of pure ceramics. The impurities seem to be dissolved causing no change in the number of charge carrier of pure ceramics.

(ii) The resistivity of ceramics increases when the amount of impurities such as $CaCO_3$ is small (5%), but decrease when the amount becomes greater. The increase of the resistivity seems to be caused by the compensation of hole conduction. In order to explain the decrease of resistivity, the ceramics are assumed to consist of grain and thin impurity layer.

(iii) The temperature variation of the resistivity of ceramics containing 0.10 to 0.15 wt % $BaCO_3$ is close to that of pure ceramics as shown in Fig. 4.

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