

Anomalous d.c. conductance in Nd⁺³-doped ferroelectric lead germanate single crystal

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Abstract. Pure lead germanate (LG), 0.1 wt% Nd⁺³-doped lead germanate (LG.1Nd⁺³), 0.2 wt% Nd⁺³-doped lead germanate (LG.2Nd⁺³) were grown by controlled cooling of melt. Variation of d.c. conductivity was studied in the temperature range 293°K–523°K. Conductivity increases with increasing temperature, showing semiconducting behaviour for all the compositions under study. The activation energy in ferroelectric phase is larger than in paraelectric phase for all the compositions. The result suggests polaron hopping to be a significant contributor to conduction mechanism.

Keywords. d.c. conductivity; Nd⁺³ doping; activation energy; polaron hopping.

1. Introduction

Lead germanate is a suitable material for pyroelectric detector because of its small dielectric constant and a high pyroelectric coefficient (Watton *et al* 1976; Otto *et al* 1980; Monya *et al* 1981; Bravina *et al* 1989). It is of particular interest because of its promising applicability in acousto electronic and opto-electronic devices. It is well known that tailor-made additives (Devořak and Gloger 1966; Yanorskil 1980; Dergunova *et al* 1988) can be planned to modify the ferroelectric behaviour. Nd⁺³ doping in lead germanate also provides laser active host material (Kaminskii *et al* 1983). Information on conductivity behaviour is a prerequisite for ferroelectric materials to be used as ferroelectric solid state devices. It was therefore necessary to undertake the d.c. conductivity study alongwith structural modification, dielectric and pyroelectric study.

Conduction in pure and doped lead germanate have been studied extensively (Goto and Samaguchi 1979; Polomska *et al* 1979, 1981; Mansingh *et al* 1979; Mansingh and Kripanidhi 1980; Otto *et al* 1980; Dhuley and Katpatal 1985; Levstik *et al* 1992; Ghulghule 1996). While most investigations reveal higher activation energy in ferroelectric phase, Dhuley and Katpatal (1985) and Mansingh *et al* (1979) report lower activation energy in ferroelectric phase compared to paraelectric phase. Anomalous hump at transition temperature is another significant observation (Goto and Sawaguchi 1979; Mansingh *et al* 1979; Dhuley and Katpatal 1985). Kaminskii *et al* (1982) predicted Nd⁺³ to enter one or more Pb sites because of similar ionic radii of Pb⁺² and Nd⁺³. Moiseenko *et al* (1985) also reported replacement of Pb ion with La and Bi in lead germanate single crystal. In this paper we report the effect of Nd⁺³ doping on d.c. conductivity in lead germanate single crystal.

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2. Experimental

High purity starting materials (PbO 99.99% Aldrich USA, GeO₂ 99.999% Reachim USSR and Nd₂O₃ 99.9%) were used to grow pure lead germanate (LG), 0.1 wt% Nd³⁺ doping (LG.1Nd³⁺) and 0.2 wt% Nd³⁺ doping (LG.2Nd³⁺) single crystals by controlled cooling of melt in a platinum crucible. A chromel–alumel thermocouple along with SCR Module controller was used to monitor the temperature. The molten charge was cooled slowly at the rate of 1°C/h to few degrees below the melting point. Then subsequently at the rate of 2°, 5° and 10°C/h the charge was cooled down to room temperature. The crystals were cut, polished and electroded with air drying silver paste. The size of the crystals used in the measurement were about 0.3 × 0.3 × 0.2 cm. A specially designed spring-loaded crystal holder with highly insulating alumina tubes and silver electrodes was used. Aplab make power supply and SES make picoammeter with ± 0.3% accuracy were used to measure d.c. conductivity along *c*-axis.

3. Results and discussion

Temperature dependence of d.c. conductivity for pure and doped lead germanate is shown in figure 1. The summary of similarities in the conductivity behaviour of LG, LG.1Nd³⁺ and LG.2Nd³⁺ is as follows: (i) all the three samples exhibit semiconductive behaviour, (ii) in all the three compositions variation of log σ with $10^3/T$ is linear except in the vicinity of the respective transition temperature i.e. at 175°C for LG, 165°C for LG.1Nd³⁺ and at 150°C for LG.2Nd³⁺, (iii) a small hump is observed in all the three cases near their respective transition temperatures and (iv) existence of two activation energies above and below the transition temperatures are observed for all the three compositions.

Doping increases the conductivity of pure lead germanate marginally and shifts the anomalous conductivity region to lower temperature side but the nature of hump remains the same. Calculated values of activation energy using the formula

$$\sigma = \sigma_0 \exp(-E/2kT),$$

for the three compositions is shown in table 1 alongwith other reported values. Our values closely agree with the values reported by Goto and Sawaguchi (1979) and Ghulghule (1996).

The conductivity in ferroelectrics is a complex phenomenon. It is affected by the presence of defects, vacancies, imperfections and change in lattice parameters.

Wojcik (1988) suggested three possibilities of defects in PbTiO₃: (i) due to loss of PbO at higher temperature, vacancies may be created at Pb and O sublattices. Vacancy at Pb may give two holes whereas vacancy at O may give two free electrons, (ii) if the reaction takes place in reducing atmosphere the precipitation of Pb is possible and (iii) if PbO is in excess then Ti deficiency is obtained and vacancies appear in Ti sublattices.

Extending Wojcik's model to our lead germanate system, the possibility of producing vacancies at Pb and O sublattices is more. As PbO is highly volatile, therefore

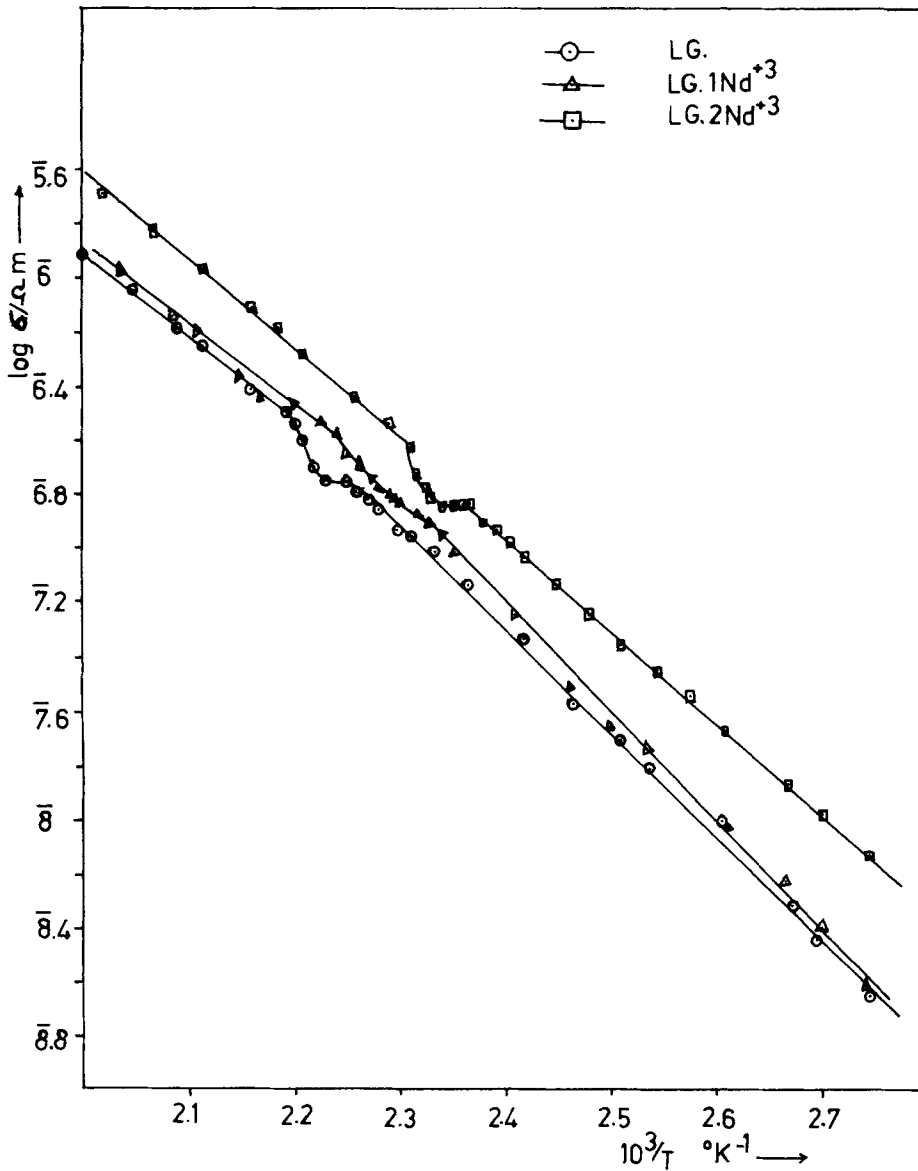
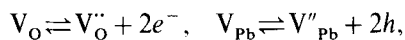
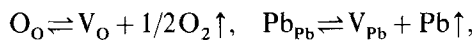
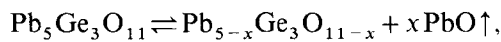


Figure 1. Variation of dc conductivity with temperature.

despite all the precautions taken during growth process, lead losses are expected to occur in lead germanate crystals. The reaction may be written as



and the charge neutrality condition may be written as:

$$2(V_{Pb}'') + 2(V_O'') + e + h = 0.$$

Table 1. Activation energy in eV for ferroelectric and paraelectric phases.

Material	AE-ferro	AE-para	Formula	References
LG	1.544	1.271	$\exp - E/2kT$	Our data
LG.1Nd ⁺³	1.51	1.373	$\exp - E/2kT$	Our data
LG.2Nd ⁺³	1.484	1.329	$\exp - E/2kT$	Our data
LG	1.6	1.41	$\exp - E/2kT$	Goto (1979)
LG	1.412	0.918	$\exp - E/2kT$	Glulghule (1996)
LG.5L	1.46	1.154	$\exp - E/2kT$	Glulghule (1996)
LG1 La	1.453	1.124	$\exp - E/2kT$	Glulghule (1996)
LG	0.31	0.54	$\exp - E/kT$	Dhuley and Katpatal (1985)
LG:Sm	0.36	0.66	$\exp - E/kT$	Dhuley and Katpatal (1985)
LG	0.83	0.71	$\exp - E/kT$	Polomska <i>et al</i> (1981)
LG:Si	0.8	0.67	$\exp - E/kT$	Polomska <i>et al</i> (1981)
LG:Si	0.74	0.66	$\exp - E/kT$	Polomska <i>et al</i> (1981)
LG:Nd	1.06	0.75	$\exp - E/kT$	Polomska <i>et al</i> (1981)
LG	0.62	0.91	$\exp - E/kT$	Mansingh <i>et al</i> (1979)
LG	0.96	0.82	$\exp - E/kT$	Polomska <i>et al</i> (1979)
LG ceramic	0.87	0.7	$\exp - E/kT$	Levstik <i>et al</i> (1992)

Vacancies are thus created at Pb and O sublattices. As our reaction is not carried out in a reducing atmosphere, precipitation of metallic Pb is not possible. Since we have prepared lead germanate by taking exact stoichiometric ratio 5 PbO:3GeO₂, so the excess of PbO is not expected. Thus occurrence of Ge vacancy is not possible in our system. Therefore Pb and O losses in lead germanate leads to (i) creation of vacancies at Pb and O sublattices and (ii) increase in the concentration of charge carriers.

Thus the conduction process in lead germanate is significantly contributed by vacancies formed at Pb and O sites. It is evident that doping enhances conductivity. The Nd⁺³ rare earth is likely to go to Pb (1) and Pb (2) sites. Nonisovalent substitution of Nd⁺³ at Pb⁺² results in corresponding excess charge carriers. The observed increase in conductivity due to doping is because of these excess charge carriers.

Dergunova *et al* (1988) reported semiconductive behaviour of BaTiO₃ with the addition of rare earth elements by examining distribution of rare earth cation between A and B sites of a crystal lattice. According to them substitution induces local lattice distortion around the impurity atoms and change in overall lattice constant. For a crystal to be in equilibrium it must have the lowest elastic energy, E , i.e. energy due to misfit between the unstrained bond lengths and the corresponding cation-anionic distances in the crystal. For low-doping level, $x < 0.1$ at.%, as $E > 0$, then the elements from La to Tm will substitute for Ti and $E < 0$ for Yb and Lu will substitute for Ba.

Stretching Dergunova's (1988) model to our system of lead germanate, in LG.1Nd⁺³, the Nd⁺³ is about 0.066 at.% as confirmed by inductive coupled plasma analysis. Calculated E in our case is positive. Therefore Nd⁺³ may replace Ge⁺⁴ making lead germanate p type semiconductor. However in LG.2Nd⁺³ the impurity Nd⁺³ is about 0.133 at.%. According to Dergunova, for $x > 0.1$ at.% this higher doping concentration leads to overlapping of local lattice distortion and to interaction

between impurity atoms. Then the difference between unstrained bond length or corresponding ionic radii becomes energetically more favourable and hence impurity cation Nd^{+3} will replace Pb^{+2} making it *n*-type semiconductor.

The temperature dependence of conductivity can be understood by intrinsic semiconductor model at low temperature and by polaron hopping at higher temperature for pure and doped lead germanate. The conduction is given by

$$\sigma = \sigma_0 \exp(-E/2kT),$$

where E is the intrinsic band gap.

At higher temperatures the conduction may also be contributed by polaron hopping. The effective mass of polaron is large compared to electron. The polaron formation is caused by dynamical electron-lattice interaction. If the interaction is sufficiently large electron will move through the lattice along with the associated polarization and the mobility will be very low. Electrical conductivity in this polaron model occurs when in the course of thermal fluctuation a site with the self-trapped electron attains a configuration equivalent to a neighbouring unoccupied site. The electron transfer can take place between the two sites.

In lead germanate due to loss of Pb and O during growth, vacancies are expected to form at Pb and O sublattices. Electrons trapped at Pb sites may form polarons. Different polarons formed at Pb(1), Pb(2) and Ge strain field sites are likely to hop with different activation energy of hopping. In doped compositions more vacancies are created because of nonisovalent Nd^{+3} doping. Therefore there is more probability of formation of polarons and increased polaron conduction in the doped samples. Both effective mass and associated local polarized field will be different in pure and doped samples. The mobility is of the form (Mott and Davis 1971)

$$\mu = (e/kT)pR^2 \exp(-Wh/kT),$$

where $p = w_0 \exp(-2\alpha R)$, where $\exp(-2\alpha R)$ is the rate at which the wave function of the electron in one of the localized states falls off with distance. R is the distance through electron transfer, Wh , the hopping activation energy. The observed existence of two activation energies may be associated with the structural changes taking place at transition temperature i.e. from space group P3 (trigonal) at ferroelectric phase to $P\bar{6}$ (hexagonal) in paraelectric phase, as reported by Iwata (1977). At below transition temperature i.e. in ferroelectric phase the conduction is contributed by intrinsic process, higher value of activation energy is expected. At higher temperatures along with intrinsic process conduction is contributed by hopping of different types of polarons which may have different activation energies of hopping. Thus lower value of activation energy can be expected for both pure and doped compositions.

Doping does not change the nature of hump observed at their respective transition temperatures. Following Goto *et al* (1979), the observed hump can be correlated to the response of domain wall movement with applied field which effectively decreases the impedance and causes hump. The coercive field along c-axis is very small near transition temperature, so applied field for conductivity measurement is sufficient to cause movement of domains through polarization reversal. The interaction of charge carriers with such mobile domain boundaries may give rise to hump in our case. However the shape of the hump could not be understood properly.

4. Conclusion

The conduction process in pure and doped lead germanate is of intrinsic nature at lower temperature. The thermally activated polaron may contribute conductivity at higher temperature. Both pure and doped compositions possess negative temperature coefficient and the conductivity of doped compositions increases marginally.

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