

Electrical conductivity and stimulated thermocurrent studies in dicalcium lead propionate single crystal

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Abstract. Electrical conductivity and stimulated thermocurrent (STC) studies are carried out in dicalcium lead propionate (DLP) in pure, Cu^{2+} , Fe^{3+} and acetate doped single crystals over a temperature range of 303° to 503° K. Conductivity measurements on pure and doped single crystals of DLP indicate that both propionate anions and metallic cations are responsible for the transition occurring at 333° K. Thermoelectric power measurements from 340° to 500° K in DLP (pure) indicate that the transport charge carriers are electrons. A model for the conduction mechanism is proposed on the basis of hopping of π or resonating electrons of carboxyl groups through tunnel paths involving metal ions (Pb^{2+} and Ca^{2+}). From activation energies estimated from conductivity and STC measurements, the STC peak in DLP (Fe^{3+}) occurring at 513° K is attributed to impurity vacancy jump mechanism.

Keywords. Electrical conductivity; ferroelectric transitions, thermoelectric power; hopping mechanism; stimulated thermocurrent; impurity-vacancy jump mechanism.

1. Introduction

Electrical conductivity and stimulated thermocurrent measurements yield information (Ah Mee Hor *et al* 1976; Hor and Jacobs 1977; Matsui and Wagner 1977) about the structural changes, activation energy, effects of impurities, frequency factor and mechanism of conduction. In particular, such studies on ferroelectric crystals are interesting, since they are associated with phase transitions, from ferroelectric to paraelectric phase. The $\log \sigma$ vs $(1/T)$ graph indicates a kink at the transition temperature (Zheludev 1971; Rao and Rao 1978), associated with the appearance or disappearance of spontaneous polarization. Phase transitions are generally investigated using dielectric measurements, differential scanning calorimetric measurements and specific heat measurements (Sawada *et al* 1978a; Nakumara *et al* 1965). Although experimental data corresponding to changes in structure and spontaneous polarization along with changes in electrical conductivity are available, the nature of their relationship is not yet clearly established.

The measurement of stimulated thermocurrent (STC) is one of the most direct and sensitive methods of determining the reorientation kinetics of dipolar complexes. This technique is more sensitive than the technique of dielectric relaxation and has the additional advantage that the temperature of measurement is well below the temperature of the break-up of the complexes. The correlation between the conductivity and STC measurements provides information about the nature of conduction

mechanism. Thermoelectric power measurements on single crystals can yield information about the nature of charge carriers and also about the charge transport mechanism in a given sample.

The present paper reports our studies on electrical conductivity, STC and thermoelectric power measurements in dicalcium lead propionate (DLP) single crystals (both pure and doped), to investigate the nature of phase transition occurring at 333°K (Nakumara *et al* 1965; Takashige *et al* 1976) in this crystal and the nature of transport mechanism.

2. Crystal structure

Dicalcium lead propionate $\text{Ca}_2\text{Pb}(\text{CH}_3\text{CH}_2\text{COO})_6$ is a tetragonal crystal, belonging to the space group $D_4^4-P_{41}2_12$ or $(D_4^3-P_{43}2_12)$ (Ferroni and Orioli 1959). Only the positions of metallic cations were reported and no attempt was made to determine the positions of the organic groups in the above studies. DLP crystal was reported to be isostructural with dicalcium strontium propionate (DSP). As in the case of DSP, Pb^{2+} and Ca^{2+} metallic cations should have dodecahedral and octahedral coordinations respectively, with the oxygens of carboxyl groups. Each oxygen atom coordinates a lead ion on the one side and a calcium on the other side and plays a major role in conduction process. DLP crystal is ferroelectric along the tetragonal *c*-axis up to 333°K.

3. Crystal growth

The crystals are grown from aqueous solutions by slow evaporation. Lead carbonate is dissolved in aqueous solution of propionic acid by slow heating. Calcium oxide is dissolved in the above solution in their molar ratios. The crystals grow in two morphological forms, pyramidal-tabular, and octahedral. Crystals of both the forms are chosen for the experimental work. Ferric chloride, cupric chloride and calcium acetate are used as dopants, while growing doped crystals. The crystallographic directions are identified by Laue x-ray photographs.

4. Experimental details

Electrical conductivity and stimulated thermocurrent studies are carried out using a cell as shown in figure 1a, which is designed and fabricated in this laboratory. The conductivity cell consists of two stainless steel hollow cylinders fastened together by an o-ring, the upper double-walled cylinder acting as a container of liquid nitrogen. The sample is cooled to low temperatures by cold-finger method. The crystal mount is a cylindrical brass rod which serves as one of the electrodes. A small brass rod in juxtaposition—spring-loaded and insulated from the main body by a teflon piece—acts as the second electrode. A third electrode known as *guard ring* is provided [figure 1b] to prevent the surface conduction effects in the measurements. In addition, the conductivity unit is standardized, using triglycine sulphate single crystals (TGS) whose currents are in the range of 10^{-13} amps. The results obtained in the electrical

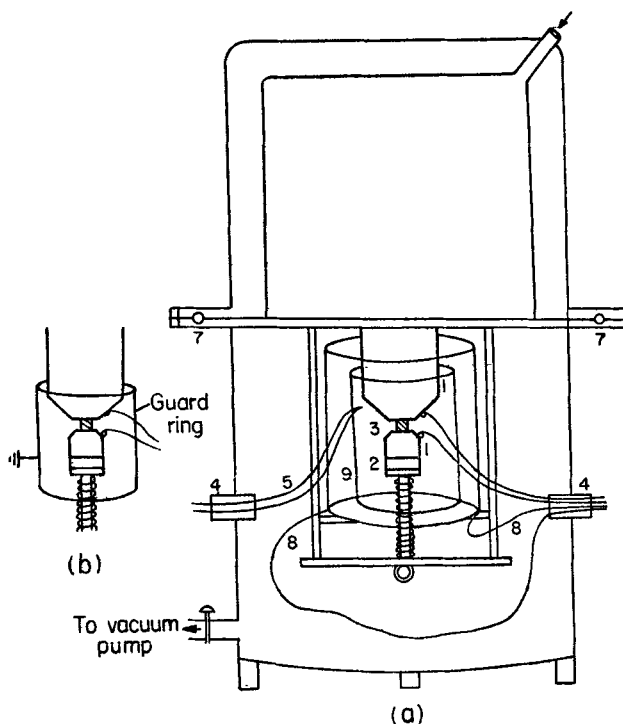


Figure 1. (a) Conductivity cell. (b) Guard-ring arrangement. 1, 1, Electrodes, 2-teflonpiece, 3-sample, 4, 4 teflon taper plugs, 5-thermocouple, 6-Liquid nitrogen container, 7, 7 o-rings, 8, 8 heater leads, 9-guard ring.

conductivity measurements (including the transition at 322° K) on TGS single crystals agree with those reported in literature (Zheludev 1971). The temperature of the sample is raised using a concentric heater wound on split ceramic tube. Shielded teflon coaxial cables are used from electrodes to the input of the electrometer. A double-pole double-throw switch on a teflon base is used to make and break the circuit. The vertical winding of heating element on ceramic split cylinder and heating with AC supply yielded no background. The whole equipment is placed on teflon sheets covered with metallic sheets to avoid leakage currents. By proper isolation and shielding the noise level is reduced to less than 10^{-14} amps. Current measurements are made by a sensitive electrometer (Anadigi Co. Model DE 5202), which was also calibrated against a Keithley electrometer (type 610C). The accuracy of current measurements is within $\pm 2\%$. The current variation by reversing the battery terminals is $\pm 2\%$, which indicates an ohmic contact between the crystal surface and the electrodes. Silver paint is used for the contact between the crystal surfaces and the electrodes. The current measurements are carried out both while cooling and heating the sample, which avoids the electrode effects, surface charges and establishes repeatability of measurements. Linear heating rate in STC experiment is provided with a slow moving motor, which in turn rotates the wheel fixed to an auto-transformer. The STC spectrum is recorded on two strip chart recorders (one for current versus time and the other for temperature versus time). A program written for TDC-12 computer is used to find the best fitting values of STC spectra. A sensitive differential scanning calorimeter of Dupont model 910 is employed to investigate either the endothermic or exothermic peaks on powder samples of DLP (both pure

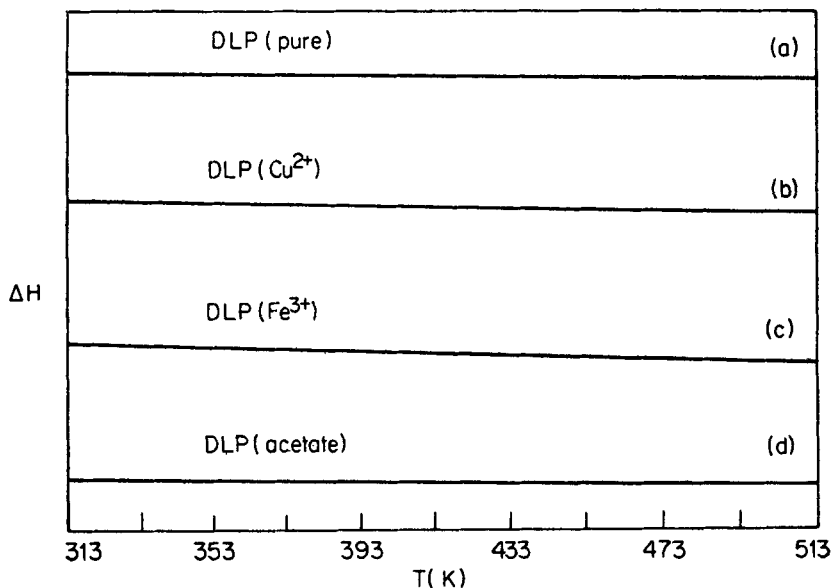


Figure 2. (a), (b), (c), (d) thermograms of DSC on powders of pure, Cu^{2+} , Fe^{3+} , acetate doped DLP.

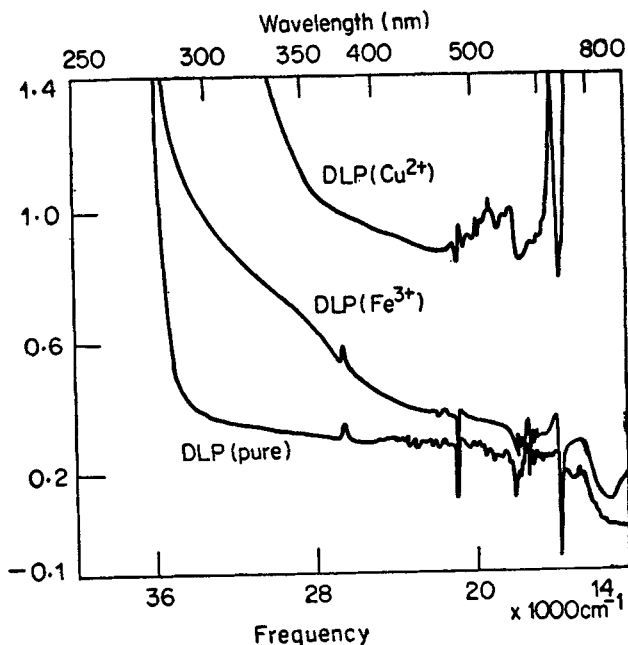


Figure 3. Optical absorption spectra DLP (pure), DLP (Cu^{2+}) and DLP (Fe^{3+}).

and doped) [figures (2a, b, c, d)] and the rate of heating is $10^\circ/\text{min}$. Differential thermal analysis measurements on powder sample of DLP (pure), employing a DTA unit (Leeds and Northrope) are carried out to determine the melting point, which is found to be 730°K . No evidence of decomposition below this temperature is observed in this experiment. The rate of heating in this experiment is $12.5^\circ/\text{min}$. The thermo-electric power at various temperatures from 340° to 500°K is determined by a hot

probe method (Bruk *et al* 1969; Kireev 1974) with respect to hot junction. A minimum temperature difference of 30°K is always maintained between the hot and the cold junctions of the crystal. In addition, optical absorption measurements are carried with Specord spectrophotometer on DLP (pure) DLP (Fe³⁺) and DLP (Cu²⁺) single crystals, wherein a broad peak at 350 nm in UV region (corresponding to Fe³⁺ impurity) and another peak around 550 nm in visible region (corresponding to Cu²⁺ impurity) are indicated (figure 3). The presence of ferric ion in DLP (Fe³⁺) single crystal is confirmed by chemical analysis also. A weighed portion of DLP (Fe³⁺) crystal is dissolved in HCl (4M), and is added to the solution of potassium thiocyanate (of 20 g) dissolved in 100 ml of water (2M concentration) resulting in an intensely red colour complex, confirming the presence of Fe³⁺ ion (Vogel 1968). Besides, concentrations of dopants Fe³⁺ and Cu²⁺ in doped crystals are estimated, employing an atomic absorption spectrophotometer (Perkin Elmer, model -373) which are found to be 20 and 170 ppm respectively.

5. Results and discussion

5.1 Electrical conductivity

The conductivity measurements are carried out from room temperature 303°K to 503°K across [100], [010] and [001] planes of single crystal of DLP (pure). Log σ vs (1/T) graph of DLP (pure) single crystal across [001] plane indicates two peaks (figure 4), one at 330°K and another at 370°K. Besides, discontinuities are observed in log σ versus (1/T) graph (figure 4) around 312°K across [100] and [010] planes

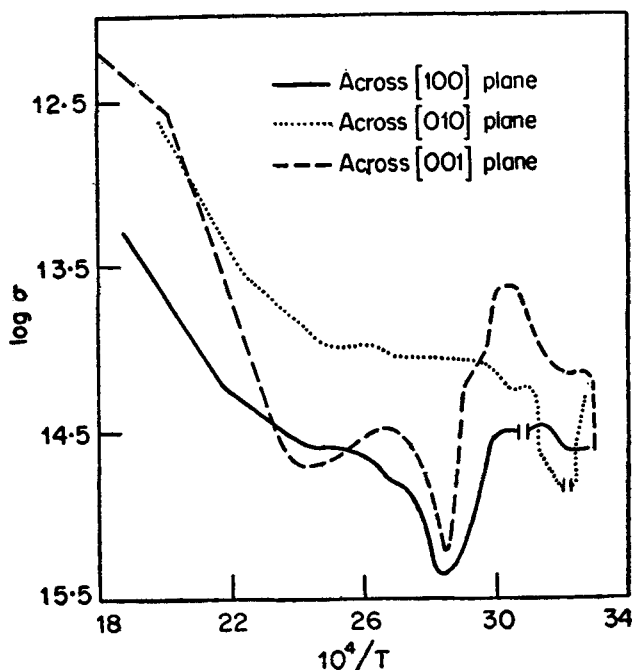


Figure 4. log σ versus 1/T graph of DLP (pure) single crystal across [100], [010] and [001] planes.

of DLP (pure). Nakumara *et al* (1965) and Takashige *et al* (1976) reported the ferroelectric transition at 333°K using dielectric measurements. The above transition is of the second order, associated with spontaneous polarization, since no peak (either exothermic or endothermic) is observed at 333°K in differential scanning calorimetric measurements in DLP (pure), Fe³⁺, Cu²⁺, acetate doped powder samples (figure 2). The observed discontinuities around 312°K across [100] and [010] planes in DLP (pure) can be attributed to some features, typical of first order transitions. A similar case is that of triglycine sulphate single crystal, which undergoes a second order transition at 322°K (Zheludev 1971) and indicates not only a peak at the transition temperature but a discontinuity also.

Shifts in transition peak temperatures are observed in $\log \sigma$ vs $(1/T)$ graphs of DLP (Cu²⁺), DLP (Fe³⁺) and DLP (acetate) across [001] plane (figure 5) and are indicated in table 1.

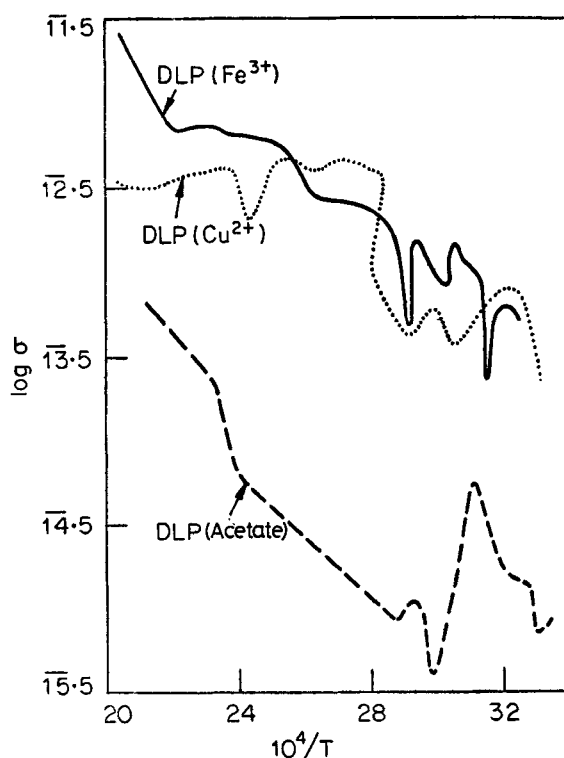


Figure 5. $\log \sigma$ versus $1/T$ graph of DLP (Cu²⁺), DLP (Fe³⁺) and DLP (acetate) across [001] plane.

Table 1. Shifts of transition peak temperatures.

Sample	Low temperature peak (°K)	High temperature peak (°K)
DLP (Pure)	330	370
DLP (Cu ²⁺)	345	385
DLP (Fe ³⁺)	308	363
DLP (Acet)	323	343

It is most probable that Cu^{2+} and Fe^{3+} impurity ions enter the lattice substitutionally for Ca^{2+} ion, which is octahedrally coordinating with six oxygens of carboxyl groups. It is unlikely to substitute the Pb^{2+} site, which has larger ionic radius of 0.99 Å. However, even this radius is larger than those of Fe^{3+} (0.64 Å) and Cu^{2+} ion (0.72). Hence Fe^{3+} and Cu^{2+} ions may loosely be held in Ca^{2+} site. The substitution of Fe^{3+} ion in Ca^{2+} site in DLP (Fe^{3+}) causes an anion and cation vacancy pair in the lattice. In the case of DLP (acetate), the partial substitution of acetate ions to the propionate anions might be responsible for the shift in the transition peak temperatures. The conductivity measurements on DLP (Cu^{2+}), DLP (Fe^{3+}), DLP (acetate) suggest that both cations and anions might be responsible for the transition occurring at 333°K in DLP (pure).

The positive sign in thermoelectric power (Bruk *et al* 1969; Kireev 1974) measurements of DLP (pure) from 340° to 500° K (figure 6) indicate that the majority charge carriers are electrons.

DLP (pure) crystal can be classified as an organic semiconductor (of ionic type) having its conductivity in the range of $10^{-14} \Omega^{-1} \text{cm}^{-1}$. Electrical conduction in these crystals can be explained by a hopping process (because of low mobility $10^{-7} \text{cm}^2/\text{V sec}$ determined from conductivity and thermoelectric power measurements, Hannay 1959). The electrons hop from one molecule to the other. The two metallic cations (Pb^{2+} and Ca^{2+}) coordinating to one another through oxygens of carboxyl groups that are bridging Pb^{2+} and Ca^{2+} , have resonating electrons (resonating between the two oxygens) and the latter play a major role in the conduction process. Assuming that a hopping mechanism is involved in the electrical conduction, the charge carriers (electrons) move from one carboxyl group to another through a tunnelling path

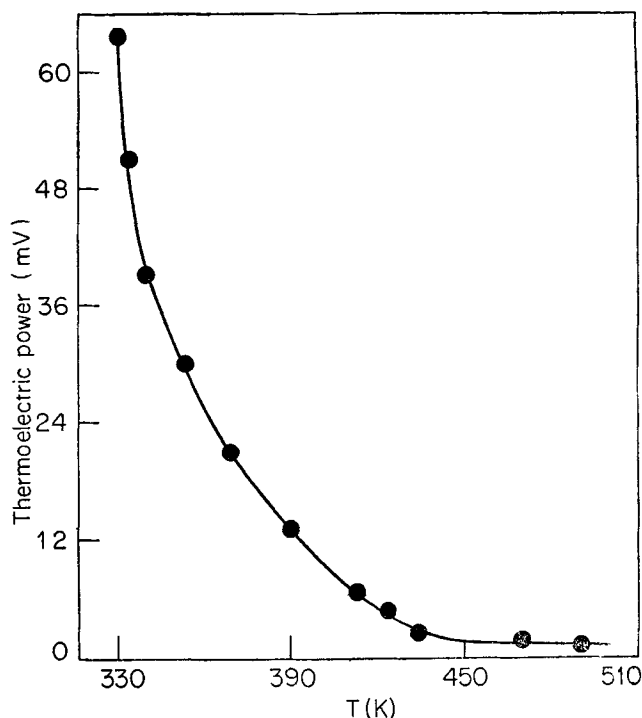


Figure 6. Thermoelectric power versus temperature graph of DLP (pure).

involving metal ions (figure 7), around which the ethyl groups are situated. The latter consisting of saturated carbons do not contribute to the conductivity. The results obtained by the present authors in a similar compound namely dicalcium barium propionate (Madhusudan *et al* 1980) could also be explained by the above conduction mechanism.

5.2 Stimulated thermocurrent measurements

The thermally stimulated thermocurrent (STC) experiment is carried out on pure, Cu^{2+} , Fe^{3+} and acetate doped single crystals of DLP, across [001] plane. The STC experiments are carried out both above and below the room temperature (upto 150°K below room temperature), with various polarizing voltages, polarizing times, and heating rates, some of which are indicated in table 2. Pure, Cu^{2+} and acetate doped single crystals did not indicate any STC peak either below or above room temperature (figures 8b, c, d). The STC peak for all polarizing voltages, times, and heating rates in the case of DLP (Fe^{3+}) single crystal, is observed around 513°K only.

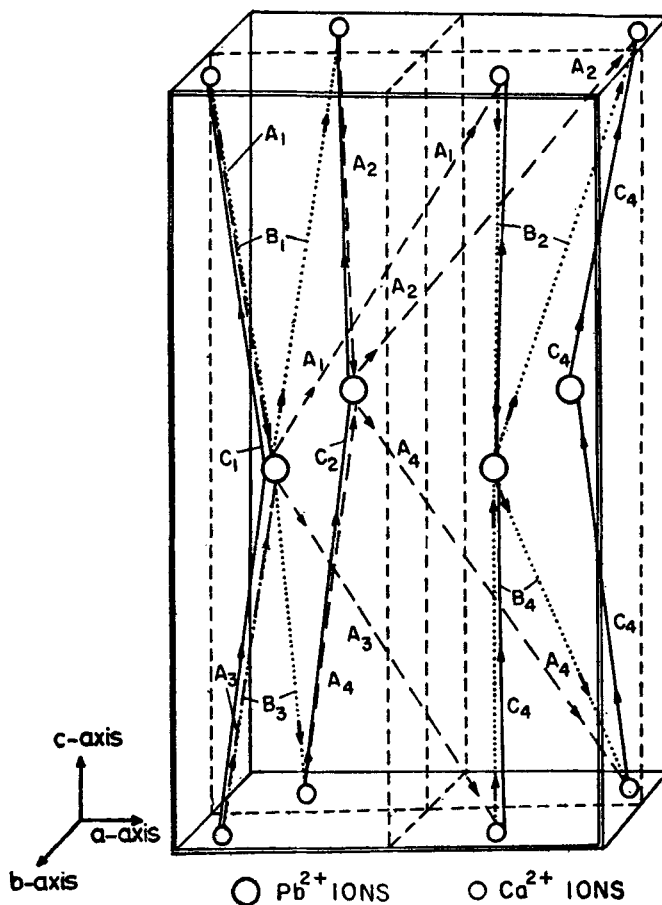


Figure 7. Conducting paths in a unit cell across [100] plane — A_1, A_2, A_3, A_4 , across [010] plane B_1, B_2, B_3, B_4 , across [001] plane — C_1, C_2, C_3, C_4 .

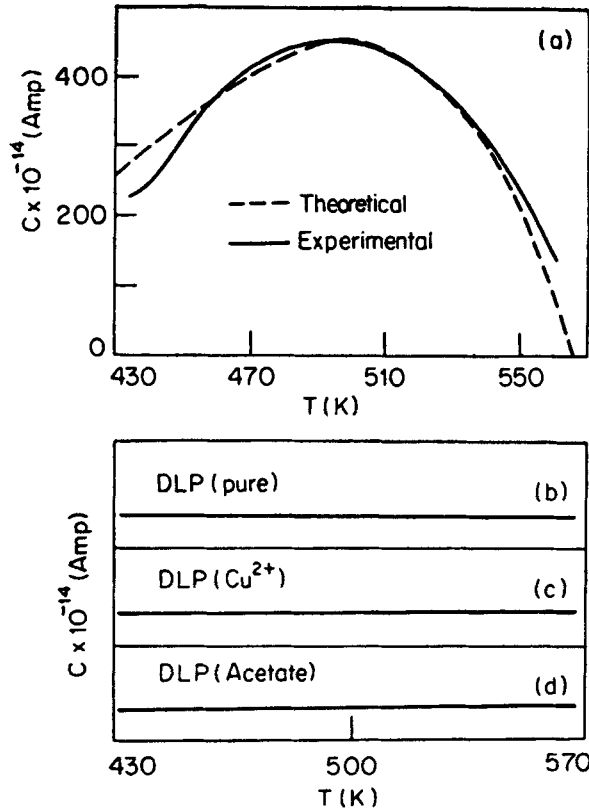


Figure 8. (a) STC spectra of DLP (Fe³⁺) single crystal across [001] plane. (b), (c) and (d) STC spectra of pure, Cu²⁺, acetate doped DLP single crystals.

Table 2. STC peak with various polarizing voltages and heating rates

Samples	Polarizing voltage kV/cm	Polarizing time (min.)	Heating rate (°/m)	Peak temperature (°K)
DLP (Fe ³⁺)	1.6	30	7.5	508
	1.6	30	10	510
	1.6	30	16	513
	1.0	30	16	510

When the sample is heated at $\beta = dT/dt$, the instantaneous value of polarization current (Bucci and Fieschi 1964; Bucci *et al* 1966 and Bucci 1967), is given by

$$J(t) = \left(\frac{P_0}{\tau_0}\right) \exp \left[-(E/kT) - (1/\beta\tau_0)\right] \int_{\tau_0}^{\tau} \exp(-E/kT) dT$$

where P_0 = initial polarization, k = Boltzmann's constant, E = activation energy. The polarization current has a peak at the temperature (T_m) where

$$\tau_0 = kT_m/\beta E [(E/kT_m)].$$

Figure (8a) indicates one of the typical STC spectra of DLP (Fe^{3+}) with a peak at 513°K. The linear dependence of STC maxima on the polarizing voltages, and μg ($=\delta/\omega$) = 0.42 suggests (Reuven 1977) the applicability of the first order thermoluminescence kinetics to the STC curve of DLP (Fe^{3+}). The value of activation energy and the pre-exponential factor evaluated from different methods for the STC curve are indicated in table 3. As mentioned earlier, substitution of Fe^{2+} ion in DLP (Fe^{3+}) single crystal causes vacancy pairs of cation and anion and the propionate anion vacancy is equivalent to an electron vacancy (figure 9) (caused by the absence of resonating or π -electron of oxygens of carboxylic group). In pure Cu^{2+} and acetate-doped DLP single crystals such vacancy pairs are not formed and the absence of STC spectra in these crystals can be understood on this model. Thus in the case of DLP (Fe^{3+}) the STC peak occurring at 513°K might be due to impurity-vacancy jump mechanism. The observed broad peak indicates the participation of large number of dipoles in this type of jump mechanism. As the activation energy of the STC peak of DLP (Fe^{3+}) and the activation energy evaluated from conductivity measurements in the intrinsic region across [001] plane (figure 4, table 3) agree with

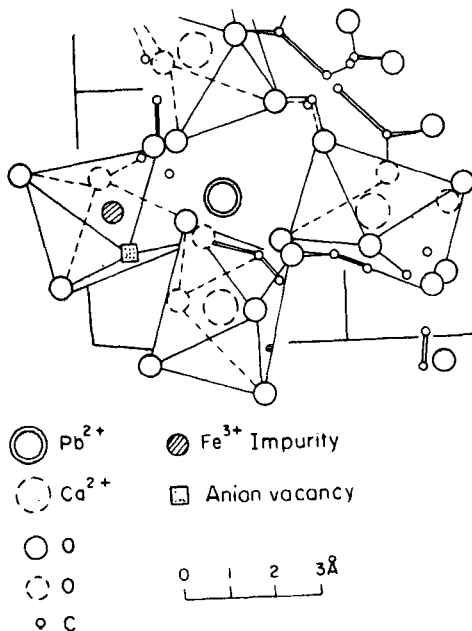


Figure 9. The location of cation impurity and an anion valency in the unit cell of DLP (Fe^{3+}) single crystal projected on [001] plane.

Table 3. Activation energy and pre-exponential factor evaluated by various methods.

Method	Activation energy (eV)	Pre-exponential factor (τ_0)S
Initial rise	0.36	0.72×10^{-7}
Chen's	0.38	
Curve fitting	0.37	
Conductivity	0.36	

each other, the STC peak can be attributed to impurity-vacancy jump mechanism. Such examples with broad peaks at high temperature, with low τ_0 value, have not been reported earlier.

Formation of dipolar complexes, when the trivalent ions are doped in divalent sites, have however been reported in other systems. Kitts *et al* (1973) and Kitts and Crawford (1973) have carried out ITC experiments on alkaline earth fluorides MF_2 (where M stands for Ca, Ba, Sr) doped with trivalent rare-earth impurities such as Gd^{3+} , Y^{3+} . Normally the trivalent ion substitutes for a host lattice (M^{2+}). Charge compensation is attained by a fluoride interstitial in a nearest neighbour (nn) position. This forms a dipolar complex, which can orient by means of a thermally activated jump of F_1^- to another (nn) site. The ITC peak occurs at a sufficiently low temperature for the above said fluoride structures. On the other hand, the STC peak for DLP (Fe^{3+}) is at a higher temperature (513°K) with an activation energy of 0.36 eV. The conductivity and thermoelectric power measurements on DLP (pure) indicate that the charge carriers are electrons, supporting the above argument.

6. Conclusions

(i) The activation energy evaluated from both conductivity and STC measurements agree with each other. This indicates that the transport charge carriers in DLP (pure) sample are electrons, which is further supported by thermoelectric power measurements.

(ii) Conductivity studies on DLP (Cu^{2+}), DLP (Fe^{3+}) and DLP (acetate) indicate that both cations and anions are responsible for ferroelectric transition occurring at 333°K in DLP (pure) crystal.

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References

- Bruk V, Garshenin V and Kunosov A 1969 *Semiconductor technology* (Moscow: Mir Publishers) p. 309
- Bucci C 1967 *Phys. Rev.* **164** 1200
- Bucci C and Fieschi R 1964 *Phys. Rev. Lett.* **12** 16
- Bucci C, Fieschi R and Guidi G 1966 *Phys. Rev.* **148** 816
- Ferroni Von E and Orioli P 1959 *Z. Kristallogr. Bd.* **111** 362
- Hannay N B 1959 *Semiconductors* (New York: Reinhold) p. 600
- Hor A M and Jacobs P W M 1977 *J. Solid State Chem.* **22** 77
- Hor A M, Radhakrishna S and Jacobs P W M 1976 *Can. J. Phys.* **54** 1669
- Kireev P S 1974 *Semiconductor physics* (Moscow: Mir Publishers) p. 309
- Kitts Jr E L and Crawford Jr J H 1973 *Phys. Rev. Lett.* **30** 443
- Kitts Jr E L, Ikeya M and Crawford J H 1973 *Phys. Rev.* **138** 5840
- Madhusudan V, Sathyanarayan S G and Sivarama Sastry G 1980 *Phys. Status Solidi A* **62** 299
- Matsui T and Wagner Jr J 1977 *J. Electrochem. Soc.* **124** 610

- Nakumara N, Suga H, Chihara H and Seki S 1965 *Bull. Chem. Soc. Jpn.* **38** 1779
- Rao C N R and Rao K J 1978 *Phase transitions in solids* (New York & London: Mc-Graw Hill) p. 286
- Reuven C 1977 *J. Electrostat.* **3** 15
- Sawada S, Shiroishi Y, Yamamoto A, Takashige M and Matsuo M 1978a *Phys. Lett.* **A67** 56
- Sawada S, Shiroishi Y, Yamamoto A, Takashige M and Matsuo M 1978b *J. Phys. Soc. Jpn.* **44** 687
- Takashige M, Iwamura H, Hirotsu S and Sawada S 1976 *Ferroelectrics* **11** 431
- Vogel A I 1968 *A textbook of quantitative inorganic analysis*, (London: English Language Book Society) (3rd ed.) p. 785.
- Zheludev I A 1971 *Physics of crystalline dielectrics* (New York/London: Plenum Press) Vol. 2 p. 495