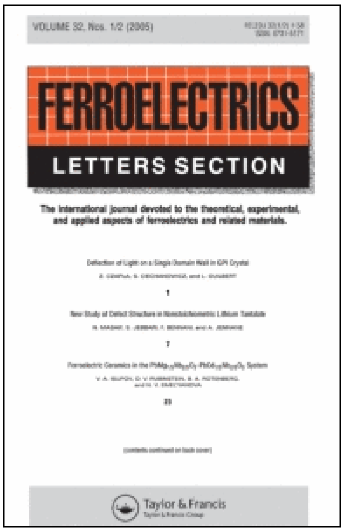
This article was downloaded by: *[INFLIBNET India Order]*
On: *13 December 2010*
Access details: *Access Details: [subscription number 920455929]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Ferroelectrics Letters Section

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713871498

Thermal Properties of Dicalcium Lead Propionate Across the Prominent Transition Temperatures

M.V. MANJUSHA[a]; J. PHILIP[a]
[a] Department of Instrumentation and STIC, Cochin University of Science & Technology, Cochin, India

To cite this Article MANJUSHA, M.V. and PHILIP, J.(2008) 'Thermal Properties of Dicalcium Lead Propionate Across the Prominent Transition Temperatures', Ferroelectrics Letters Section, 35: 5, 107 — 118
To link to this Article: DOI: 10.1080/07315170802520102
URL: http://dx.doi.org/10.1080/07315170802520102

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ferroelectric Letters, 35:107–118, 2008

ISSN: 0731-5171 print / 1563-5228 online
DOI: 10.1080/07315170802520102

Thermal Properties of Dicalcium Lead Propionate Across the Prominent Transition Temperatures

M. V. MANJUSHA and J. PHILIP*

Department of Instrumentation and STIC, Cochin University of Science & Technology, Cochin 682 022, India

Communicated by Dr. George W. Taylor

(Received October 20, 2007)

The thermal transport properties, thermal diffusivity, thermal conductivity and specific heat capacity of Dicalcium Lead Propionate (DLP) crystal have been measured following a modified photopyroelectric thermal wave method. The measurements have been carried out with thermal waves propagating along the three principal symmetry directions, so as to bring out the anisotropy in these parameters. The variations of the above parameters through two prominent phase transition temperatures of this crystal have also been measured to understand the variation of these parameters as it undergoes ferroelectric phase transitions. In addition, complete thermal analysis and FTIR measurements have been done on the crystal to bring out the correlation of these results with the corresponding thermal transport properties. All these results are presented and discussed. The data presented in this paper form a comprehensive set of results on the thermal transport properties of this crystal.

Keywords: Dicalcium lead propionate; thermal diffusivity; thermal conductivity; specific heat capacity; thermal analysis

INTRODUCTION

Dicalcium Lead Propionate (DLP, chemical formula $Ca_2Pb\ (C_2H_5COO)_6$), which belongs to the family of double propionates, is ferroelectric below 333K along the c- axis [1]. It undergoes a para to ferro electric phase transition at 333K (Tc_1), which is a second order one. Upon decreasing the temperature further, it undergoes another phase transition at 191 K (Tc_2), which is first order. The transition at Tc_1 is associated with the movement

---

*Corresponding author. E-mail: jp@cusat.ac.in of the ethyl group (C_2H_5) [2], but the one at Tc_2 is still not understood well. Even below this transition temperature the material continues to remain ferroelectric. Based on the measurement of the hydrostatic pressure dependence of the crystal structure of DLP above and below the respective phase transitions, Gesi and Ozawa [3] have proposed that the phases above and below Tc_2 are isomorphous to each other. However, on the basis of polarizing microscopic observations and dielectric constant measurements Gesi has concluded that the two phases above and below Tc_2 are not isostructural [4].

The crystal structure of DLP is tetragonal at room temperature [5]. The space group associated with this is $D_4^4(P4_32_12)$. The lead atoms are located at $4a$ positions and calcium atoms at $8b$ positions. It is also interesting to note that the position of organic group has not yet been identified. Studies on the pyroelectric properties of DLP associated with its phase transitions by Osaka et al. have led to the conclusion that DLP crystal between Tc_1 and Tc_2 is tetragonal and polar, the point group in this phase being C_4 or C_{4v} [6].

The Raman, infrared and dielectric properties of this crystal have been studied by earlier workers [7, 8]. Earlier EPR studies on DLP, doped with $Mn^{2+}_,$ by Bhat et al. suggest that Mn^{2+} enters the plane of Ca^{2+} substitutionally, and are loosely held in the lattice sites of Ca^{2+}, as the ionic radius of Mn^{2+}(0.08 nm) is small compared to Ca^{2+}(0.09 nm) [9]. From the results on the temperature dependence of electrical conductivity and dielectric constant, Badarinath et al have concluded that the para to ferroelectric transition in Mn^{2+} doped DLP is a defect controlled property, and is dependent on the concentration of the dopant [10]. The phase diagram of mixed crystal system DSP-DLP, where DSP stands for Dicalcium Strontium propionate, was determined for the first time by Nagae et al. from dielectric and dilatometric measurements [7]. They confirmed that the space groups of DLP are $D_4^4(D_8^4)$ above Tc_1 and $C_2^4(C_4^4)$ below this temperature. Work done by Standnicka et al. showed how much more accurately the transition temperature could be established for DSP-DLP mixed crystal through high precesion measurements of optical retardation [11]. Nage et al. have reported Raman scattering spectra of DSP and DLP between 73 and 423 K [7]. They concluded that both the phase transitions of the two materials are of the order–disorder type since no soft modes were observed implying that these transitions are most probably isomorphous [7]. Takashige et al. has reported the piezoelectric and elastic properties of ferroelectric DLP over a wide temperature region, including the ferroelectric-paraelectric phase transition point (Tc_1) [8].

Even though the specific heat of DLP was reported way back in 1965 [1], other thermal properties such as thermal conductivity have not been reported so far. Moreover, systematic thermal analysis following thermogravimetry or scanning calorimetry through $Tc_1$and Tc_2have not yet been reported. In this work we report thermo gravimetric and scanning calorimetric analysis of DLP through these transition temperatures. The FTIR spectrum at room temperature is also reported. The thermal transport properties of the sample, thermal diffusivity (α), effusivity (e), thermal conductivity (k) and specific heat capacity (c_p) of the sample have been measured as a function of temperature following an improved photopyroelectric (PPE) thermal wave technique. The anisotropy in thermal diffusivity/conductivity along the principal axes as well as their variation through these transition temperatures have been measured. The experimental methods followed, results obtained and a discussion of the results are given in the following sections.

EXPERIMENTAL METHOD

Sample Preparation

DLP crystals were grown by slow evaporation method [12]. PbO was gradually dissolved in an aqueous solution of propionic acid, to which calcium salt of propionic acid was added in stochiometric proportion. The best resulting crystals were dissolved in water for recrystalisation. This process is repeated three or four times. In about four to five weeks time, colorless DLP crystals with sizes in the range of 1 cm^3 were obtained. The so obtained crystals were cut with a slow speed diamond wheel saw such that they have faces perpendicular to the [100], [010] and [001] orientations. The samples were carefully polished and made into a thickness of about 0.5 mm for photopyroelectric measurements. The density of the sample was measured to be 1.7474 g/cm^3. The morphology of the crystal is shown in Fig. 1. Lumps or pieces of sufficient volume were used for FT IR and thermal analysis experiments.

Photopyroelectric Thermal Wave Measurements

An improved photopyroelectric method has been used to determine the thermal properties of single crystals of DLP [13, 14]. For this measurement the sample dimensions should be such that the sample, the pyroelectric detector and the backing material should be thermally thick during the whole measurement. The sample is illuminated with an intensity-modulated beam of light, which gives rise to periodic temperature variation in the sample by

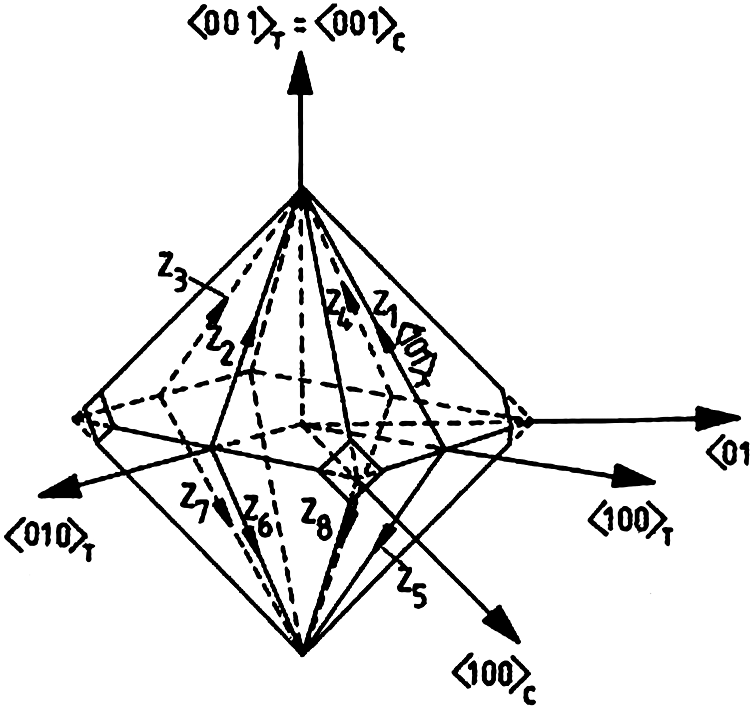


Figure 1. Morphology of DLP crystal.

optical absorption. The thermal waves so generated propagate through the sample and are detected with a pyroelectric detector.

A 70 mw He-Cd laser of wavelength $\lambda = 442$ nm has been used as the optical heating source and the intensity modulation is done with a mechanical chopper (Model SR540). A PVDF film of thickness 28 μm, with Ni-Cr coating on both sides, with pyroelectric coefficient $P = 0.30 \times 10^{-8}$ Vcm^{-1}K^{-1}, is used as the pyroelectric detector. The output signal is measured using a lock-in amplifier (Model SR830). Modulation frequency is kept above 30 Hz in all our experiments to ensure that the detector, the sample and the backing medium are all thermally thick during measurements. The thermal thickness of DLP sample has been verified by plotting the PPE amplitude and phase with frequency at room temperature. Since the optical absorption in DLP is low, a light coating of carbon black is provided on the face of the sample to enhance optical absorption and consequent thermal wave generation.

Measurement of the PPE signal phase and amplitude enables one to determine thermal diffusivity (α) and thermal effusivity (e) respectively. Principles of this method and experimental procedures are described in detail elsewhere [13]. From the measured values of α and e, the thermal conductivity k and specific heat capacity c_p of the samples are determined, knowing densityρ, using the following relations [13].

$$k = e[\alpha]^{1/2} \tag{1}$$

$$c_p = e/[\rho[\alpha]^{1/2}] \tag{2}$$

The calibration of the experimental set up has been done with known samples prior to carrying out the measurements. A block diagram of the experimental setup used in the present experiments is shown in Fig. 2.

In photopyroelectric measurements one measures the amplitude and phase of the pyroelectric detector output with the lock-in amplifier. These parameters are measured as a function of the modulation frequency to extract the thermal diffusivity and effusivity values of the sample. The sample temperature has been kept constant during the above measurements, allowing sufficient time for the sample to reach thermal equilibrium. The variations of the detected signal amplitude and phase as a function of frequency for DLP sample at room temperature are shown in Fig. 3. In these measurements the sample has been cut and polished to such a thickness that the sample and the PVDF film detector are thermally thick at all the modulation frequencies used.

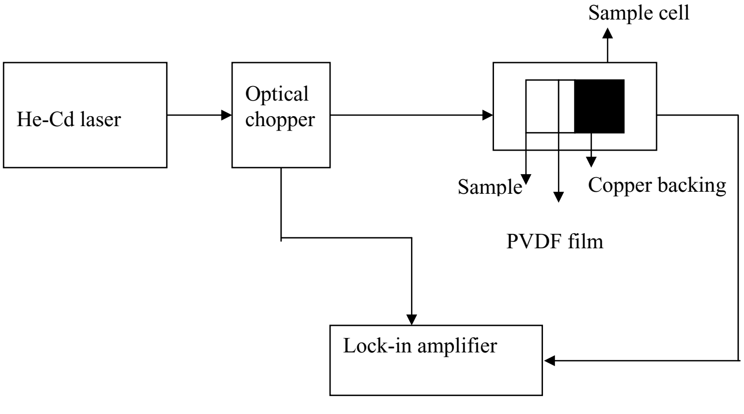


Figure 2. Block diagram of the experimental set up.

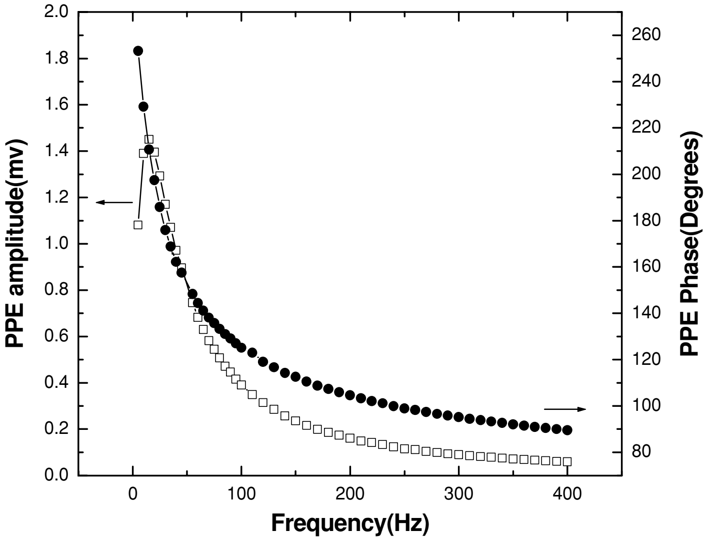


Figure 3. Frequency dependence of the photopyroelectric amplitude and phase for DLP crystal with faces cut normal to the c-axis.

These measurements have been done at temperatures between 170 K and 360 K at temperature intervals of 2 K normally and at intervals of 1 K at temperatures in the vicinity of the two transition points. At each measurement temperature, the sample has been kept at constant temperature during measurements. From the frequency dependence of the pyroelectric amplitudes and phases, the thermal diffusivity and effusivity of the sample have been determined at each temperature. The temperature variations of these parameters along the c-axis of DLP are shown in Fig. 4. From the diffusivity and effusivity values, the corresponding values of thermal conductivity and specific heat capacity have been computed and plotted in Fig. 5.

These measurements have been repeated for samples cut with faces normal to the a- and b-axes as well. Since these results are comparable to the corresponding results for the c-axis, they are not reproduced here. The values of thermal conductivity of DLP along the three symmetry axes at room temperature, as well as at 191 K and 333 K, are given in Table I. From this Table one can estimate the anisotropy in thermal conductivity for DLP at room temperature as well as at the two transition points. One can see that the thermal conductivity along the c-axis is more than those along a and b axes.

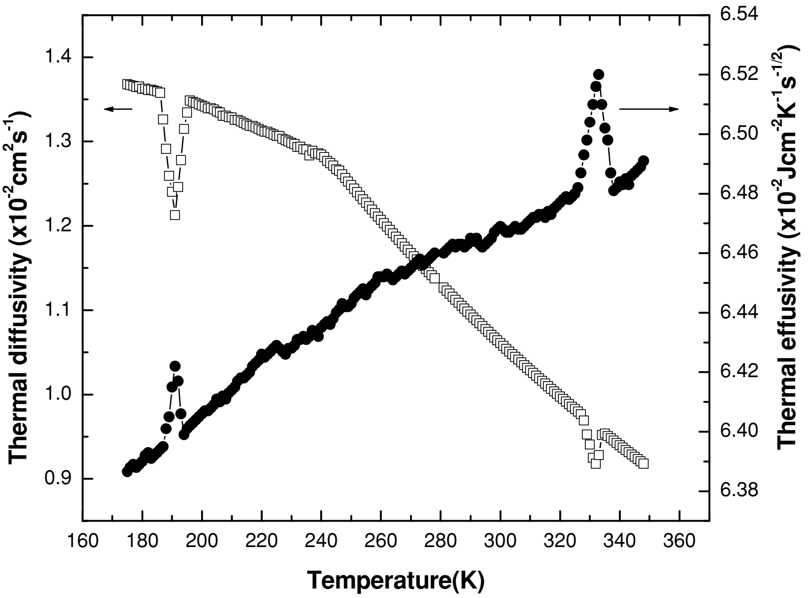


Figure 4. Variation of thermal diffusivity and thermal effusivity for DLP crystal, cut with faces normal to the c-axis.

Thermal Analysis of DLP

Thermal analysis of DLP has been carried out following thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) methods. Simultaneous TGA and differential thermal analysis (DTA) on DLP have been carried out with a Perkin Elmer Diamond TG/DTA instrument from room temperature to 1000°C at a heating rate of 10°C/min. The TG/DTA curves are shown in Fig. 6. The loss of weight due to decomposition and the rate at which the sample decomposes at different temperatures are evident from these curves. The DSC curve of the sample has been plotted

TABLE I Thermal conductivity of DLP along the three principal axes, in units of $\times 10^{-2}$Wcm^{-1}K^{-1}

Temperature K	c-axis	a-axis	b-axis
Room Temperature (302)	0. 656 ± 0.01	0. 592 ± 0.01	0. 549 ± 0.01
191	0. 703 ± 0.01	0. 626 ± 0.01	0. 566 ± 0.01
333	0. 615 ± 0.01	0. 578 ± 0.01	0. 541 ± 0.01

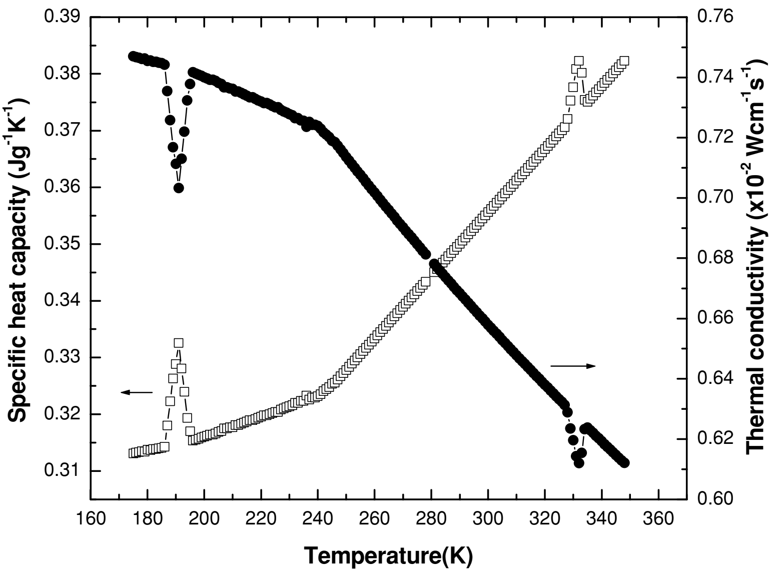


Figure 5. Variation of thermal conductivity and specific heat capacity for DLP crystal, cut with faces normal to the c-axis.

over a temperature range encompassing the two transition temperatures, with a Mettler Toledo DSC 822^e at a heating rate of 10°C/min. The DSC curve during the heating cycle is shown in Fig. 7. The DSC peaks occurring at –80.39°C (192 K) and +61.4°C (334 K) clearly show that the phase transitions at these temperatures are endothermic.

FTIR Measurements

The Fourier-transform infrared absorption measurements in the sample in the wave number range 4000–400 cm^{-1} have been carried out at room temperature with a Thermo-Nicolet Avtar 370 Spectrometer. The FTIR spectrum is shown in Fig. 8. The absorption peaks in the spectrum correspond to the prominent rotations and vibrations of the molecular groups in this crystal as discussed in the following section.

RESULTS AND DISCUSSION

We have presented a comprehensive set of results on the thermal transport properties of DLP crystal. The variation of thermal diffusivity (α),

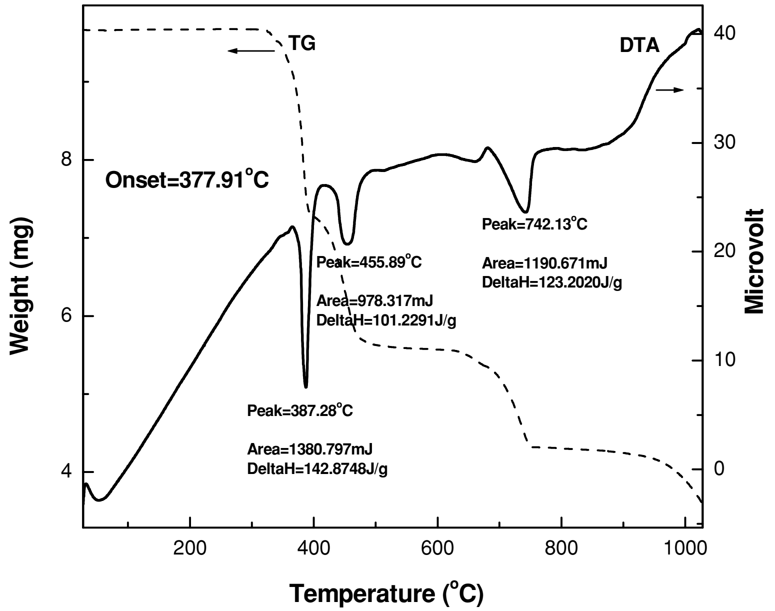


Figure 6. TG/DTA curves for DLP crystal.

effusivity (e), thermal conductivity (*k*) and specific heat capacity (c_p) of DLP, shown in Figs. 4 and 5, clearly indicate that the above thermal properties undergo anomalous variations during the phase transitions at 191 K and 333 K. In general, the thermal diffusivity and thermal conductivity show an anomalous decrease during transitions, whereas the heat capacity shows a corresponding anomalous increase. Being an electrical insulator crystal, the major contribution to the heat capacity of DLP is expected from the lattice phonons and the electronic contribution to heat capacity is very small. As the phonon modes undergo variations due to mode instability at the transition points, they absorb excess energy giving rise to enhancement in heat capacity. This is getting reflected in the DSC curve as well. Again, during the transitions, the phonon mean-free path increases, resulting in a decrease in thermal resistance or a corresponding increase in thermal diffusivity and thermal conductivity. As is evident from Table 1, the anisotropy in thermal conductivity is not very high for this crystal. The maximum thermal conduction occurs along the c-axis for this crystal, which is the direction of spontaneous polarization.

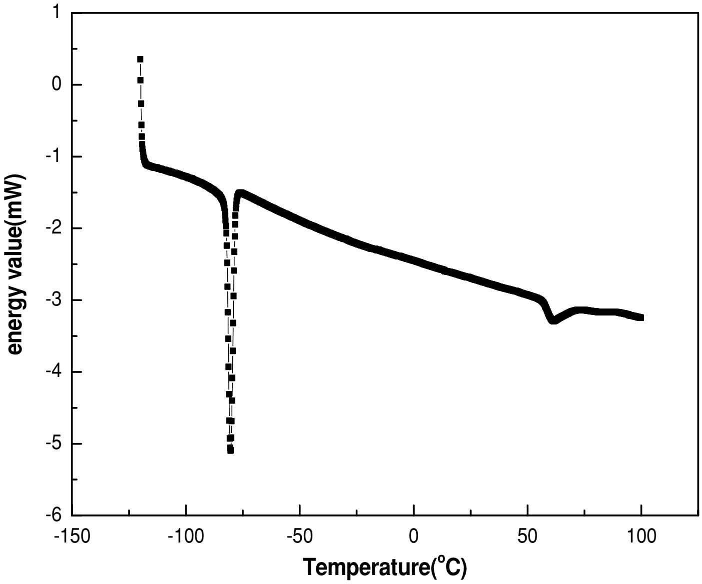


Figure 7. DSC curve for DLP crystal during heating cycle.

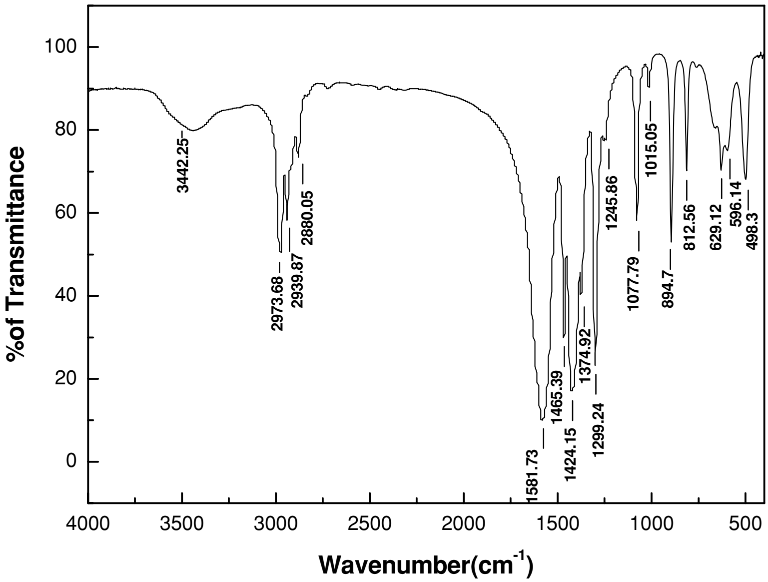


Figure 8. FTIR Spectrum of DLP.

From the FTIR spectrum of the DLP crystal we can get information about the chemical bonds and their motions in the crystal. The peaks in the range 2280–2971cm^{-1} correspond to the C—H stretch mode. Peak at 1581 cm^{-1} represent the asymmetric stretching mode of C—O bond and the one at 1484 cm^{-1} represents symmetric stretching of the C—O bond. Scissoring mode of CH_2 is reflected in the peak at 1465 cm^{-1} and the peak at 1077 cm^{-1} corresponds to twisting and wagging modes. The C—O stretching, coupled with C—C stretching is manifested by the peak at 1299 cm^{-1}. Peaks from 590 cm^{-1} to 890 cm^{-1} correspond to rocking modes and the peak at 498 cm^{-1} is possibly due to metal-oxygen bond. Thus all the chemical bonds and their motions are revealed by the FTIR spectrum.

From the TG/ DTA curves it is evident that the decomposition of the sample is maximum at 387°C, and the rate of decomposition is also maximum at this temperature. The heat capacity of DLP reported earlier at 191 K compares well with the value obtained from our thermal wave measurements [1]. Our results indicate that photopyroelectric thermal wave measurements can bring out the variation of thermal transport properties such as thermal diffusivity, thermal conductivity and heat capacity of crystalline samples during their phase transitions. These measurements help to understand the lattice properties of such crystals and their variations with temperature.

ACKNOWLEDGMENTS

One of the authors (MVM) thanks Cochin University of Science and Technology for a fellowship. The authors thank Dr. S. Pratapan for fruitful discussions. SAIF, Cochin is acknowledged for TG/DTA/DSC/FTIR measurements.

REFERENCES

[1] N. Nakamura, H. Suga, H. Chihara, and S. Seki, Phase transitions in crystalline divalent metal diclacium propionates.I.Calorimetric and dielectric investigations of strontium and lead dicalcium propionates. *Bull. Chem. Soc. Jpn.* **8**, 1779–1787 (1965).

[2] N. Nakamura, H. Suga, H. Chihara, and S. Seki, Phase transitions in crystalline divalent metal diclacium propionates. II. Proton magnetic resonance investigation. *Bull. Chem. Soc. Jpn.* **41**, 291–296 (1978).

[3] K. Gesi, and K.Ozawa, Effect of hydrostatic pressure on the phase transitions in ferroelectric $Ca_2Sr\ (C_2H_5COO)_6$and $Ca_2Pb(C_2H_5COO)_6$. *J. Phys. Soc. Jpn.* **39**, 1026–1031 (1975).

[4] K. Gesi, Reinvestigation of pressure-induced II-III transitions in ferroelectric $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$. *J. Phys. Soc. Jpn.* **53**: 1602–1605 (1984).

[5] E. Ferroni, and P. Orioli, Zur kristallstruktur von $PbCa_2$ (CH3CH2COO)$_6$. *Z. Krist.* **111**, 362 (1959).

[6] T. Osaka, Y. Makita, and K. Gesi, Pyroelectricity of dicalcium lead propionate associated with its phase transitions. *J. Phys. Soc. Jpn.* **38**: 292–292 (1975).

[7] Y. Nagae, M. Wada, Y. Ishibashi, and Y. Takagi, Raman scattering spectra of $Ca_2Sr(C_2H_5CO_2)_6$and $Ca_2Pb(C_2H_5CO_2)$. *J. Phys. Soc. Jpn.* **41**, 1659–1662 (1976).

[8] M. Takashige, S. Hirotsu, S. Sawada, and K. Humano, Piezoelectric and elastic properties of dicalcium lead propionate. *J. Phys. Soc. Jpn.* **45**, 558–564 (1978).

[9] S. V. Bhat, V. Dhar, and R. Srinivasan, ESR studies on phase transitions in double propionates. *Ferroelectrics (GB)* **39**, 1167–1167 (1981).

[10] K. V. S. Badarinath, and S. Radhakrishna, Studies on the ferroelectric-paraelectric transition of dicalcium lead propionate. *Jour. Mat. Sci. Lett.* **3**, 575–577 (1984).

[11] K. Standnicka, A. M. Glazer, and U. Bismayer, The phase diagram of dicalcium strontium/lead propionate: *Phase transitions* **27**, 73–80 (1990).

[12] K. Sushil Misra, and Stainslaw Jerzak, Mn^{2+} EPR study of phase transitions in dicalcium lead propionate Ca_2Pb $(C_2H_5COO)_6$: Determination of critical exponent below the ferroelectric phase transition and comparison with EPR studies on $Ca_2Ba(C_2H_5COO)_6$ and $Ca_2Sr(C_2H_5COO)$. *Phy. Rew. B* **39**, 2041–2050 (1989).

[13] C. P. Menon, and J. Philip, Simultaneous determination of thermal conductivity and heat capacity near solid-state phase transitions by a photopyroelectric technique. *Meas. Sci. & Tech.* **11**, 1744–1749 (2000).

[14] M. Marinelli, F. P. Murtas, M. G. Mecozzi, U. Zammit, R. Pizzoferrato, F. Scudierri, S. Maerwllucci, and M. Marinelli, Simultaneous determination of specific heat, thermal conductivity and thermal diffusivity at low temperature via the photopyroelectric technique. *Appl. Phys. A: Solid Surf.* **51**, 387–393 (1990).