




# Enhanced linear and non-linear optical activity of lead onto L-threonine cadmium acetate crystal

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## ABSTRACT

Herein, we describe the growth and characterization of new crystal lead-doped L-threonine cadmium acetate (LTCA). The supramolecular coordination compounds are crystallized by slow evaporation technique at ambient temperature. The X-ray diffraction techniques confirm monoclinic crystal system. The presence of lead and the LTCA lattices were identified using EDAX analysis. L-Threonine amino acids have unique properties like zwitterionic nature and molecular chirality, which improve the optical properties of the lead-doped crystal. The linear optical parameters such as optical band gap and refractive indexes are estimated at lower cutoff wavelength from UV–Vis analysis. The variation of dielectric constant, dielectric loss with frequency is studied using LCR meter. Due to the electropositive character of lead the static permittivity increases. Magnetic behavior changes to paramagnetic nature due to the inclusion of lead. TG/DTA analysis suggests that the crystal is thermally stable up to 135.32 °C. Using Nd-YAG laser, the NLO property was studied and the lead-doped LTCA crystal shows higher SHG efficiency than the LTCA crystal.

## 1 Introduction

The development of new organometallic crystals attains a great interest in crystal growth and technology owing to its applications in various fields like non-linear optics, optical communication, solid-state electronics, medicine, optoelectronic device fabrications, and optical data storage technology [1]. These crystals are used in shorter wavelength laser technology, electro-optical devices, optical parametric

oscillator, and optical waveguide [2]. Organometallic materials are excellent second harmonic generators due its charge transfer character between metal–organic ligands and its multiple electronic states. Organometallic materials differ from other materials because the organic ligand undergoes  $\pi \rightarrow \pi^*$  transitions, charge transfer between metal–organic ligands, and  $d-d$  transitions [3]. Higher non-linear optical responses are attained in organometallic compounds as a result of interaction between incident light and

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electrons present in the individual molecular units [4]. L-Threonine is considered as a bifunctional [5] neutral amino acid, dipolar in nature useful for non-linear optical properties [6]. Even though the cadmium compounds are toxins, when L-threonine amino acids are incorporated they combine together and modify the properties. LTCA compounds stand for vast industrial applications such as pigments, ceramics, glasses, cigarettes, beverages corrosion preventer in vehicles, refineries, electronic products, additives, and biocompatible materials [7–10]. Lead being a chalcophile metallic element has the advantage of high density, excellent thermal stability, good NLO candidate, and low strength and can be of great importance in corrosion-resistant material, drier in paints, light industry, radiation protection, gas sensors, IR detectors, and insecticides. Lead can also be used as water repellent which also prevents mildew and  $Pb^{2+}$  ion as selective sensors [11–13]. By doping lead in L-threonine cadmium acetate one can enhance the optical, thermal, and magnetic properties and second harmonic generation efficiency.

The typical layered structure with supramolecular organization of L-threonine cadmium acetate monohydrate (LTCA) crystal has been crystallized and its structure was reported [14]. The initial investigation is extended to fetch the physicochemical properties of the crystal, which shows lower transmittance percentage and SHG efficiency [15]. Trying to improve the properties of the grown crystals, different dopants are incorporated and their properties are studied. We recently reported the effect of zinc on the structural, optical, and magnetic properties of L-threonine cadmium acetate crystal. In this paper, the brief description of a newly grown crystal lead doped with enhanced optical, thermal, dielectric, magnetic and non-linear optical properties are reported.

## 2 Experimental methods

### 2.1 Materials

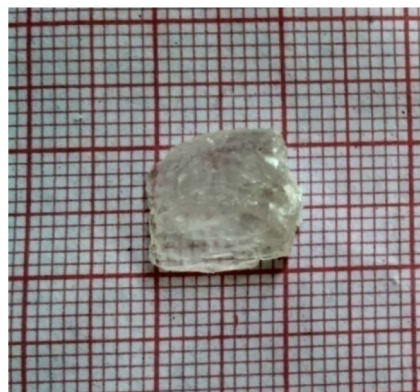
Lead-doped L-threonine cadmium acetate crystals were grown using the following chemical reagents purchased from NICE company (99% purity) and used as received; cadmium acetate dihydrate ( $Cd(CH_3COO)_2 \cdot 2H_2O$ ) and lead acetate trihydrate ( $Pb(CH_3COO)_2 \cdot 3H_2O$ ). L-Threonine ( $C_4H_9NO_3$ ) was purchased from HPLC company with 99% purity.

### 2.2 Synthesis

An organometallic crystal, lead-incorporated L-Threonine cadmium acetate was crystallized by slow evaporation crystal growth technique. The commercially available L-threonine, cadmium acetate dihydrate, and lead acetate dehydrate were taken as a raw materials. The stoichiometric quantities of L-threonine and cadmium acetate salts were completely dissolved in double-distilled water separately followed by stirring for 2 h. The two solutions are completely mixed together followed by adding to the above solution 0.6 mol percentage of lead acetate. The resulting solution was stirred thoroughly for 3 h and heated at 45 °C for drying the mixture. The dried mixture was totally dissolved with the solvent (double-distilled water) until the solution saturated. The saturated solution was filtered and allowed for free evaporation. Good quality  $Pb^{2+}$ -doped L-threonine cadmium acetate crystals were obtained in around 45 days. The picture of harvested crystal is displayed in Fig. 1.

### 2.3 Characterization

The structural and elemental confirmations were carried out using X-ray analysis. XRD was analyzed to characterize the purity [16], crystallinity and natures of the samples are analyzed with X'Pert pro family of multipurpose PAN analytical diffractometer and the resultant diffracted peaks were indexed using INDEX software package. The powdered  $Pb^{2+}$ -doped LTCA sample was continuously scanned in the range of  $10^\circ$ – $70^\circ$  with a step time of 10.16 s using  $CuK\alpha$  radiation. The lattice parameters of  $Pb^{2+}$ -doped LTCA crystals were computed from Bruker



**Fig. 1** Grown  $Pb^{2+}$ -doped LTCA crystal

Kappa APES II single-crystal X-ray diffractometer with MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Elemental analysis has been carried out using EDAX analysis associated with scanning electron microscope OXFORD XMX N model with the accelerating voltage 200 kV. The grown Pb<sup>2+</sup>-doped LTCA crystal of 3 mm thickness was chosen for UV–Vis analysis and their transmittance spectra has recorded using UV spectrophotometer (ELICO) in the range between 200 and 1200 nm. Optical band gap of the doped crystal is estimated from the following relation:

$$E_g = \frac{hc}{\lambda}. \quad (1)$$

Refractive index of the crystal is considered as the most important optical property which plays a major criterion in optical device fabrication. Refractive index ( $n$ ) is evaluated from the reflectance ( $R$ ) as follows:

Reflectance,

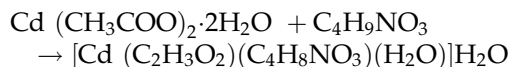
$$R = \frac{\exp(-\alpha t) + \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad (2)$$

$$\text{The refractive index, } n = -(R + 1) + \frac{2\sqrt{R}}{R - 1} \quad (3)$$

Dielectric measurements were carried out in the frequency range between 1 kHz and 2 MHz for a perfectly graphite-coated Pb<sup>2+</sup>-doped LTCA crystal of 4.78 mm thickness using LCR impedance analyzer at normal air pressure. The magnetic behavior was depicted at room temperature using Lakeshore model: 7410 in an average time of 3 s. In order to fetch the knowledge about texture, stability, and chemical degradation, thermogravimetric measurements were taken by PerkinElmer STA 6000 thermal analyzer apparatus. Pb<sup>2+</sup>-doped LTCA samples were taken in the platinum crucible and heated between 50 and 750 °C in nitrogen atmosphere. The second harmonic generation of Pb<sup>2+</sup>-doped LTCA crystal was determined by modified technique of Kurtz and Perry [17].

### 3 Results and discussion

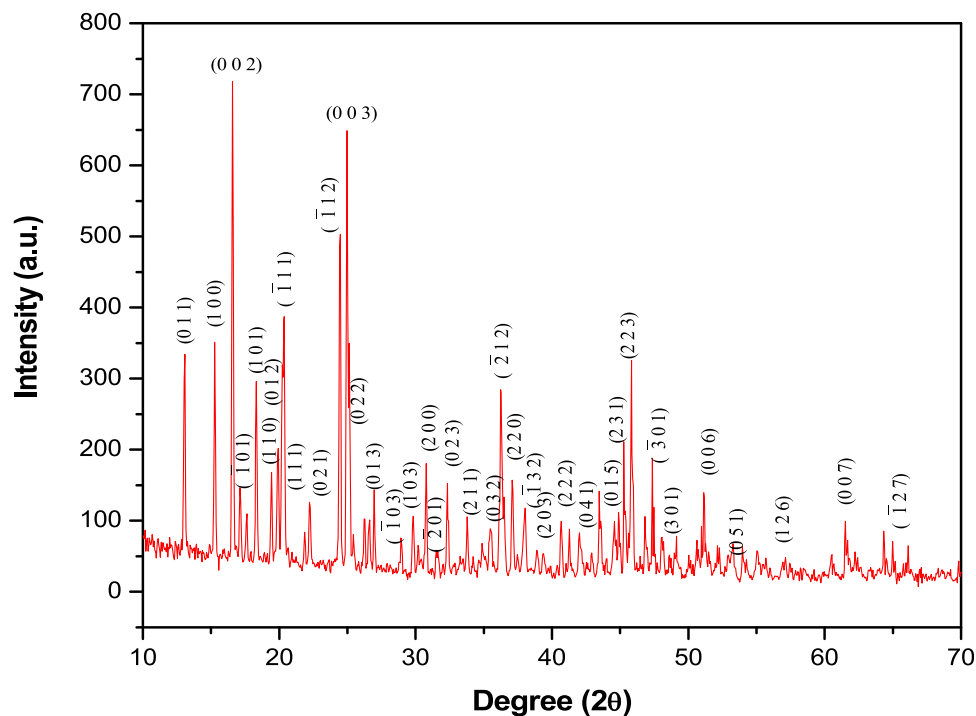
Organometallic compound, L-threonine cadmium acetate has been obtained as a result of chemical reaction between L-threonine and cadmium acetate dihydrate at 45 °C.



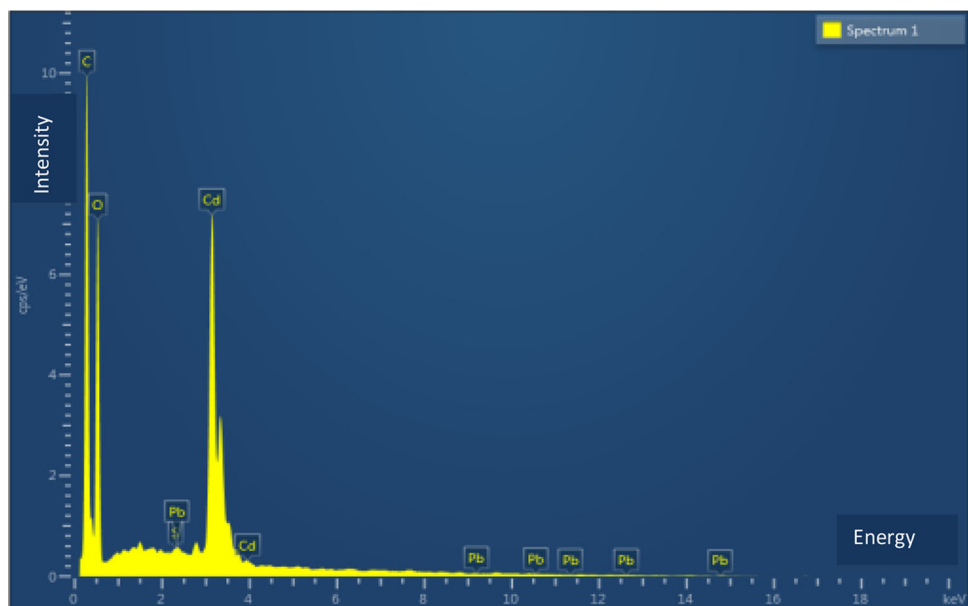
The host compound shows hydrophilic interactions due to the influence of solvent. Pb<sup>2+</sup>-doped LTCA crystallized by doping 0.6 mol percentage lead acetate trihydrate in the host compound. Figure 2 illustrates the powder XRD spectrum of Pb<sup>2+</sup>-doped LTCA, from the spectrum it can be seen that all the sharp recorded peaks confirm the crystalline and single phase nature. Due to doping larger size molecule lead, it causes strain in the lattice and creates small variation in intensity and diffraction angles comparing to pure LTCA [15]. Moreover, Pb<sup>2+</sup>-doped LTCA shows the maximum intensity of 716 arbitrary units diffracted peak recorded at  $2\theta = 16.7^\circ$  in the (002) plane. Single-crystal XRD study reveals that Pb<sup>2+</sup>-doped LTCA crystal belongs to monoclinic crystal system with  $a = 5.84 \text{ \AA}$ ,  $b = 8.85 \text{ \AA}$ ,  $c = 10.72 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 91.84^\circ$ , volume =  $554 \text{ \AA}^3$ , and space group P2<sub>1</sub>. The monoclinic crystal structure of Pb<sup>2+</sup>-doped LTCA with two crystallographic axes was inclined at an oblique angle and the third axis was perpendicular to the other two axes. Thus the crystal is mainly recommended for prism fabrication.

The single-crystal X-ray analysis [14] shows small variations in lattice parameters and crystallographic axes which confirms the influence of lead on the parent compound LTCA. Furthermore, the presence of lead on the host LTCA compound was verified using EDAX analysis. Energy peaks corresponding to various elements present in Pb<sup>2+</sup>-doped L-threonine cadmium acetate are shown in Fig. 3. The energy peaks obtained for Pb<sup>2+</sup>-doped LTCA confirms that Pb<sup>2+</sup> metal ions were successfully incorporated in the crystal lattice of L-threonine cadmium acetate. In Pb<sup>2+</sup>-doped LTCA, the atomic percentage of carbon presented is 50.4, oxygen 43%, cadmium 6.6%, and lead 0.06%. The Pb/Cd stoichiometric ratio obtained from EDAX analysis is 0.59 and the calculated stoichiometry applied in the preparation process is 0.623.

**Fig. 2** XRD pattern of  $\text{Pb}^{2+}$ -doped LTCA crystal



**Fig. 3** EDAX spectrum of  $\text{Pb}^{2+}$ -doped LTCA

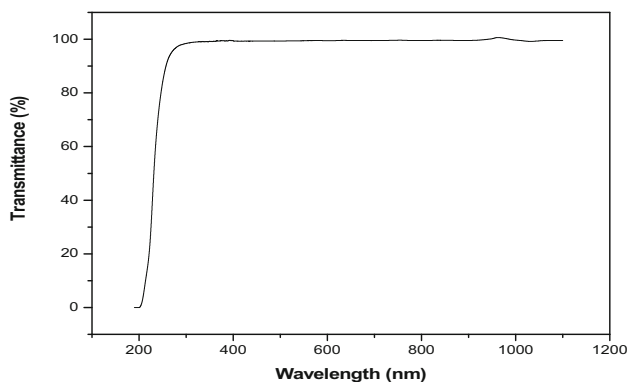
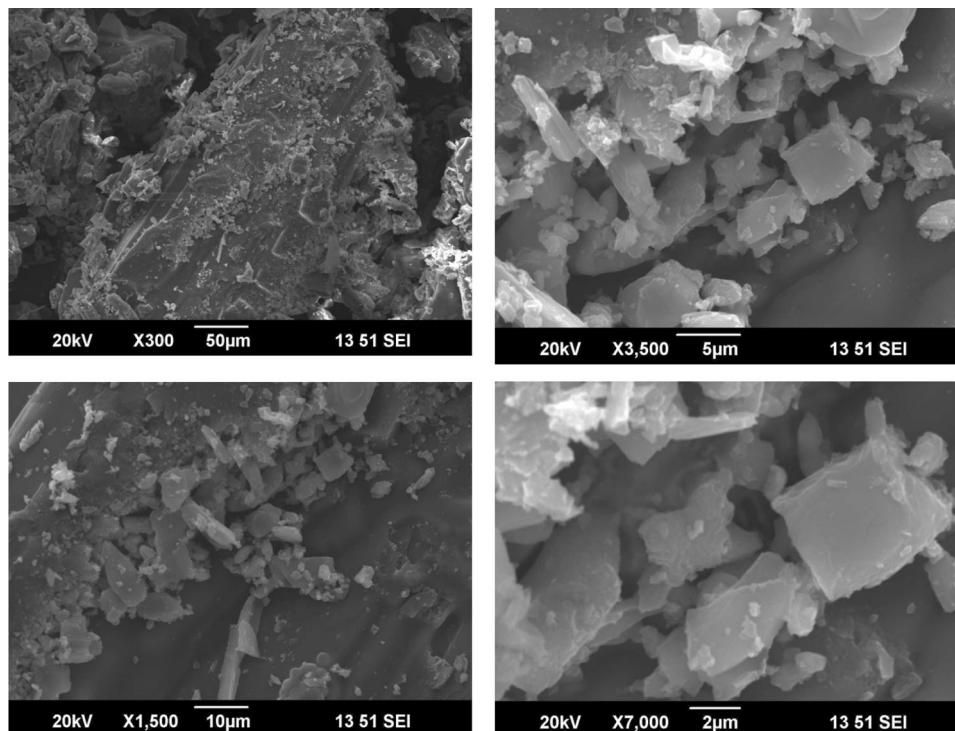


Thus, EDAX analysis confirms the successful doping of LTCA (Fig. 4).

To investigate the influence of lead on the shape of LTCA, SEM images of lead-doped LTCA were taken and illustrated in Fig. 5. It was noted that irregularly shaped particles with large grain size were obtained. Moreover, the particles were not uniform and they were highly aggregated in some planes [18].

Figure 5 illustrates the UV–Visible transmittance spectrum recorded for  $\text{Pb}^{2+}$ -doped L-threonine cadmium acetate. From the spectra, it was confirmed that the crystal has lower cutoff wavelength of 236 nm near the UV region and exhibits absorption in the range of blue light. These properties arise due to the combination of  $\pi \rightarrow \pi^*$  transitions and charge transfer between metal–organic ligands. The lower cutoff wavelength in the order of 200–400 nm is the

**Fig. 4** SEM image of  $\text{Pb}^{2+}$ -doped LTCA



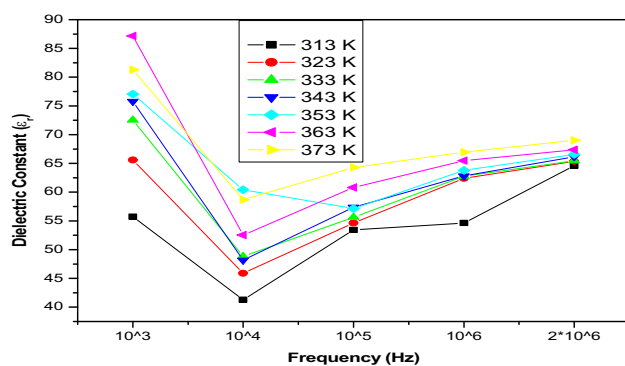
**Fig. 5** Optical transmission spectrum of  $\text{Pb}^{2+}$ -doped LTCA

necessary requirement of the crystal capable for blue light by second harmonic generation from diode laser [19]. Hence, lead-doped crystal is a better one for NLO application. As observed in the transmittance spectrum, the transmittance percentage is higher (compared to pure LTCA); this property is mainly due to the higher optical density and higher electron affinity of lead compared to cadmium crystal. Good percentage of optical transmittances around 99% can be used in UV tunable laser, optoelectronic applications, and second harmonic generation (SHG) device applications [20, 21].

Band gap and refractive index value evaluated with respect to lower cutoff wavelength are 5.247 eV

and 3.14, respectively, which confirms that the doped crystal is a perfect dielectric and a better corrosion-resistant material. Energy gap is the most important property for photocatalytic yield [22–24]. Compared to the band gap of pure LTCA (4.8 eV), the doped crystals shows higher band gap. Higher values of optical band gap crystals are suitable for electro-optical device fabrications and photocatalyst under UV light [25, 26]. Therefore, the grown  $\text{Pb}^{2+}$ -doped LTCA is highly recommended for photodiode fabrications, information processing. Refractive index also increases after doping because it has the ability to polarize under powerful radiation therefore the material can be used as an antireflection coating in solar thermal devices, and glasses of computer and television [27]. The variation of band gap in a doped crystal was due to different electronic state of doped crystal and the non-centrosymmetric nature of the material which affects the optical polarization of the crystal.

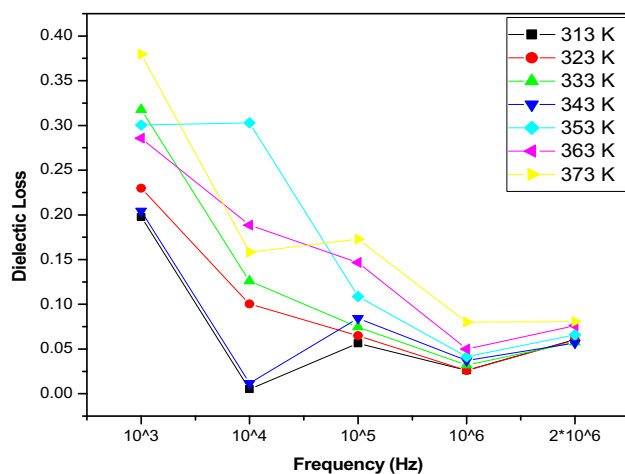
To study the ability of the material to store energy due to relaxation process, dielectric constant was measured with respect to the frequency as shown in Fig. 6. In  $\text{Pb}^{2+}$ -doped LTCA, as the frequency increases the static permittivity decreases and then increases for all the measured temperature and the maximum value of dielectric constant experienced at lower frequency. The polarization of crystal is



**Fig. 6** Frequency vs dielectric constant of  $\text{Pb}^{2+}$ -doped LTCA

attributed due to the presence of electronic, ionic, and dipole polarization. Ionic polarization is caused by the relative displacement of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ , and  $\text{C}_4\text{H}_8\text{NO}_3^-$  ions, which results in lattice vibrations in the crystal. The dipole polarization requires greater time compared to electronic and ionic polarization, therefore the static permittivity begins to drop at certain frequency due to the fact that dipoles cannot orient themselves at low temperature. The orientation polarization arises due to the polar water molecules present in crystals, which creates distortion in asymmetry bonds due to permanent dipole. As the temperature increases the orientation of the dipole creates increase in dielectrics. The asymmetric charge distribution raises the secondary bonds between the amino acid groups present in the crystal. Organometallic amino acid crystal with higher dielectric constant can be utilized as a capacitor for energy storage applications.

Frequency dependence of dielectric loss is a measure of heat energy dissipated due to the mobility of

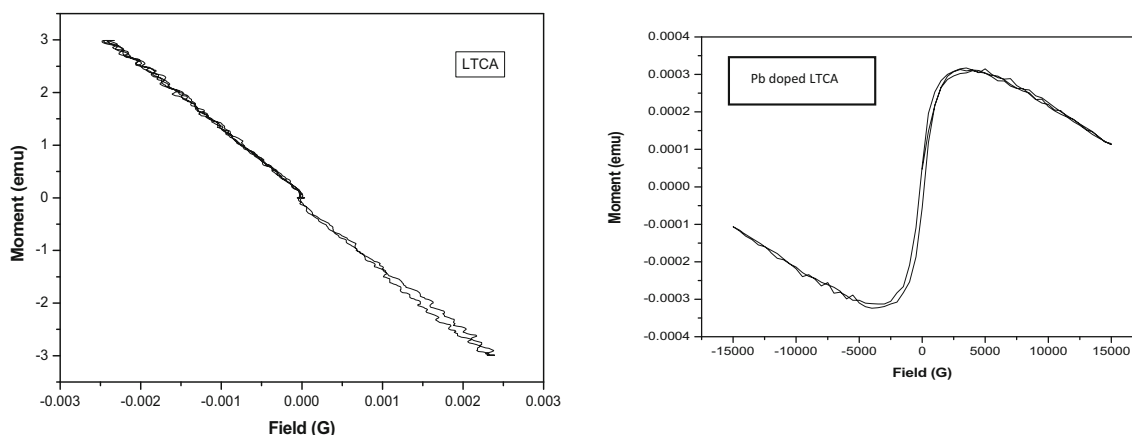


**Fig. 7** Frequency vs dielectric constant of  $\text{Pb}^{2+}$ -doped LTCA

charge carriers (Fig. 7). As the frequency of the crystal increases dielectric loss decreases up to 100 kHz and then increases for 323 K, 333 K, and 363 K and the higher value of dielectric loss experienced at lower frequency. This property is ascribed due to the presence of space charge polarization near the grain boundary interfaces [28, 29].  $\text{Pb}^{2+}$ -doped LTCA shows that the lowest minimum position of dielectric loss shifts towards the higher frequency range and experiences high static permittivity. This property is mainly due to the influence of lead ( $1.19 \text{ \AA}$ ) with higher ionic radii than that of cadmium with ionic radii  $0.95 \text{ \AA}$ . A monoclinic crystal system with polar non-Centrosymmetric point group possesses polar dielectrics having finite dipole in the absence of electric field. This property can be utilized as electronic applications such as cable insulator, frequency filters, and dielectric ceramics [30]. Higher value of dielectric constant for  $\text{Pb}^{2+}$ -doped LTCA is due to higher polarization of the  $\text{Pb}^{2+}$  ions [31]. Due to the metal compound lead doping, the dielectric loss and static permittivity increased. Thus, the material confirms excellent dielectrics. In the case of organocadmium coordination complexes, the organic ligands play a dominant role in dielectric effects which is mainly recommended for gate dielectrics in an organic transistor.

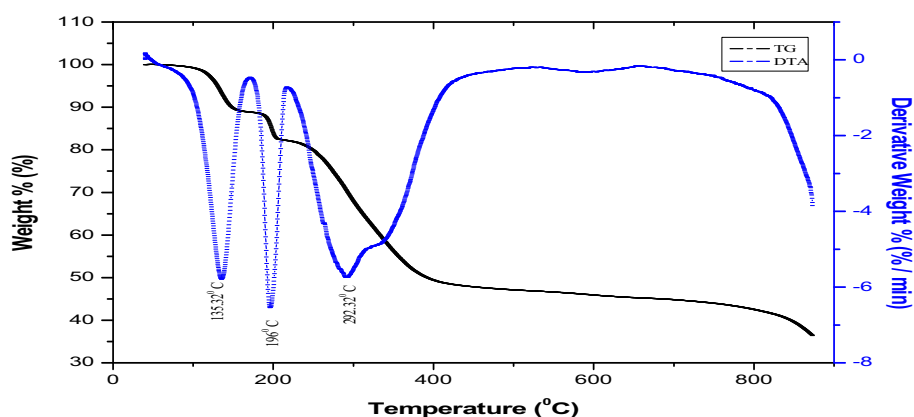
The magnetic behavior was recorded to a sample of mass  $17.000\text{E}^{-3} \text{ g}$  at room temperature by the applied magnetic field in an average time of 3 s with the field increment of 500 G. The corresponding field with moment graph is depicted in Fig. 8. Pure LTCA crystal shows diamagnetic nature since the metal cadmium has closed s-shell. Due to the addition of  $\text{Pb}^{2+}$  on LTCA crystal it shows paramagnetic nature with saturated magnetization  $320.53\text{E}^{-6} \text{ emu}$ , coercivity  $159.96 \text{ G}$ , and retentivity  $55.47\text{E}^{-6} \text{ emu}$ . Paramagnetic nature of  $\text{Pb}^{2+}$ -doped LTCA is due to the partially filled electron in p-shell of  $\text{Pb}^{2+}$  ion, where the total spin is not zero. When an external magnetic field is applied, the electron spins to align the direction parallel to the applied field. The main application of paramagnetic semiorganic complex is as a contrast agent in magnetic image experiments, drug carriers, and organic capacitors.

The TG/DTA data for  $\text{Pb}^{2+}$ -doped LTCA (Fig. 9) are obtained and it seems that the first endothermic peak takes place at  $135.32 \text{ }^\circ\text{C}$  which confirms that the material has retained its texture till  $135.32 \text{ }^\circ\text{C}$  without any decomposition up to this temperature.



**Fig. 8** VSM graph

**Fig. 9** TG/DTA plot of  $\text{Pb}^{2+}$ -doped LTCA



Comparing pure LTCA doping lead enhances the thermal stability about 30°. This endothermic peak corresponds to the liberation of two molecules of water. Another endothermic peak obtained at 196 °C and 292 °C illustrates the liberation of two molecules of carbon and  $\text{C}_5\text{H}_{18}\text{NO}_2$ , respectively. From the analysis it was confirmed that  $\text{Pb}^{2+}$ -doped LTCA is more stable than LTCA crystal.

NLO study has been performed using modified Kurtz and Perry powder technique, since the technique is mostly used for confirming the SHG efficiency from prospective second-order NLO material [25]. A Q-switched high-energy Nd:YAG laser beam of wavelength 1064 nm radiates with an input power of 0.70 J irradiation with  $\text{Pb}^{2+}$ -doped LTCA, and as a result green light from the sample is emitted which confirms SHG generation. The powder form of KDP was used as a reference and the SHG conversion efficiency of KDP is 8.94 mV and  $\text{Pb}^{2+}$ -doped LTCA is 4.85 mV. It was found that the SHG conversion efficiency of 0.6 mol%  $\text{Pb}^{2+}$ -doped LTCA was found

to be 0.54 times that of reference KDP crystal. This shows that lead doping has increased the SHG efficiency. The increase in SHG efficiency is due to the variation in the electronic configuration of the  $\text{Cd}^{2+}$  ion and  $\text{Pb}^{2+}$  metal ion. The  $\text{Cd}^{2+}$  ion has  $3d^{10}$  configuration as well as these electrons are too tightly held while  $\text{Pb}^{2+}$  ions that have  $6p^2$  configuration with  $2p$  electrons are more free to interact with electromagnetic radiation and so they are easily polarized by the incoming laser pulse and hence SHG efficiency increases in the  $\text{Pb}^{2+}$  ion-doped LTCA crystal.

## 4 Conclusion

Supramolecular frame of lead doped catena –poly [[(acetato- $\kappa^2\text{O},\text{O}'$ ) aquacadmium (II)]- $\mu$ -L-threoninato- $\kappa^3\text{N},\text{O},\text{O}'$ ] monohydrate has been successfully crystallized by slow evaporation technique. X-ray analysis confirms the crystalline nature, monoclinic crystal system, and the presence of lead on the LTCA

lattice. EDAX analysis confirms the inclusion of lead. UV–Vis studies show good optical transparency in the entire region and the calculated optical properties reveal dielectric nature of the crystal. The UV transmission ability suggested that the crystal can be a better optical and corrosion-resistant material for optical device fabrications. The static permittivity increases by doping a Pb with more electropositive character, thus the metal organic frame plays a key role in solid-state dielectrics applications due to its relative permittivity. Magnetic behavior changes to paramagnetic nature due to the inclusion of lead on the host lattice can be used for magnetic image experiments, and gate dielectrics for organic transistor and organic capacitors. It was observed that the thermal stability of the Pb-doped crystal rises about 30°. NLO study indicates that lead doping increases the polarization ability which in turn enhances their SHG efficiency.

## References

- J. Kido, Y. Okamoto, *Chem. Rev.* **102**, 2357 (2002)
- A. Kanthasamy, R. Siddeswaran, P. Mirugakoothan, P.S. Kumar, R. Mohan, *Cryst. Growth Des.* **7**, 183 (2007)
- Y. Qian, M. Cai, S. Wang, Y. Yi, Z. Shuai, G. Yang, *Opt. Commun.* **283**, 2228 (2010)
- T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, S. Li, Y. Zhai, S. You, Q. Wang, J. Qin *Chem. Phys. Lett.* **451**, 213 (2008)
- J.H. Joshi, S. Kalainathan, D.K. Kanchan, M.J. Joshi, K.D. Parik, *Arab. J. Chem.* **13**, 1532 (2020)
- R.L. Madan, *Organic Chemistry*, 1st edn. (Tata McGraw Hill Education private Limited, New Delhi, 2013).
- K. Sloane Tilley, C. Rebecca Fry, *Systems Biology in Toxicology and Environmental Health* (Academic Press, Boca Raton, 2015), pp. 117–216
- A.R. Chowdhury, D. Sarkar, *Green Chemistry* (Elsevier, Amsterdam, 2018).
- C.A. McQueen, *Comprehensive Toxicology*, 2nd edn. (Elsevier, Amsterdam, 2010).
- P. Patnaik, *Handbook of Inorganic Chemicals Compounds* (McGraw Hill Professional, New York, 2002).
- A. Mohamad Ghazi, J.R. Millette, *Environmental Forensics* (Elsevier, Amsterdam, 1964).
- F. Ray, *Clinical Neurotoxicology* (Saunders, Elsevier, 2009), pp. 675–691
- Z. Meng, *Powder Technol.* **02**, 035 (2019)
- M. Abila Jeba Queen, K.C. Bright, S. Mary Delphine, *IUCr Data* **3**, 181770 (2018)
- M. Abila Jeba Queen, K.C. Bright, S. Mary Delphine, P. Aji Udhaya, *Spectrochim. Acta. A* **228**, 117802 (2019)
- S. Zinatloo-Ajabshir, M. Salavatti-Nissari, *Int. J. Appl. Ceram. Technol* **13**, 108 (2016)
- S.K. Kurtz, T.T. Perry, *J. Appl. Phys* **39**, 3798 (1968)
- S. Zinatloo-Ajabshir, M. Salavatti-Nissari, *J. Mater. Sci.* **26**, 5812 (2015)
- Y. Le Fur, R. Masse, M.Z. Cherkaoui, J.F. Nicoud, *Cryst. Mater.* **210**, 856 (1995)
- K. Kanagasabapathy, R.J. Rajasekaran, *Opto. Electron. Adv. Mater.* **6**, 218 (2012)
- T.K. Kumar, S. Janarthanan, S. Pandi, M.V. Raj, A.J. Kana-galakshmi, D.P. Anand, *J. Miner. Mater. Charact. Eng.* **9**, 916 (2010)
- S. Zinatloo-Ajabshir, M. Salavatti-Nissari, *Ultrason. Sonochem.* **72**, 105420 (2021)
- S. Zinatloo-Ajabshir, M. Salavatti-Nissari, *Ultrason. Sonochem.* **71**, 105776 (2021)
- M. Mousavi-Kamazani, S. Zinatloo-Ajabshir, M. Ghodrati, *J. Mater. Sci.* **31**, 17332 (2020)
- F. Razii, S. Zinatloo-Ajabshir, M. Salavatti-Nissari, *Mater. Lett.* **193**, 9 (2017)
- S. Zinatloo-Ajabshir, S.M. Dorazkola, *J. Mol. Liquid* **234**, 430 (2017)
- T.C. Sabari Girisun, S. Dhanuskodi, *Cryst. Res. Technol.* **44**, 1297 (2009)
- C.P. Smyth, *Dielectric Behaviour and Structure* (McGraw-Hill, New York, 1965).
- K.C. Bright, T.H. Freeda, *Appl. Phys. A* **99**, 935 (2010)
- B.S. Benila, K.C. Bright, S. Mary Delphine, R. Shabu, *Opt. Quant. Electron.* **50**, 202 (2018)
- A. Ben Rhaïem, F. Hlel, K. Guidara, M. Gargouri, *J. Alloys Compd.* **485**, 718 (2009)

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