Enhanced Linear and Non Linear Optical Activity of Lead Onto L-Threonine Cadmium Acetate Crystal

Abila Jeba Queen M (jeba.abi@gmail.com)
Holy Cross College https://orcid.org/0000-0001-5929-139X
K.C. Bright
St John's College
S. Mary Delphine
Holy Cross College
P. Aji Udhaya
Holy Cross College

Research Article

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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 and the presence of lead onto the LTCA lattice. L-Threonine amino acids have the unique properties like zwitter ionic nature and molecular chirality, which improves the optical properties of the crystal. The linear optical parameters such as optical band gap and refractive indexes are estimated 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, the crystal is thermally stable up to 135.32°C. Using Nd-YAG laser the NLO property was studied and the 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 its applications in various fields like non linear optics, solid state electronics, medicine, optoelectronic device fabrications etc., [1, 2]. Organometallic materials are excellent second harmonic generators due its charge transfer character between metal-organic ligands and its multiple electronic states [3]. Organometallic materials differ from other materials because of the reason that: organic ligand undergoes $\pi \rightarrow \pi^*$ transitions, charge transfer between metal-organic ligands and d-d transitions [4]. Higher non linear optical responses are attained in organometallic compounds as a result of interaction between incident light and electrons present in the individual molecular units [5]. L-threonine is considered as a 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 combined together and modifies the properties. LTCA compounds stands for vast industrial applications such as pigments, ceramics, glasses, cigarettes, beverages corrosion preventer in vehicles, refineries, electronic products, additive and bio compatible material [7–10]. Lead be a chalcophile metallic element has the advantage of high density and low strength 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 used as water repellant which also prevents mildew and Pb^{2+} ion as selective sensors [11–13].

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 physico chemical 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 [16]. 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. Materials And Methods

2.1. 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 dihydrade 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 following by stirrering 2 hours. In addition to the above solution 0.6 mole percentage of lead acetate was added as a dopant. The resulting solution was stirred thoroughly for 3 hours and allowed heating at 45^0 C to dry the mixture. The dried mixture was totally dissolved with the solvent until the solution saturates. 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.

2.2. Characterization

The structural and elemental confirmations were carried out using X-ray analysis. The crystalanity 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 lattice parameters of Pb^{2+} doped LTCA crystals were computed from Bruker Kappa APES II single crystal X-ray diffractometer with MoKα (λ=0.71073 Å) radiation. Elemental analysis has been carried out using EDAX analysis OXFORD XMX N model. The grown Pb^{2+} doped LTCA crystal of 3 mm thickness has chosen for UV-Vis analysis and their transmittance spectra has recorded using UV spectrophotometer (ELICO). Optical band gap of the doped crystal was estimated from the following relation;

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

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

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

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

Dielectric measurements were carried out for a graphite coated Pb^{2+} 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 sec. In order to fetch the knowledge about the texture, stability and chemical degradation, thermo gravimetric measurements were taken by Perkin Elmer STA 6000 thermal analyzer apparatus. Samples were taken in the platinum crucible and heated between 50-750°C in nitrogen atmosphere. The second harmonic generation of Pb^{2+} doped LTCA crystal was determined by modified technique of Kurtz and Perry.

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^{0} C.

$Cd\ (CH_3COO)_2.\ 2H_2O + C_4H_9NO_3 \rightarrow [Cd\ (C_2H_3O_2)\ (C_4H_8NO_3)(H_2O)]H_2O$

The host compound shows hydrophilic interactions due to the influence of solvent. Pb^{2+} doped LTCA crystallized by doping 0.6 mole percentage lead acetate dihydrate in the host compound. Fig. 2 illustrates the powder XRD spectrum of Pb^{2+} doped LTCA. From the spectrum it can be seen that all the sharp recorded peaks confirm the crystalline and single phase in nature. Due to the influence of lead small variation in intensity and diffraction angles appear comparing to pure LTCA [15]. Moreover Pb^{2+} doped LTCA shows the maximum intensity of 716 arbitrary units diffracted peak recorded at 2θ = 16.7° in the (0 0 2) plane. Single crystal XRD study reveals that Pb^{2+} doped LTCA crystal belongs to monoclinic crystal system with a = 5.84 Å, b = 8.85 Å, c=10.72 Å, α = γ = 90°, β=91.84°, volume = 554 $Å^3$ and space group $P2_1$. The monoclinic crystal structure of Pb^{2+} doped LTCA with two crystallographic axes was inclined at an oblique angle and the third axes are perpendicular to the other two axes. Thus the crystal is mainly recommended for prism fabrication.

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

Fig.4 illustrates the UV-Visible transmittance spectrum recorded for Pb^{2+} doped L-threonine cadmium acetate. From the spectra, it was confirmed that the crystal have lower cutoff wavelengths of 236nm near the UV region and exhibits absorption in the range of blue light. These properties arises due to the combination of $\pi \rightarrow \pi^*$ transitions and charge transfer between metal-organic ligands. The lower cut off wavelength in the order of 200-400 nm is the necessary requirement of the crystal capable for blue light by second harmonic generation from diode laser [17]. 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, opto-electronic applications and second harmonic generation (SHG) device applications [18, 19].

Band gap and refractive index value evaluated with respect to lower cut off wavelength are 5.247 eV and 3.14 respectively, which confirms that the doped crystal is a perfect dielectric and a better corrosion resistive material. Therefore the grown Pb^{2+} doped LTCA is highly recommended for photodiode fabrications, information processing, antireflection coating in solar thermal devices, glasses of computer and television [20]. The variation of band gap in a doped crystal was due to different electronic state of doped crystal and the non centro symmetric 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. 5. In 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 attributed due to the presence of electronic, ionic and dipole polarization. Ionic polarization is caused by the relative displacement of Cd^{2+}, Pb^{2+}, $C_2H_3O_2^-$ and $C_4H_8NO_3^-$ ions, which results 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 rises the secondary bonds between the amino acid groups present in the crystal.

Frequency dependence of dielectric loss is a measure of heat energy dissipated due to the mobility of charge carriers (Fig. 6). As the frequency of the crystal increases dielectric loss decreases up to 100 KHz and then increases for 323K, 333K and 363K 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 [21, 22]. 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 Å) with higher ionic radii than that of cadmium with ionic radii 0.95 Å. A monoclinic crystal system with polar non-Centro symmetric 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 [23]. Higher value of dielectric constant for Pb^{2+} doped LTCA is due to higher polarization of the Pb^{2+} ions [24]. In the case of organocadmium coordination complexes the organic ligands plays a dominant role in dielectric effects which is mainly recommended for gate dielectrics for organic transistor.

The magnetic behavior was recorded to a sample of mass 17.000 E^{-3}g at room temperature by the applied magnetic field in an average time of 3 sec with the field increment of 500 G. The corresponding field with moment graph is depicted in Fig.7. Pure LTCA crystal shows diamagnetic nature since the metal cadmium has closed s-shell. Due to the addition of Pb^{2+} on LTCA crystal it shows paramagnetic nature with saturated magnetization 320.53E^{-6} emu, coercivity 159.96 G and retentivity 55.47E^{-6} emu. Paramagnetic nature of Pb^{2+} doped LTCA is due to the partially filled electron in p-shell of 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 semi organic complex as a contrast agents in magnetic image experiments, drug carrier and organic capacitors.

The TG/DTA data for Pb^{2+} doped LTCA is obtained and it seems that the first endothermic peak take place at 135.32°C which confirms that the material have retain its texture till135.32°C without any decomposition up to this temperature. 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 $C_5H_{18}NO_2$ respectively. From the analysis it was confirmed that 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 0.70J irradiate with Pb^{2+} doped LTCA 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 Pb^{2+} doped LTCA is 4.85 mV. It was found that the SHG conversion efficiency of 0.6 mol% 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 Cd^{2+} ion and Pb^{2+} metal ion. The Cd^{2+} ion have $3d^{10}$ configuration as well as these electrons are too tightly held while Pb^{2+} ions 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 Pb^{2+} ion doped LTCA crystal.

4. Conclusion

Supramolecular frame of lead doped catena –poly [[[(acetato-κ^2O,O’) aquacadmium (II)]-μ-Lthreoninato-κ^3N,O:O’] monohydrate has been successfully crystallized by slow evaporation technique. X-ray analysis confirms the crystalline nature, crystal system and the presence of lead on the LTCA lattice. UV-Vis studies shows good optical transparency in entire region and the calculated optical properties reveals dielectric nature of the crystal. The UV transmission ability suggested that the crystal can be a better optical material for optical device fabrications. The static permittivity increases by doping a metal 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, gate dielectrics for organic transistor and organic capacitors. It was observed that the thermal stability of the crystal rises due to doping. NLO study indicates that lead doping increases SHG efficiency.

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Figures

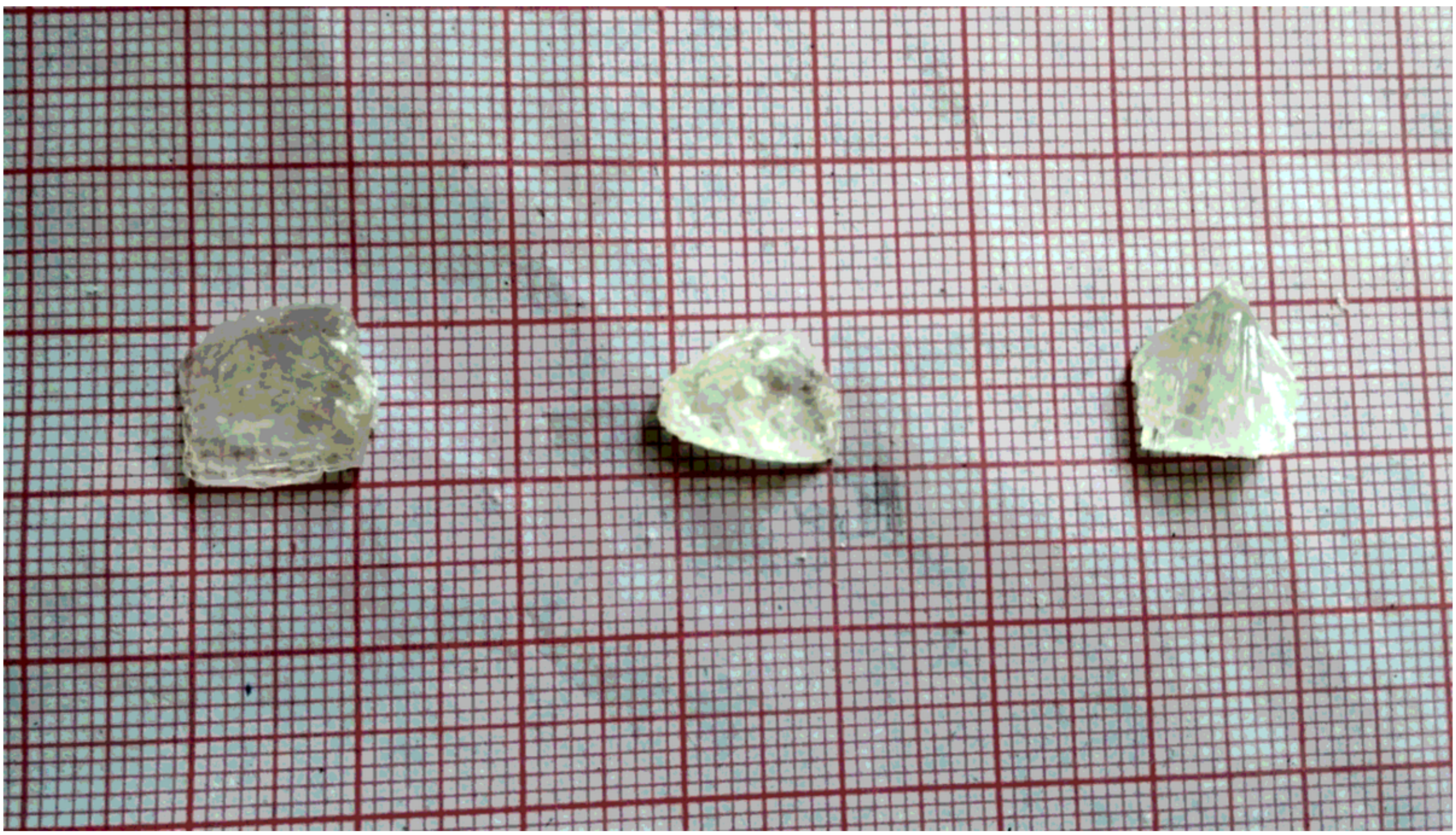

Figure 1

Grown Pb2+ doped LTCA crystal.

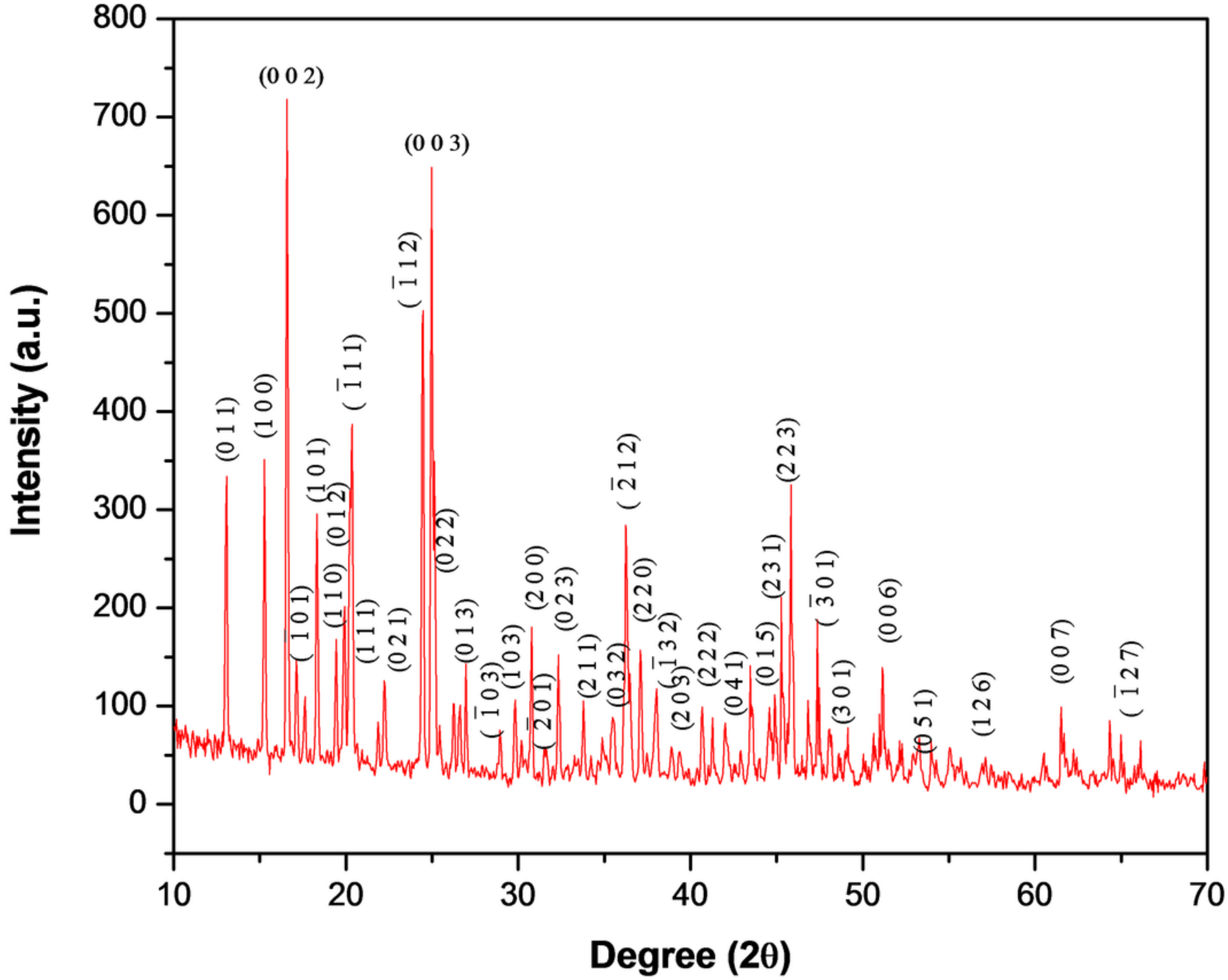

Figure 2

XRD pattern of Pb2+ doped LTCA crystal.

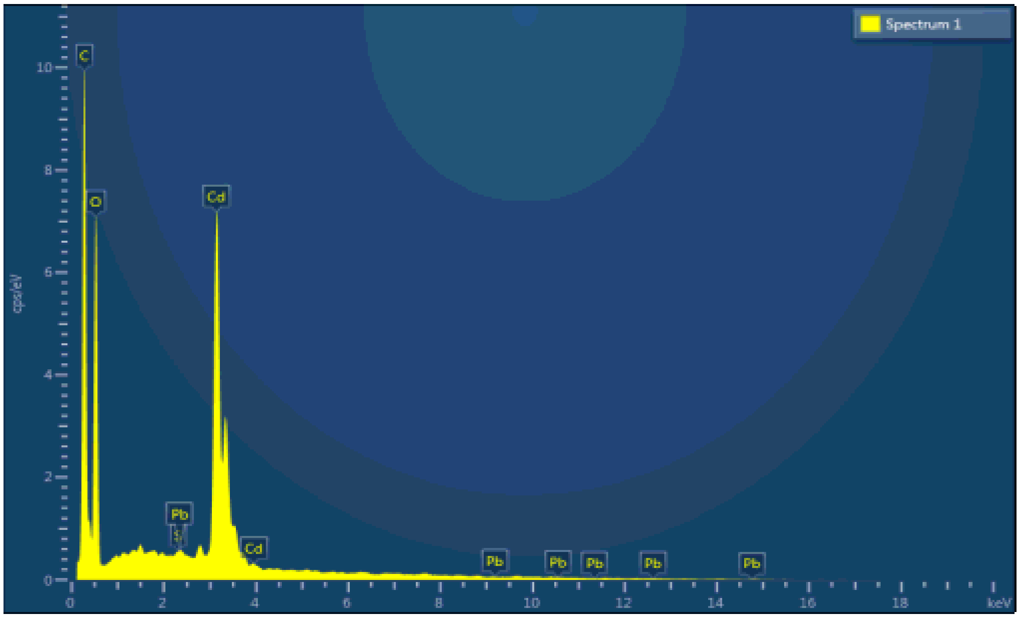

Figure 3

EDAX spectrum of Pb2+ doped LTCA.

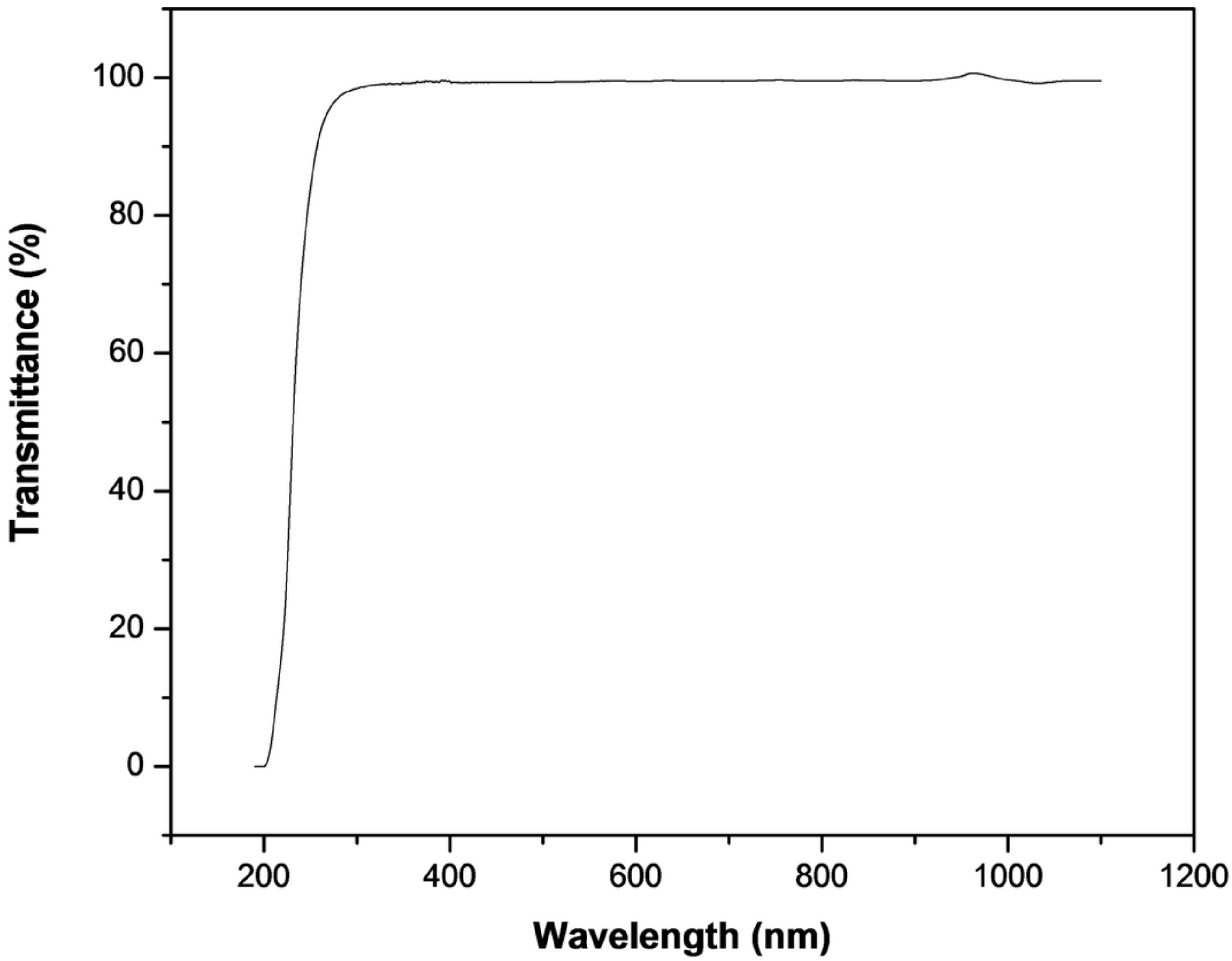

Figure 4

Optical transmission spectrum of Pb2+ doped LTCA.

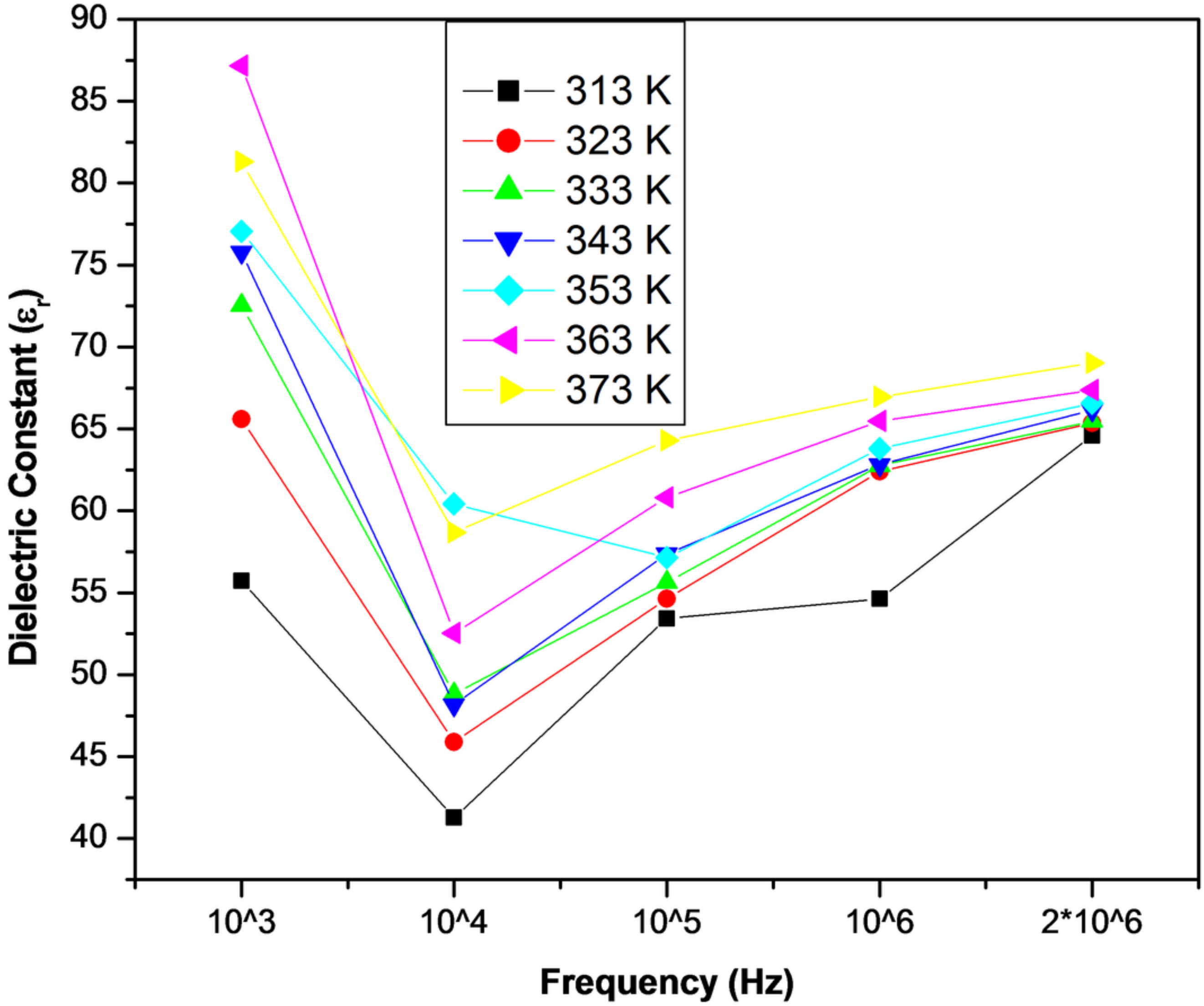

Figure 5

Frequency vs dielectric constant of Pb2+ doped LTCA.

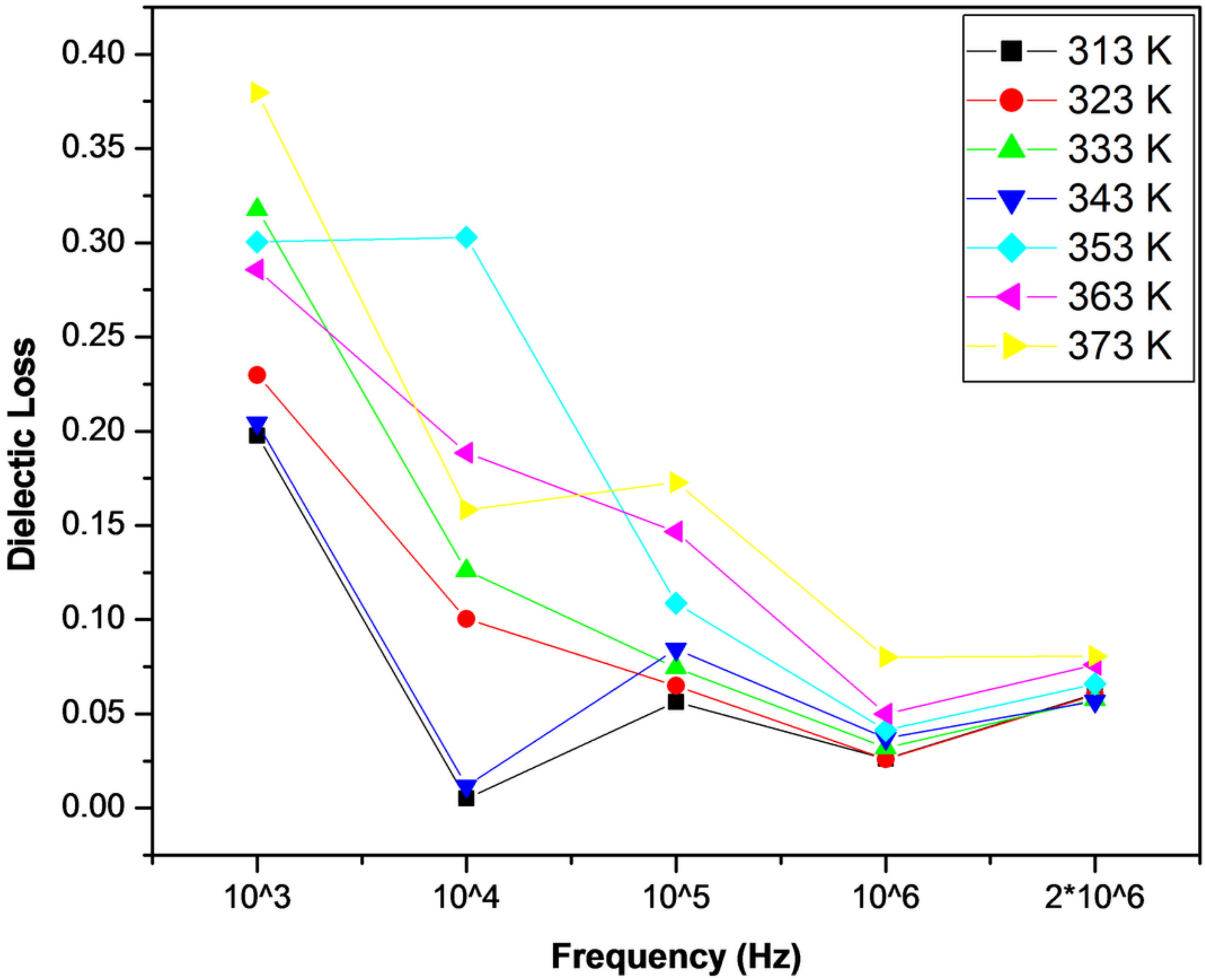

Figure 6

Frequency vs dielectric constant of Pb2+ doped LTCA.

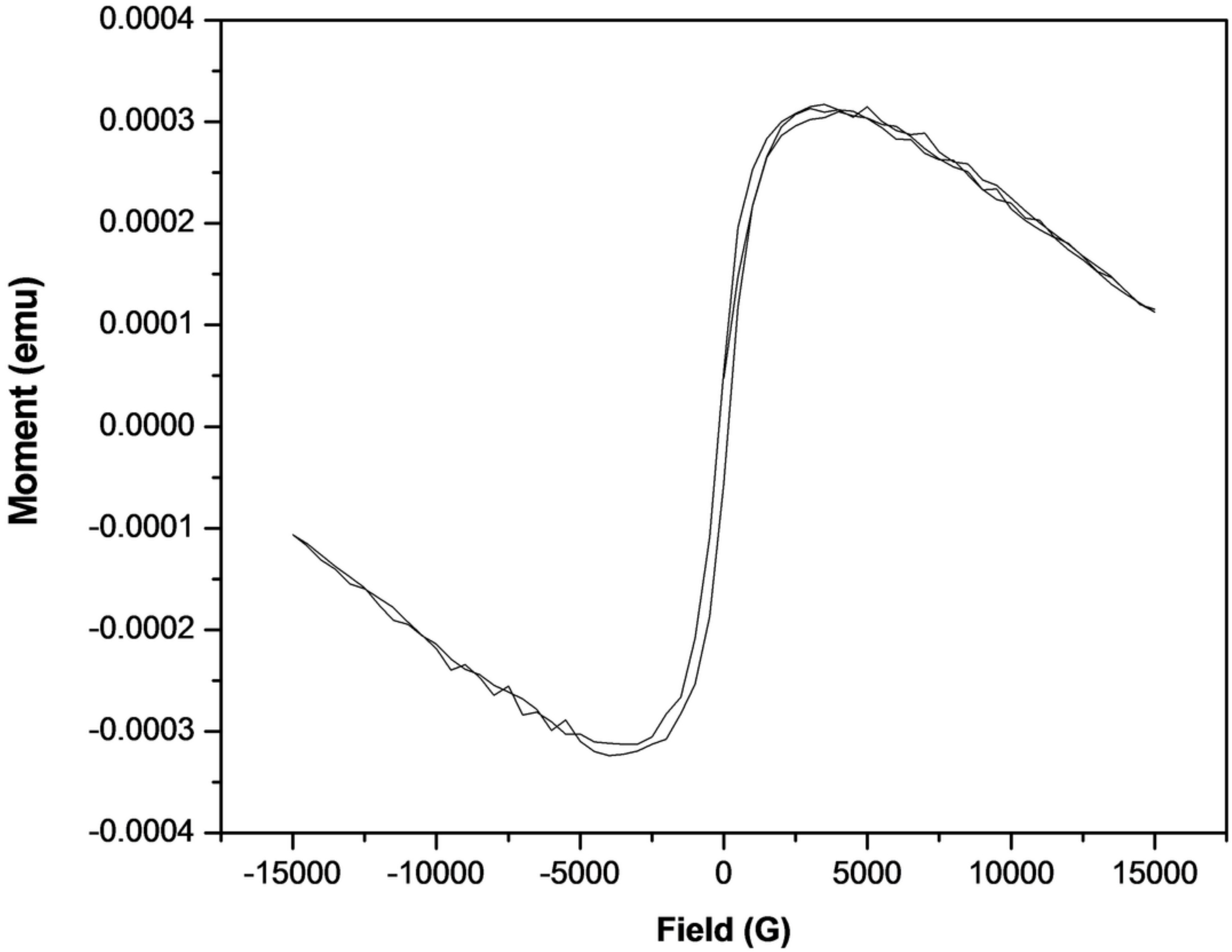

Figure 7

VSM graph of Pb2+ doped LTCA.