

Spectroscopic and analytical studies of lead mixed cadmium oxalate crystals

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Abstract

Lead mixed cadmium oxalate (LMCO) crystals were grown in oxalic acid impregnated silica hydro gel. Optimal growth condition was established by varying specific gravity of sodium meta silicate (SMS), gel pH, gel temperature and concentration of reactant solutions. The grown crystals were found to be transparent, hard and water insoluble. The LMCO crystals were characterized in succession by Energy dispersive X-ray (EDX) spectroscopy, Fourier transform infrared (FTIR) spectral technique, Thermogravimetric analysis (TGA), Powder X-ray diffraction (P-XRD) and UV-visible spectroscopy. Occupation of lead (Pb^{2+}) ions in the vacancies of cadmium (Cd^{2+}) ions was confirmed by EDX. FTIR spectrum identified the presence of oxalate ($C_2O_4^{2-}$) ions and metal-oxygen linkage in the novel crystals. TG analysis betrayed the stable oxide state of LMCO crystals after decomposition. P-XRD pattern depicted the high crystallinity. Optical studies revealed the insulating behaviour of the grown crystals.

Keywords: EDX, FTIR, insulator, oxalate crystals

1. Introduction

Crystal growth is a trust area of research, fascinated by many investigators [1]. As per the literature, mixed crystals find their applications in opto-electronics. Studies on crystal growth in gel media unveil inherent physical and chemical properties of oxalate crystals. Modern day science and technology requires fabrication of high-quality defect free semiconductors, electrical components and optical devices [2]. Gel technique is the established tool, with the aid of that variety of pure, doped, co-doped and mixed crystals are grown. Crystals grown in gel are water insoluble, possess special dielectric properties and exhibit outstanding thermal stability. The investigation propounded by us deals with the growth of lead mixed cadmium oxalate (LMCO) crystals in oxalic acid impregnated silica (OIS) hydro gel and its characterization.

2. Materials and methods

2.1 Growth of Lead mixed cadmium oxalate crystals

Single test tube gel diffusion method was employed to grow LMCO crystals in oxalic acid impregnated silica (OIS) hydro gel. Chemicals used were sodium meta silicate (Na_2SiO_3), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$) of AR grade.

Growth of LMCO crystal required optimization of gel media. OIS gel was accomplished by mixing oxalic acid (0.75M) with sodium meta silicate (SMS) solution of specific gravity 1.0375 g/cm^3 in 5:4 ratio and allowed to set for gelling. After 8 days, above the set gel the reactant mixture of $\text{Cd}(\text{NO}_3)_2$ (0.5M) and $\text{Pb}(\text{NO}_3)_2$ (0.5M) in the ratio 3:3 added slowly by sideways of the test tube. Reagent cations diffused through the set gel, nucleated with oxalate ions which initiated crystallization. Crystal growth accomplished in 10 days for LMCO crystals and grown crystals were extracted and further subjected to characterization. The chemical process which describe the formation of LMCO crystals is as follows:



Fig. 1 illuminates the growth phase and extracted LMCO crystals. The optimized growth parameters are recorded in Table 1.

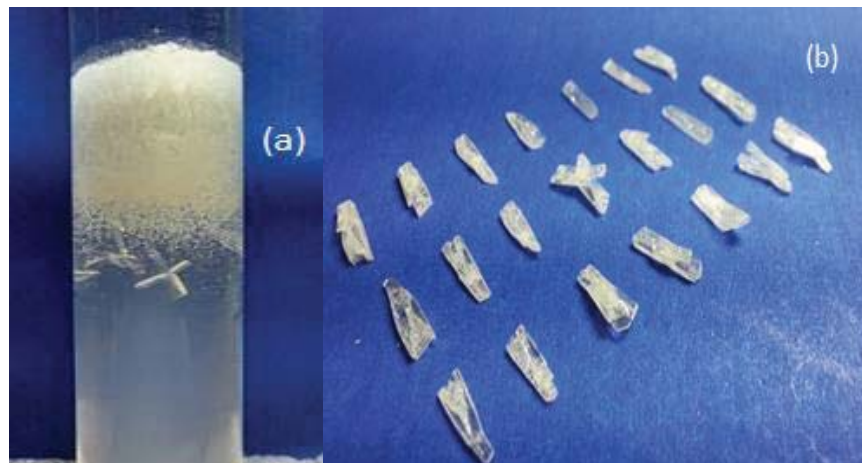


FIG 1. LMCO crystals – (a) Growth in silica gel and (b) extracted crystals.

Table 1. Optimal growth conditions of LMCO crystals.

Growth parameters	Optimum conditions
Specific gravity of SMS solution	1.0375 g/cm^3
Concentration of oxalic acid	0.75 M
Ratio of SMS : Oxalic acid	5 : 4
pH of the gel	1.5
Temperature	$20.5 \text{ }^\circ\text{C}$
Time to set gel	8 days

Concentration of supernatant solutions	0.5 M
Ratio of cationic reactants	3:3
Duration of crystal growth	10 days
Physical appearance	transparent and hard

2.2 Characterization

Chemical composition of LMCO crystal were determined using CARL ZEISS FESEM attached with EDS system (Oxford instruments). Bruker (Alpha) KBr Fourier Transform Infrared Spectrophotometer (FTIR) ($400\text{--}4000\text{ cm}^{-1}$) was used to identify the functional group associated with the grown crystals. Thermogravimetric analysis was studied using TGA-DSC (Hitachi STA 7300). Powder X-ray diffracted pattern was obtained using Bruker D8 Advance Twin-Twin diffractometer. UV-visible spectrum was obtained with the aid of UV VIS NIR $\theta/2\theta$ spectrophotometer (HO-SPA-1990P).

3. Result and discussions

In-depth characterization of LMCO crystal using Energy dispersive X-ray (EDX) measurements identified the characteristic peaks of cadmium, lead, oxygen and carbon in the EDX spectrum (Fig. 2) The mixed crystal exhibited a cationic distribution of 36.04:1 ($\text{Cd}^{2+}:\text{Pb}^{2+}$) and brought up as a good mixed crystal. The SEM image at $100\mu\text{m}$ resolution (Fig. 3) show layered deposition with valley regions. The weight and atomic percentages of elements are listed in Table 2.

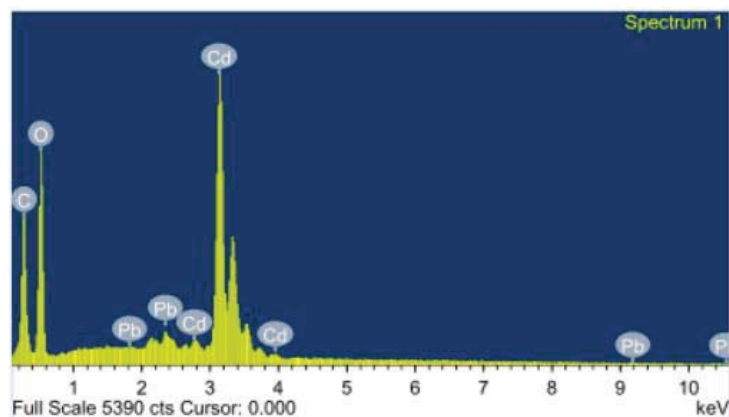


FIG 2. EDX spectrum - LMCO crystals.

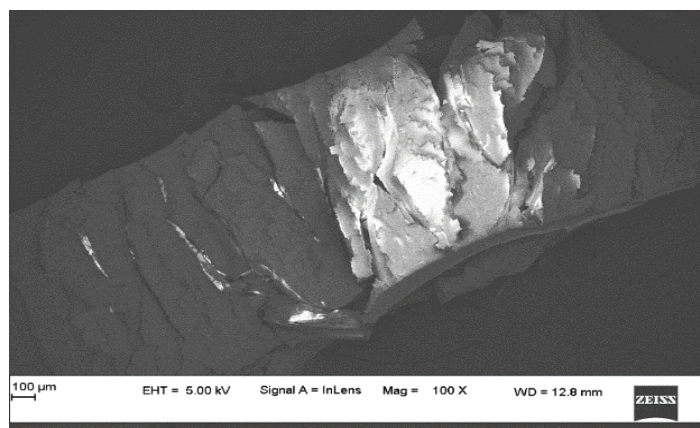


FIG 3. SEM image - LMCO crystal.

Table 2. EDX result of LMCO crystals.

Elements	Weight %	Atomic %
Cd	44.02	9.64
Pb	2.23	0.27
O	39.09	60.06
C	14.66	30.03
Total	100	100

Fig. 4 show the Fourier transform infrared (FTIR) spectrum of LMCO crystal. The possible stretching, bending vibrations and corresponding band assignments were recorded in Table 3 [3,4]. LMCO crystal armature consisted of C=O stretching (sharp absorption band at 1581.63 cm^{-1}), C-C vibrations and C-O stretching (sharp intense peak at 1311.59 cm^{-1}), OH group with broad absorption band and finger print region constituting M-O bond ($M = \text{Cd, Pb}$) at 603.72 and 513.07 cm^{-1} respectively.

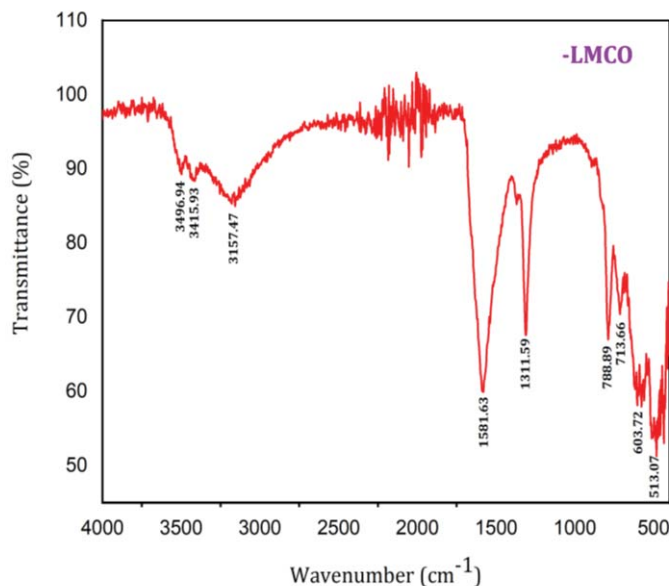


FIG 4. FTIR spectrum - LMCO crystals.

Table 3. FTIR result of LMCO crystals.

Band assignments	Wavenumbers (cm ⁻¹)
Symmetric and asymmetric stretching of OH group and water of crystallization	3496.94
	3415.93
	3157.47
C=O stretching, O-H bending	1581.63
C-C vibrations, C-O stretching	1311.59
O-H out of plane bending	788.89
	713.66
Pb-O and Cd-O stretching	603.72
	513.07

The decomposition behaviour and thermal stabilities of LMCO crystals were investigated by thermo gravimetric (TG) studies. The TG plots consisted of thermo gravimetric analysis (TGA), derivative thermo gravimetry (DTG) and differential scanning calorimetry (DSC) curves as shown in Fig. 5. The TGA studies determined the degradation temperatures, matter released, rate of weight loss (%) and chemical process involved during decomposition of LMCO crystals (Table 4). Fig 5(a) show two structural phase transformation. In the first phase of decomposition ($T_D = 48.70 - 181.53^\circ\text{C}$) the crystal lost three molecules of crystalline water showed a weight loss of 20.04% (observed) (calculated = 21.03%). In the second phase of decomposition ($T_D = 278.80 - 372.33^\circ\text{C}$) LMCO crystal lost carbon monoxide and carbon dioxide showed a weight loss of 28.1% (observed) (calculated = 28.02%) [5]. The crystal remained stable in oxide state until 1190°C , above which the crystal decomposed completely ($T_{DTG} = 1274^\circ\text{C}$). The first ($T_{DTG} = 135^\circ\text{C}$ and $T_{DSC} = 148^\circ\text{C}$ endothermic) and second degradation phases ($T_{DTG} = 349^\circ\text{C}$ and $T_{DSC} = 363^\circ\text{C}$ exothermic) were confirmed by DTG and DSC peaks.

Using EDX measurements followed by evaluation from FTIR and TG studies, LMCO crystal propounded with chemical formula $(\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and molecular weight of 257.03 (Table 5).

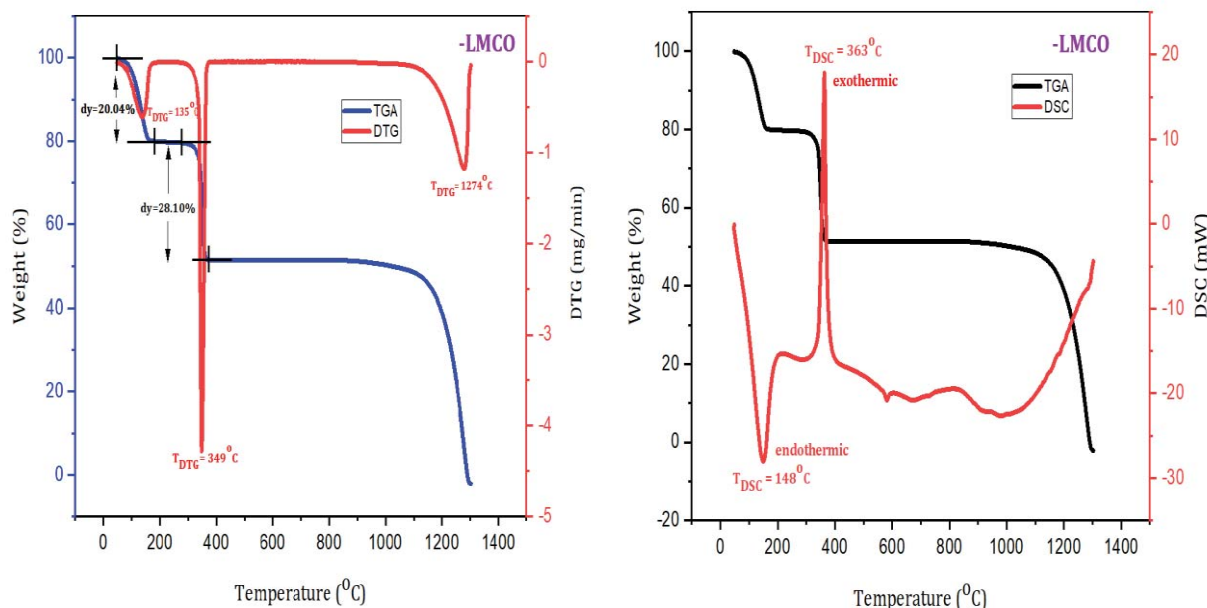


FIG 5. TG plot – LMCO crystals (a) and (b).

Table 4. Decomposition behaviour of LMCO crystals.

Phase	Decomposition Temp T_D ($^{\circ}\text{C}$)	Weight loss (%)		Decomposition phase
		Observed	Calculated	
I	48.70 - 181.53	20.04	21.03	$(\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O} \longrightarrow (\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 + 3\text{H}_2\text{O}$
II	278.80 - 372.33	28.10	28.02	$(\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 \longrightarrow (\text{Cd}_{0.973}\text{Pb}_{0.027})\text{O} + \text{CO} + \text{CO}_2$

Table 5. TG profile of LMCO crystals.

Chemical formula	Molecular weight	Phase	T_{DTG} ($^{\circ}\text{C}$)	T_{DSC} ($^{\circ}\text{C}$)	Molecule decomposed
$(\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$	257.03	I	135	148	$3\text{H}_2\text{O}$
		II	349	363	$\text{CO} + \text{CO}_2$

The Bragg’s diffraction pattern of LMCO crystals is shown in Fig. 6 for specific 2θ values. The sharp well defined peaks illuminated high crystalline nature of mixed crystal. Powder XRD pattern of the crystal was studied using PowderX software and indexed using N-TREOR09 program. After refinement with Chekcell

software, the d -spacing and lattice parameters were measured (Table 6). The observed miller indices were in agreement with the standard values [2,6]. LMCO crystal belonged to triclinic system ($P\bar{1}$ space group).

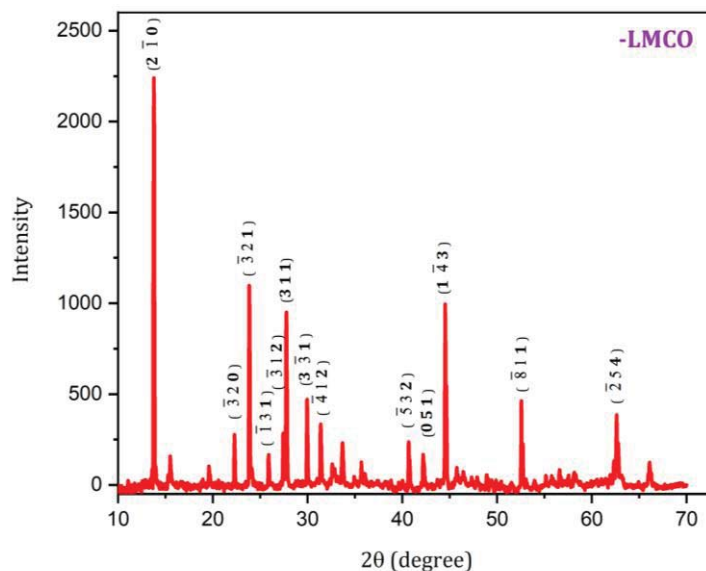


FIG 6. Powder XRD pattern of LMCO crystals.

Table 6. Cell parameters of LMCO crystals.

Cell parameters	LMCO
A	13.96 Å
B	11.79 Å
C	8.11 Å
α	93.71°
β	100.60°
γ	102.23°
Space group	$P\bar{1}$
Geometry	Triclinic

Optical properties of LMCO crystal were investigated with the aid of UV-visible spectrum. The grown crystals were brought into solution form by dissolving 10mg of LMCO crystals in 1.5N sulphuric acid heated to 80°C for 20 minutes. When crystal solution was irradiated with UV-visible light, showed absorbance in UV region with absorption maxima $A_{\max} = 1.79$ at $\lambda = 204\text{nm}$ (Fig. 7) and exhibited maximum transmittance in visible region. Tauc plot (Fig. 8) was developed to measure the band gap energy (E_g). LMCO crystal possessed a band gap energy $E_g = 5.57\text{ eV}$ and behaved as insulator [7].

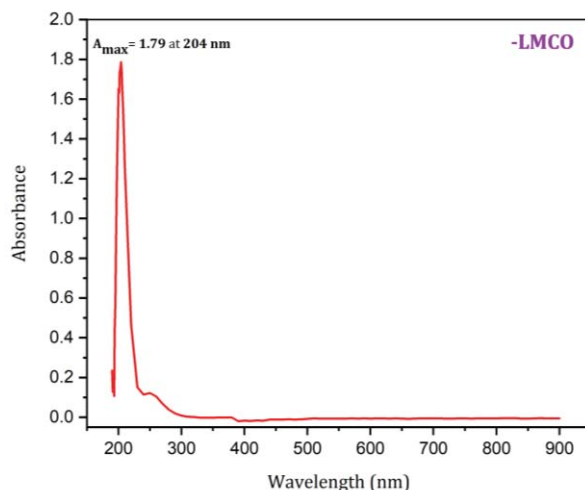


FIG 7. Absorption maxima of LMCO crystals.

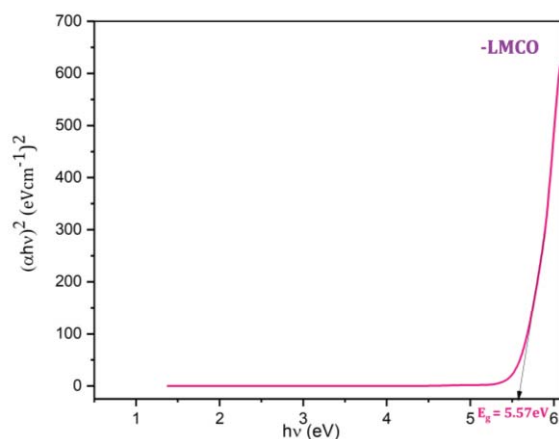


FIG 8. Band gap energy of LMCO crystals

4. Conclusion

LMCO crystals were successfully grown in oxalic acid impregnated silica hydro gel using single test tube diffusion technique. The grown mixed crystals were transparent, hard and water insoluble. EDX measurements confirmed the existence of Cd^{2+} and Pb^{2+} in 36.04:1 ratio. FTIR studies instigated C=O, C-C, C-O, Pb-O, Cd-O and OH group in the crystal armature. LMCO crystal exhibited two decomposition phases in the temperature range (48.70-372.33°C) and remained stable at Cd:PbO state, possessed good thermal stability upto 1190 °C. P-XRD measurements identified high crystalline nature and triclinic geometry with space group P1 for LMCO crystal. Overall, LMCO crystal possessed a molecular weight of 257.03 (chemical formula: $(\text{Cd}_{0.973}\text{Pb}_{0.027})\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$); ingrained a band gap energy of 5.57 eV and behaved as insulator.

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