

## Optical and thermal characterization of Nd<sup>3+</sup> doped Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O crystals

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**Abstract :** Optical And Thermal Properties Of The Neodymium (Activator) Doped Cerium (Sensitizer) Oxalate Single Crystals Grown By Hydrosilica Gel Method Were Studied At Room Temperature. The Crystals Are Bright, Transparent And Light Pink Coloured. The Emission And Absorption Spectra Of The Crystals Are Recorded And The Peaks Of The Impurity And The Host Crystals Are Identified. From The Absorption Spectra Oscillator Strengths Of This System Are Evaluated By Least Square Programming. The Emission Peak Intensities Of Cerium Decrease While That Of Nd Increases For 230 Nm-Wavelength Excitation, Which Confirms The Energy Transfer Mechanism. Ftir Spectra Show The Presence Of Water Molecules And The Number Was Measured From The Thermal Analysis.

**Keywords** – Crystal Growth, Neodymium Oxalate, Cerium Oxalate, Xrd, Ftir, Thermal Analysis

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### I. Introduction

Materials with high Energy Transfer (ET) probabilities and greater quantum efficiency are always potential candidates for the design of technologically important devices. There are several characteristics, which make these materials particularly interesting for optical active-devices applications. Rare earth ions are potential laser centers in many host materials [1-8]. The Ce<sup>3+</sup> acts as an efficient sensitizer which improves the quantum efficiency of ET in different divalent and trivalent materials in crystals and glasses [9-11]. The trivalent Ce<sup>3+</sup> could be a good sensitizer for Neodymium lasers and therefore to exploit the possibilities of Nd<sup>3+</sup> in cerium oxalate crystals we undertake this combination for the optical studies. The cerium oxalate crystals doped with different concentrations of Nd<sup>3+</sup> are grown by hydro silica gel method. The absorption and emission spectra of this oxalate single crystals are recorded and the absorption spectra show excellent variation in peak intensities in accordance with the concentration of neodymium ions. In this paper the Judd-Ofelt (J-O) analysis and the spectroscopic properties by using high resolution room temperature absorption spectra are investigated. The presence of Ce-O bond and water molecules in the crystal were identified from the FTIR spectra. Nd<sup>3+</sup> ions doped cerium oxalate crystals were subjected to thermal analysis to find out the exact number of water molecules present.

Analysis of TGA/DTA spectra shows the presence of water molecules. These large number of water molecules may greatly absorb emission radiation of Nd<sup>3+</sup> in the near IR and mid IR regions.

### II. EXPERIMENTAL

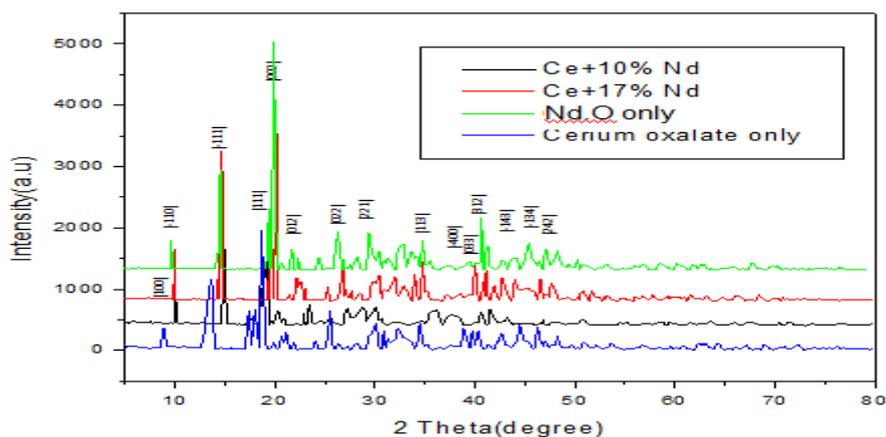
Cerium oxalate crystals with a range of impurity (Nd<sup>3+</sup>) concentrations were successfully grown in hydro silica gel technique using sodium meta silicate (SMS), cerium nitrate, neodymium nitrate, oxalic acid, nitric acid, all AR grade samples with 99.99% purity.

The volume of the cerium nitrate solution was kept constant and that of neodymium nitrate solution was varied as 10%, 15%, 17% and 20% of the total volume of the top solution. Well-grown crystals after 20 days were carefully taken out from the gel column and washed thoroughly with distilled water and then dried. These dry crystals were subjected to characterization. The emission spectra of the above samples were recorded in a Shimadzu Spectrofluorophotometer (RFPC 5301) and absorption spectra recorded in a Shimadzu Spectrophotometer (UV 2400 PC). By using KBr pellet method the FTIR spectrum for cerium oxalate crystals with 17% Nd<sup>3+</sup> concentration was recorded in a Shimadzu IR-84000 spectrometer. All measurements were done at room temperature. The chemical composition of the crystals was measured using energy dispersive X-ray fluorescence analysis (EDAX). Thermal analyses of the sample have been done by using TGA/DTA, DSC techniques. The TG analysis was done using Mettler TA 3000 system and the DSC curve was obtained by using Perkin-Elmer differentiating scanning calorimeter.

### III. Results and Discussion

#### 3.1 Characteristic analysis of XRD

X-ray powder diffraction is used to confirm the crystallinity of the sample. The sample was scanned over a range  $5^\circ$  to  $80^\circ$  at a scan rate of step size  $0.02^\circ$  with scan step time 0.5sec. Measurement temperature is  $25^\circ\text{C}$ . The obtained results of undoped and  $\text{Nd}^{3+}$  doped cerium oxalate crystals have been shown in Figure.1. The lattice parameters for 10%  $\text{Nd}^{3+}$  doped samples are  $a= 10.310 \text{ \AA}$ ,  $b= 10.101 \text{ \AA}$  and  $c= 10.213 \text{ \AA}$   $\beta= 118^\circ$  and its unit cell volume is  $939 \text{ \AA}^3$  and for 17%  $\text{Nd}^{3+}$  doped samples are  $a= 10.312 \text{ \AA}$ ,  $b= 10.110 \text{ \AA}$  and  $c = 10.241 \text{ \AA}$   $\beta= 110^\circ$  and its unit cell volume is  $960 \text{ \AA}^3$ . The (h,k,l) values have been determined and compared with the JCPDS data (20.0268 and 89.2029). The peak values are indexed and given in the Table 1. These values suggest that it is a monoclinic unit cell with space group  $\text{P2}_1/\text{c}$ .

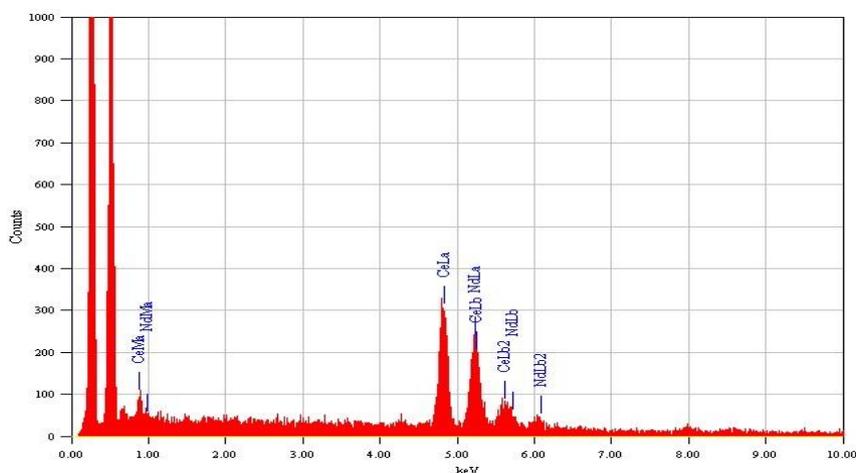


**Fig. 1** XRD Spectra of undoped and  $\text{Nd}^{3+}$  ions doped cerium oxalate crystals

All the diffraction curves show similar sharp peaks which are the characteristic of crystalline materials. The peaks in the diffraction pattern of  $\text{Nd}^{3+}$  ions doped samples are slightly shifted as compared to undoped cerium oxalate crystals. This shows that small variation in lattice parameters occur as the  $\text{Nd}^{3+}$  ions concentration increases. The lattice parameters values for this sample agreed well with the results obtained for lanthanum oxalate crystals measured by H. Sheng-Hua, C.D.Zhou and T.C.W.Mak [12].

#### 3.2 Energy Dispersive X-Ray Analysis (EDAX)

The chemical composition measured from energy dispersive X-ray analysis spectra for the crystals doped with 17%  $\text{Nd}^{3+}$  concentration with respect to  $\text{Ce}^{3+}$  ions are shown in the Figure.2. The presence of  $\text{Ce}^{3+}$  and  $\text{Nd}^{3+}$  is evident from the characteristic L peaks for these elements. The peak at 4.8 and 5.04 keV correspond to  $\text{Ce}^{3+}$  and  $\text{Nd}^{3+}$  respectively and their respective percentage in the crystal is in the same proportion of the corresponding rare earth supernatant solution.



**Fig.2.** EDAX spectra  $\text{Nd}^{3+}$  ions doped cerium oxalate crystals

### 3.3 Absorption Spectra

The  $^2F_{5/2}$  and  $^2F_{7/2}$  manifolds of 4f electronic states of cerium ions contribute much to the absorption spectra of the cerium based systems. The absorption spectra of the samples are shown in Fig.3. The peaks at 210nm, 257nm and 298nm are assigned to 4f-5d transitions of  $Ce^{3+}$  ions. The absorption peaks at 330nm, 378nm, 471nm, 528 nm, 581nm, 682 nm and 742 nm are due to the transition from  $^4I_{9/2}$  to  $^2D_{5/2}$ ,  $^2G_{11/2}$ ,  $^2G_{9/2}$ ,  $^4G_{9/2}$ ,  $^4G_{7/2}$ ,  $^4G_{5/2}$  and  $^4F_{9/2}$  respectively from the neodymium ions. Figure 3a shows the magnified peak at 581nm of Figure. 3. The absorption peaks intensities of this sample increase from 10%  $Nd^{3+}$  concentration to 17% and then starts to decrease at 20 %. That is in the  $Nd^{3+}$  sensitized cerium system there are three interdependent variables such as the concentration of cerium ions, concentration of neodymium ions and excitation pulse duration affecting the intensities. The energy levels observed from the absorption spectra are given in the Table 1.

Increasing the concentration of  $Nd^{3+}$  may improve the transfer efficiency however concentration quenching at higher  $Nd^{3+}$  concentrations reduces the gain of the system. This self-quenching of the  $Nd^{3+}$  ion concentration can lead to reduction in the over-all efficiency. Here the host considerably influences the absorption spectra of the dopant mainly in the UV region without affecting the visible region. Also the absorption spectra show that  $Nd^{3+}$  has no appreciable absorption around 230 nm, which implies that energy transfer in this system is nonradiative. Experimental and calculated oscillator strengths of various absorption transitions are given in Table 2. Oscillator strength for  $^4I_{9/2} \rightarrow ^4G_{7/2}$  transition has larger value compared with other transitions.

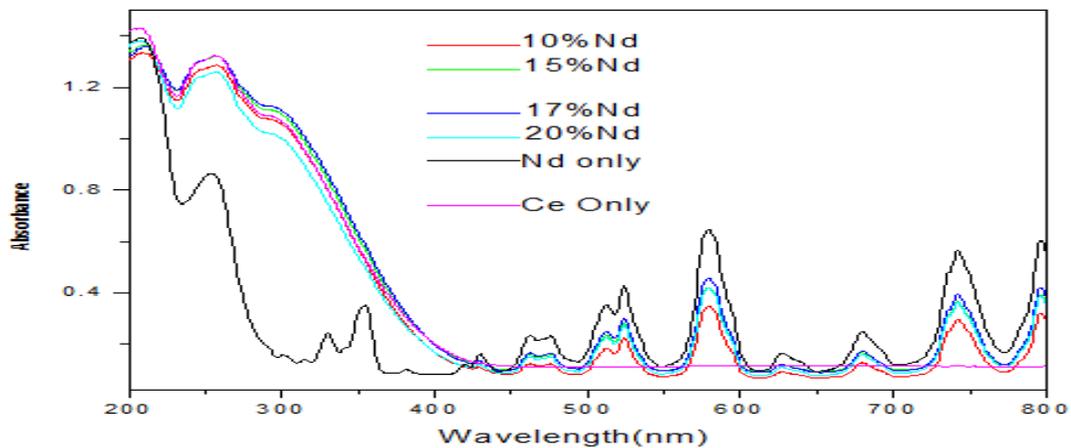


Fig.3. Absorption spectra of undoped and  $Nd^{3+}$  ions doped cerium oxalate crystals

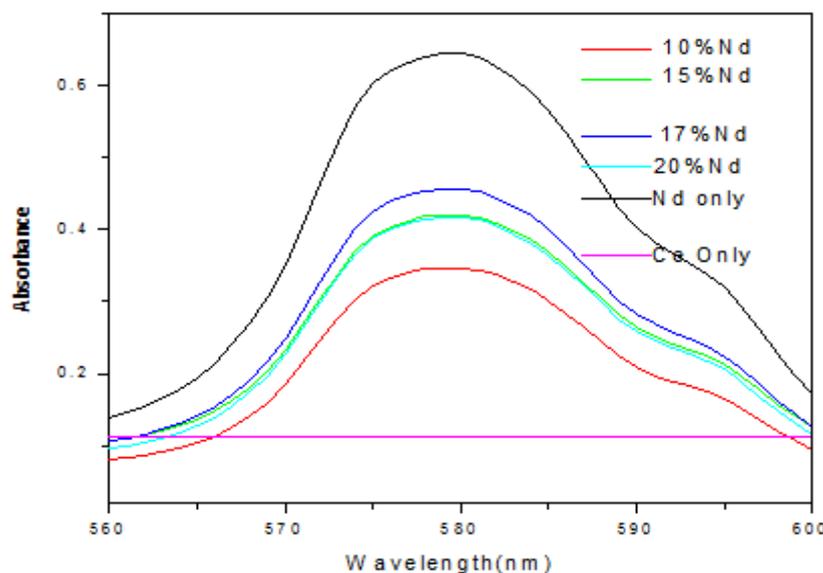


Fig 3a Magnified peak of undoped and  $Nd^{3+}$  ions doped cerium oxalate crystals

**Table 1:** Energy level assignment of Ce<sup>3+</sup> and Nd<sup>3+</sup> ions absorption spectra

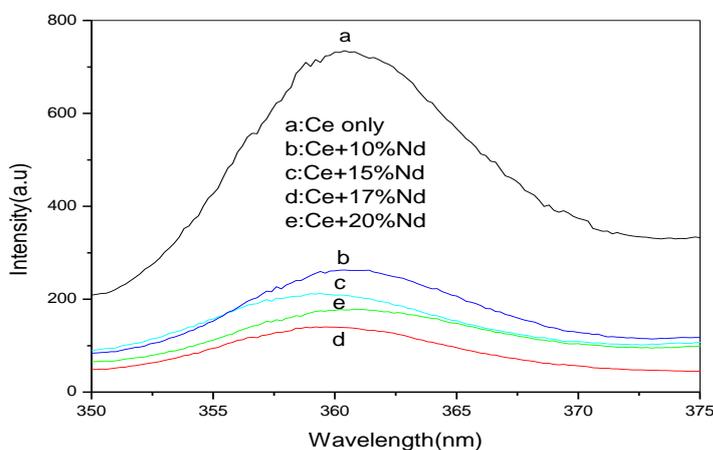
Ions	Wave length (nm)	Energy (cm <sup>-1</sup> )	Energy level Assignments
Ce	298	33557	<sup>2</sup> D <sub>5/2</sub>
	330	30303	<sup>2</sup> D <sub>5/2</sub>
Nd	378	26455	<sup>2</sup> G <sub>11/2</sub>
	471	21231	<sup>2</sup> G <sub>9/2</sub>
	528	18939	<sup>4</sup> G <sub>9/2</sub>
	581	17211	<sup>4</sup> G <sub>7/2</sub>
	682	14663	<sup>4</sup> G <sub>5/2</sub>
	742	13477	<sup>4</sup> F <sub>9/2</sub>

**Table 2:** Experimental and calculated oscillator strengths

Energy levels	10%		15%		17%		20%	
	F <sub>5</sub> <sup>exp</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>cal</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>exp</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>cal</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>exp</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>cal</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>exp</sup> x10 <sup>-5</sup>	F <sub>5</sub> <sup>cal</sup> x10 <sup>-5</sup>
<sup>2</sup> G <sub>9/2</sub>	0.335	0.334	0.461	0.459	0.529	0.528	0.488	0.486
<sup>4</sup> G <sub>9/2</sub>	0.314	0.396	0.377	0.466	0.426	0.529	0.393	0.493
<sup>4</sup> G <sub>7/2</sub>	2.515	2.508	3.009	3.002	3.389	3.381	3.158	3.149
<sup>4</sup> G <sub>5/2</sub>	0.416	0.149	0.518	0.176	0.591	0.199	0.516	0.186
<sup>4</sup> F <sub>9/2</sub>	2.147	0.709	2.519	0.834	2.861	0.947	2.670	0.883

### 3.4 Emission Spectra

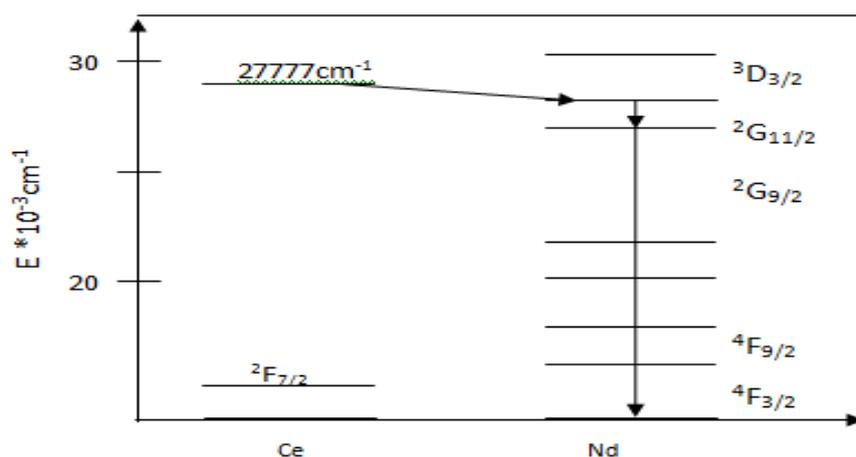
The emission spectra of cerium oxalate crystals and Nd<sup>3+</sup> doped cerium oxalate crystals are shown in Figure.5 for the excitation wavelength 230 nm. Energy transfer from Ce<sup>3+</sup> to Nd<sup>3+</sup> takes place efficiently for this 230 nm-excitation wavelength. The emission spectra for undoped cerium oxalate show only one peak at 360 nm. The emission peaks at 360 nm are corresponding to transitions from the 5d states of Ce<sup>3+</sup> and terminating on the 4f states. The Ce<sup>3+</sup> emission intensity decreases with increase of Nd<sup>3+</sup> concentration and correspondingly the intensities of emission spectra of Nd<sup>3+</sup> at 1060 nm increases initially and at 20% concentration of Nd<sup>3+</sup> it starts to decrease due to self quenching. The overall decrease in the intensities of Ce<sup>3+</sup> peaks implies that the energy transfer occurs from the Ce<sup>3+</sup> to the Nd<sup>3+</sup> ions.



**Fig.5** Emission spectra of Nd<sup>3+</sup> ions doped cerium oxalate crystals

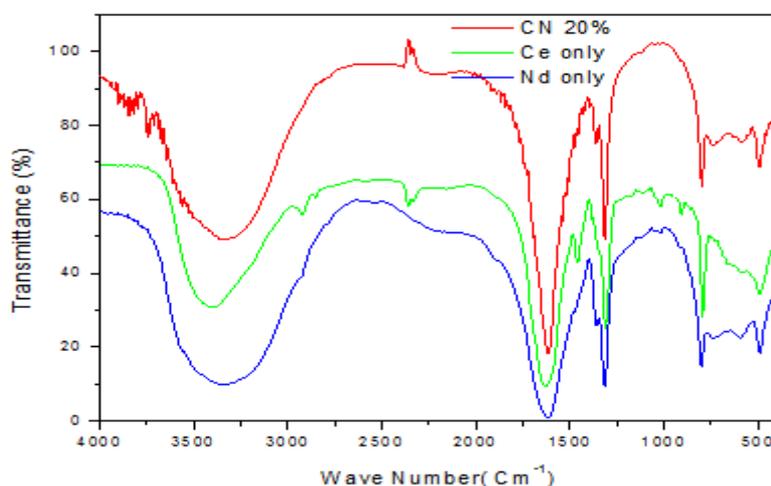
The linear variation of the transfer probabilities corresponding to the variation of concentration of dopant ions reveals the electric dipole-dipole interaction between donor and acceptor ions of this system.

The energy gap between the sensitizer and the activator varies in a small range and the closeness of these levels suggests possible energy transfer from the Ce<sup>3+</sup> to Nd<sup>3+</sup>. A simplified energy level diagram of this system is shown in Figure.6. This diagram constructed from the absorption and emission spectra of the sample is to label the different transitions involved.


**Fig.6** Simplified energy level diagram

### 3.5 FTIR spectra

We employed the KBr pellet method for the FTIR spectra. The FTIR spectra for cerium oxalate, neodymium oxalate and cerium oxalate doped with 17% of  $\text{Nd}^{3+}$  ions concentration are recorded in a Shimadzu IR-480 spectrometer and shown in Figure 7. All the three spectra show the common feature of M-O (M=Ce, Nd: Metal-oxide bond) bond formation. The intense broad bands around  $2810\text{-}3905\text{ cm}^{-1}$  centered at  $3402\text{ cm}^{-1}$  evidence the presence of water of crystallization and is assigned to asymmetric and symmetric stretching mode of vibration. The band at  $1616\text{ cm}^{-1}$  is due to asymmetric stretching of C=O. The weak band at  $1465\text{ cm}^{-1}$  is assigned to H-O-H bending mode. The sharp bands observed at  $1315\text{ cm}^{-1}$  have been assigned to C-O stretching. The band at  $799\text{ cm}^{-1}$  corresponds to M-O (M-Ce, Nd) bond. Absorbance at this wavelength for 20%  $\text{Nd}^{3+}$  cerium oxalate crystals is greater than that of undoped cerium and neodymium oxalates. The spectral data and band assignment are given in Table 3.


**Fig.7** FTIR spectra

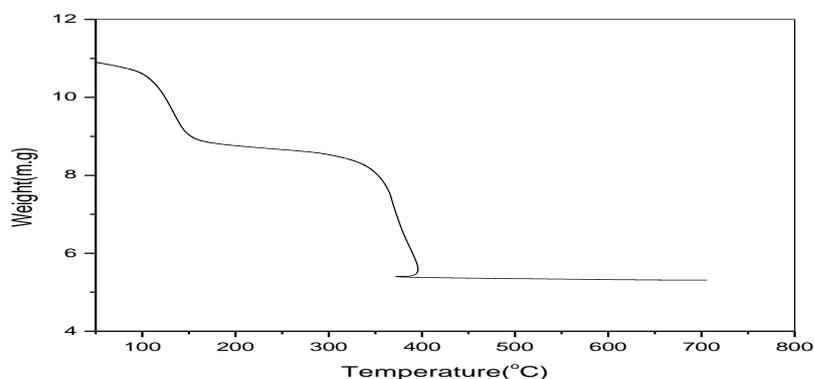
**Table 3:** Spectral data and band assignment of  $\text{Nd}^{3+}$  doped cerium oxalate crystals.

Wave number ( $\text{cm}^{-1}$ )	Intensity			Assignment
	Ce.O only	Nd.O only	Ce+Nd	
799	22.45	41.12	75.15	M-O stretching
1315	42.70	59.61	86.94	C-O stretching
1465	12.52	13.12	12.76	H-O-H bending
1616	45.12	54.39	65.47	Asym.stretch(C=O)
3402	59.97	64.86	96.67	$\text{H}_2\text{O}$ stretching

### 3.6. Thermal stability analysis

#### 3.6.1. TGA/DTA

Thermogravimetry analysis (TGA) and Differential thermal analysis (DTA) curves are recorded simultaneously on a thermal analyzer over the temperature range 28° C to 700° C. A sample of 9.988 gm is used and the recordings are carried out in oxygen atmosphere at a heating rate of 10° C/min. The TGA curve is shown in Figure.8.



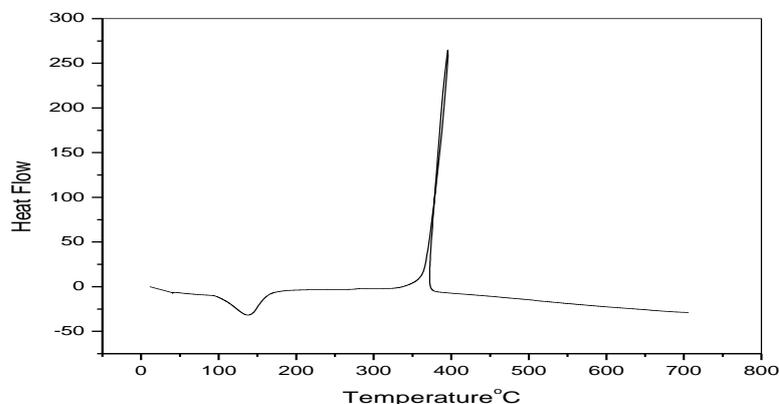
**Fig.8** TGA curve of 17% Nd<sup>3+</sup> ions doped cerium oxalate crystals

It is observed that the onset of first decomposition begins slightly at 105° C and continues up to 149° C, resulting in a weight loss of 23% of the total weight of the sample. In this stage elimination of all the 10 water molecules takes place and the sample reduced to anhydrous Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> along with Nd<sup>3+</sup> ions. After this stage of decomposition the sample remains stable for a temperature range of 149° C to 340° C. The second stage of decomposition starts at 340° C and continues up to 390° C. During this temperature range a total weight loss of 27% is observed and the sample reduced to Ce<sub>2</sub>O<sub>3</sub>. The calculated and observed mass loss is given in Table 4.

**Table 4** Calculated and observed mass loss

	Decomposition Temp(°C)	Loss of materials	Observed mass loss (%)	Calculated mass loss (%)	Endo/Exo
Stage I	105 -- 149	10H <sub>2</sub> O	23%	22%	Endo
Stage II	340-- 390	3CO & 3CO <sub>2</sub>	27%	26%	Exo

The DTA curve shows (Figure.9) an endothermic peak at 145° C corresponding to the elimination of the ten water molecules. The exothermic peak at 363° C is due to the oxidation reaction taking place along with decomposition. The thermal stability of these samples can be estimated from the DSC/DTA curves by using relation,  $\Delta t = (T_x - T_g)$ . It is determine that the transition temperature ( $T_g$ ) and onset crystallization temperature ( $T_x$ ) are 160° C and 340° C, respectively. The higher the  $\Delta t$  is, stronger the thermal stability.



**Fig. 9** DTA curve of 17% Nd<sup>3+</sup> ions doped cerium oxalate crystals

### 3.6.2. DSC analysis:

The DSC analysis was done for temperature between 20°C to 550°C. The DSC trace is shown Figure. 10. The sharp peaks at 160° C and 388° C represent its melting points. The sharpness of these peaks shows good degree of crystallinity of the sample. Thermal decomposition reactions are usually endothermic.

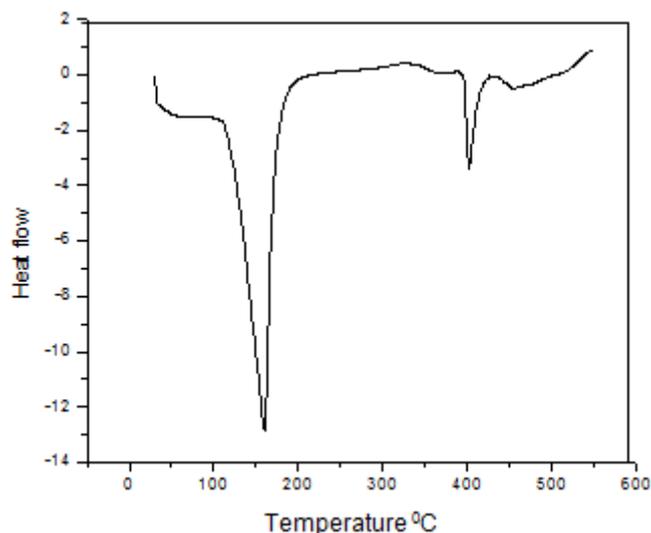


Fig. 10 DSC curve of 17% Nd<sup>3+</sup> ions doped cerium oxalate crystals

## IV. Conclusion

Impurity added cerium oxalate single crystals were grown and the energy transfer from Ce<sup>3+</sup> to Nd<sup>3+</sup> has been investigated. The mechanism of energy transfer is mainly due to dipole-dipole interaction. Fluorescence quenching has been confirmed by spectroscopic analysis and it was occurred at 17% of Nd<sup>3+</sup> concentration. The emission intensity of Ce<sup>3+</sup> around 360 nm considerably decreases with the increase in concentration of Nd<sup>3+</sup> strongly supporting the possible energy transfer from Ce<sup>3+</sup> to Nd<sup>3+</sup>. The energy transfer parameters between Ce<sup>3+</sup> and Nd<sup>3+</sup> were also calculated and analyzed based on Dexter's model. The various functional groups of impurity added cerium oxalate single crystals and vibrational modes of water molecules were identified by Fourier transform infrared spectroscopy. An intense broad band of FTIR spectra around 2810-3905 cm<sup>-1</sup> gives the evidence for the presence of water of crystallization. The presence of Ce-O bond is evidenced by the strong absorption at 799 cm<sup>-1</sup>. Thermal analysis shows endothermic peaks and the decomposition stages of these samples

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