MAGNETIC AND THERMAL PROPERTIES OF PR^{3+} DOPED ERBIUM OXALATE CRYSTALS

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Abstract: We report the magnetic and thermal properties of praseodymium ions doped erbium oxalate single crystals grown by hydro silica gel method. The rare earth oxalate crystals have attracted considerable interest in the recent years due to their greatly varying physical properties. Pr^{3+} doped erbium oxalate crystals have been studied with respect to their varying magnetic properties. Energy transfer studies and optical properties of doped rare earth oxalate crystals have already been reported. Study on magnetic properties of doped rare earth oxalate crystals is scanty and we attempt to explore the magnetic and thermal properties of Pr^{3+} doped erbium oxalate crystals in this work.

***IndexTerms* - E**rbium oxalate, Single crystals, magnetic and thermal properties, doped rare earth oxalate crystals, erbium and praseodymium ions

I. INTRODUCTION

The rare earth oxalate crystals doped with impurities have been studied with respect to their strong magnetic and thermal properties. The incorporation of rare earth ions in different host materials modifies significantly the magnetic properties of the host materials [1-6]. The erbium oxalate crystals doped with different concentrations of Pr3+ are grown by hydro silica gel method [7]. Magnetic moments for different external fields are determined by using Lakeshore- 736 VSM device. Gram susceptibility and molar susceptibility of the crystals are also measured. Hydro silica gel method is one of the suitable method, was employed for the growth of erbium oxalate crystals doped with different concentrations of praseodymium ions. The TGA/DTA and DSC analysis gives the exact number of water molecules present in these samples. The well-grown crystals are light green in colours, and the colour concentrations of these crystals are varying in accordance with the concentration of dopant materials.

II. EXPERIMENTAL

Erbium oxalate crystals with a wide range of impurities Pr^{3+} concentrations were successfully grown in hydro silica gel technique using sodium meta silicate (SMS), erbium nitrate, praseodymium nitrate, oxalic acid, nitric acid, all AR grade samples with 99.99% purity. The erbium oxalate doped with praseodymium ions for different volume composition of the top solution. Here the volume of the erbium nitrate solution was kept constant and that of praseodymium nitrate solution was varied. 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 magnetic and thermal characterization.

III. RESULTS AND DISCUSSIONS

III a. Magnetic Properties

Energy transfer studies and optical properties of doped rare earth oxalate crystals have already been reported [8-14]. The magnetic moment and gram susceptibility of erbium oxalate crystals for Pr^{3+} concentrations 12%, 18% and 21% are calculated. A summary of the calculated values of magnetic moment is given in Table 1. The variation of the magnetic moment with external field is depicted in Fig 1. These data indicate that these materials are paramagnetic and the observed magnetic moments are in agreement with the Van Vleck and others [15-17] values which indicate that the 4f-electrons well shielded by the $5S^2 5P^6$ octet, play only a small role in bonding. The observed magnetic moments of these materials are found to agree well with Hund's [18] theoretical values for first spin-orbit coupling model. Decker [19] had measured the susceptibilities of praseodymium nitrate solutions for different concentrations. He had observed that the susceptibility increases with concentrations. Fig.2 shows that the magnetic moment is decreases at 18% due to concentration quenching. The magnetic susceptibility values are corrected for diamagnetism using the values $Ee^{3+} = Pr^{3+} = 20*10^{-6}$ [20]. The molar susceptibility is calculated from the equation

$$\chi_M = \chi_g.M/n \qquad \text{----------(1)}$$

where M is the molar weight of the sample, n is the number of rare earth atoms per molecule, χ_g is the gram susceptibility [21]. Correction per diamagnetic ions can be calculated from equation (1).

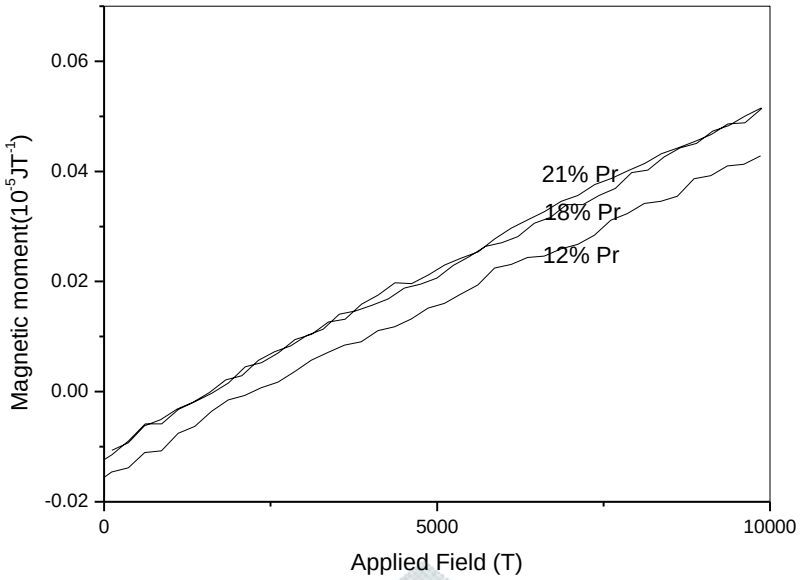

Fig.1 Magnetic curve of the Pr^{3+} doped erbium oxalate crystal

The effective magnetic moment can be calculated from the equation

$$\mu_{EFF} = 0.8942[(\chi_{M)CORR}\, T]^{1/2} \quad \text{----------(2)}$$

where χ_{Mcorr} is the corrected molar susceptibility and T is the absolute temperature. The calculated values are given in Table 1.

Table.1 Magnetic moment and gram susceptibility

Field (T) x10^4	12%		18%		21%	
	Moment $10^{-5}JT^{-1}$	χ_g $JT^{-2}Kg^{-1}$	Moment $10^{-5}JT^{-1}$	χ_g $JT^{-2}Kg^{-1}$	Moment $10^{-5}JT^{-1}$	χ_g $JT^{-2}Kg^{-1}$
0.6	0.0029	0.0456	0.0182	0.2859	0.0192	0.3016
0.8	0.0079	0.0931	0.0302	0.3558	0.0441	0.5196
1.0	0.0179	0.1687	0.0415	0.3911	0.0671	0.6324

Table.2. Effective magnetic moments

Material	Corrected molar susceptibility JT^{-2} $mole^{-1}$	Effective magnetic moment (Bohr magneton)	
		Experimental	Theoretical
Pr^{3+} doped erbium oxalate crystals	0.033	4.331	3.88
	0.108	4.826	3.88
	0.173	5.019	3.88

III b. Thermal analysis

III b.1 TGA/DTA

Thermogravimetry analysis (TGA) and Differential thermal analysis (DTA) curves are recorded simultaneously on a thermal analyser over the temperature range 50° C to 550° C. 11.3 gm sample 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.2. It is observed that the onset of first decomposition begins slightly at 102.5° C and continues up to 110° C, resulting in a weight loss of 20% of the total weight of the

sample taken. In this stage elimination of all the 8 water molecules takes place and the sample reduced to anhydrous $Er_2(C_2O_4)_3$. After this stage of decomposition the sample remains stable for a temperature range of 110° C to 170° C. The second stage of decomposition starts at 170°C and ends at 180°C. During this temperature range a total weight loss of 4% is observed and the sample reduced to Er_2O_3. The third stage of decomposition starts at 335° C and continues up to 370° C and during this temperature range the sample reduced to ErO_2. The DTA curve shows (Figure.3.) an endothermic peak at 110° C corresponding to the elimination of the eight water molecules and a second peak at 180°C. The

exothermic peak at 387.03° C is due to the oxidation reaction-taking place along with decomposition. Table 5.9 gives the calculated and observed mass loss in percentage.

Table.3. Calculated and observed mass loss.

	Decomposition Temp (°C)	Loss of materials	Observed mass loss (%)	Calculated mass loss (%)	Endo/ Exo
Stage I	105 – 112	$8H_2O$	20%	19%	Endo
Stage II	170 - 180	$3CO$ & $3CO_2$	25%	26%	Endo
Stage III	336 – 490	Ce_2O_3 to CeO_2	4%	4%	Exo

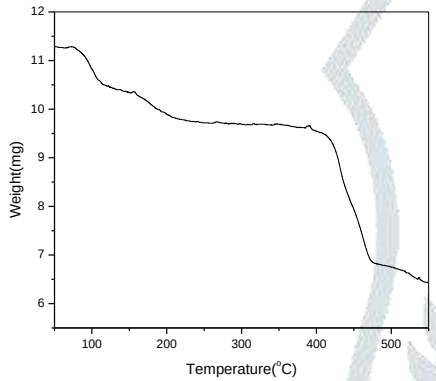

Fig.2. ***TGA curve***

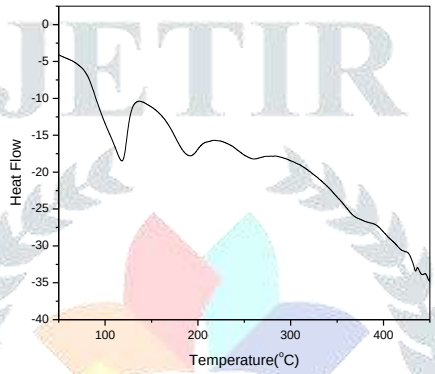

Fig.3 ***DTA curve***

III b.2. DSC analysis:

The Figure 4 shows the DSC plot of erbium oxalate crystals doped with Pr^{3+} ions. It shows thermal anomalies at temperature 105° C, 181° C and 478° C.

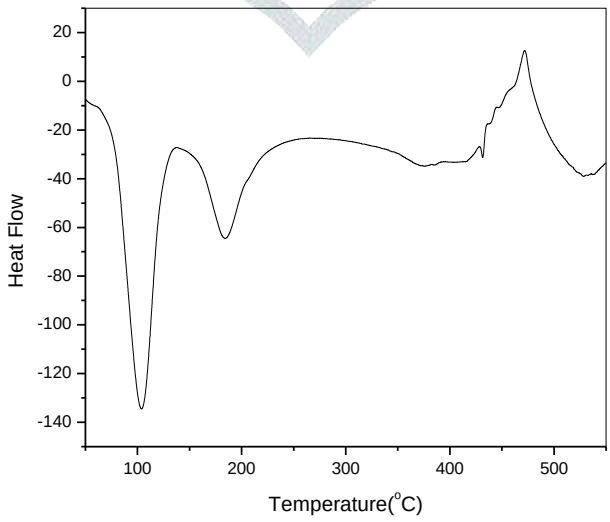

Fig.4 DSC curve

The magnetic and thermal properties of praseodymium doped erbium oxalate single crystals are presented. The doping of Pr^{3+} considerably influences the magnetic and thermal properties of the erbium oxalate single crystals. Thermal and magnetic properties are also studied. The samples decompose into metallic oxides at different temperatures. The amount of water of hydration is determined.

IV CONCLUSION

Pr^{3+} doped erbium oxalate single crystals were grown and the magnetic and thermal properties have been investigated. The variation of the magnetic moment with external field has been studied. The data indicate that these materials are paramagnetic and the observed magnetic moments are in agreement with the theoretical values which indicate that the 4f-electrons well shielded by the $5S^2 5P^6$ octet, play only a small role in bonding. The observed magnetic moments of these materials are also found to agree well with theoretical values for first spin-orbit coupling model. It has been observed that the susceptibility increases with concentrations. Studies show that the magnetic moment is decreases at 18% for Pr^{3+} doped erbium oxalate single crystals, due to concentration quenching. The magnetic susceptibility values are corrected for diamagnetism using the values $Er^{3+} = Pr^{3+} = 20*10^{-6}$

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