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Comparison of Growth and Characteristic Properties of Pure and Cobalt Doped Cadmium Oxalate Single Crystals

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The pure cadmium oxalate and cobalt doped cadmium oxalate single crystals were grown in silica gel, then compared the growth parameters. The XRD, FTIR, TGA/DTG, UV-spectrum and scanning micrographs analysis of the grown crystals confirmed the crystals to be pure and cobalt doped cadmium oxalate trihydrate. Morphology of the crystals studied from the photography while the structure of the crystals were studied from XRD. Thermal analysis reveals the decomposing temperature of the crystals.

Key Words: Doped crystal growth, Cadmium oxalate.

INTRODUCTION

Single crystals of cadmium oxalate cannot be grown by either slow solvent evaporation or melt techniques because of their insolubility in water and decomposition before melting. Cadmium oxalate single crystals grown from gel technique have been investigated by X-ray methods from which lattice constants and space group were determined[1]. Few mixed oxalate crystals were grown by gel technique[2]. Growth by hydro silica gel[3] is the most suitable method for getting perfect crystals with minimum impurities and imperfections. Cadmium oxalate trihydrate single crystals were grown in silica gel employing various nucleation controlling procedures[4] by adding impurities. Thermogravimetry of various oxalates have also been reported[5]. This paper presents the comparative study of gel grown pure and cobalt doped cadmium oxalate single crystals. The molarity of pure crystal is one while dopant's molarity is 1/100th of pure.

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EXPERIMENTAL

All the chemicals used were AR grade. Sodium meta silicate gel (sp. gravity 1.04 g cm^{-3}) was allowed to set in a corning glass tube after mixing with 1 M oxalic acid at 4 pH. One week duration needed for setting gel. For pure cadmium oxalate single crystals, cadmium chloride solution (1 M) was then added slowly along the walls of the glass tube while for doped a mixture of 1 M cadmium chloride solution and 0.01 M cobalt chloride solution (1:1 in vol) was added. The solution diffused in to the gel as indicated by the Liesegang rings and their movements. The colourless cadmium oxalate single crystals of *ca.* $4 \times 3 \times 1$ mm^3 size were obtained in about 25 d. While the pinkish coloured Co-Cd oxalate single crystals of *ca.* $7 \times 2 \times 1$ mm^3 were obtained and measured its dielectric properties[6]. The presence of cadmium in pure crystal and cadmium and cobalt in doped crystal were studied using ICPAES analysis. The following chemical reaction was employed for the growth:

$$CdCl_2 + C_2H_2O_4 \longrightarrow CdC_2O_4 + 2HCl$$

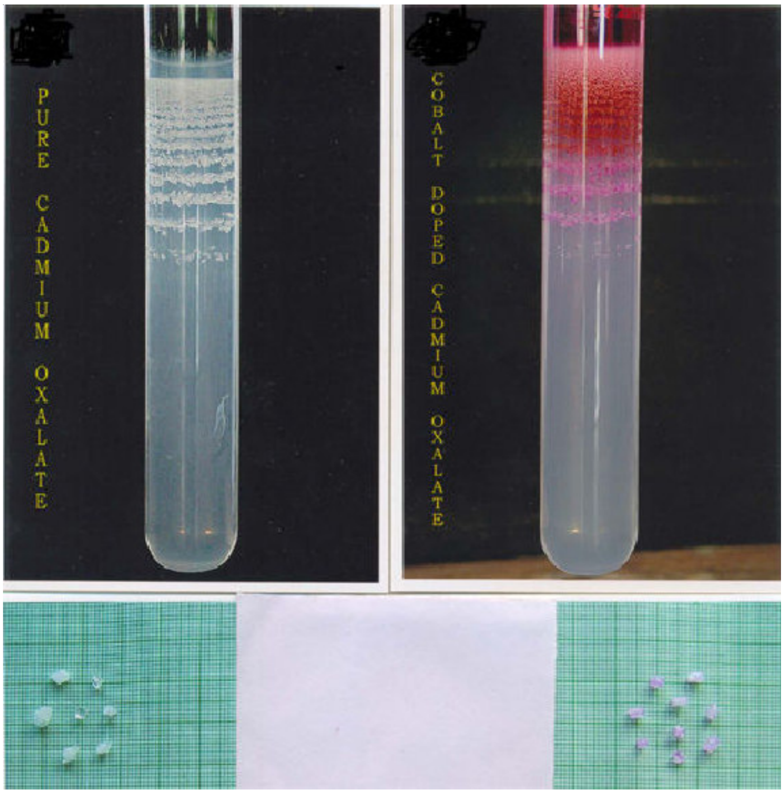
RESULTS AND DISCUSSION

Fig. 1 shows Liesegang rings and the grown crystals. The crystals are 3 to 6 mm in size. The nucleation of the crystals are due to the controlled diffusion of cadmium ions and cobalt ions through sodium meta silicate gel impregnated with oxalic acid[7]. Cadmium/cobalt chloride solution and oxalic acid function respectively as the outer and inner reactants.

The characterization of the pure and doped crystals were carried using XRD, FTIR, thermal analysis, UV absorption spectrum and scanning electron micrographs and their characteristics are compared.

X-Ray diffraction: The X-ray diffraction pattern of pure cadmium oxalate and cobalt doped cadmium oxalate crystals are shown in Fig. 2. The patterns of these two samples were taken at room temperature in order to study the structure of the materials. Both materials were found to be single crystalline. The pattern taken using Siemen X-ray diffractometer (D 5000) having CuK_α radiation ($\lambda = 1.54$ Å). Table-1 shows d-values for the prominent peaks.

FTIR: Thermo Nicolet's Avtar 370 DTGS spectrometer is used for the study of FTIR spectrum of both samples. KBr is used as the beam splitter and also as detector. The peaks are identified in comparison with earlier reports[8]. The broad peak at 3600-3400 cm^{-1} due to anti symmetric O-H stretching suggest the presence of water of crystallization in both crystals. The broad peak around 1700 cm^{-1} related to H-O-H bending is also support the presence of water. The well defined peak at 1300 cm^{-1} reveals the presence of CO_2 symmetric stretch which support the presence of oxalate ions.



(a) (b)

Fig. 1. (a) Pure cadmium oxalate crystals (b) Cobalt doped cadmium oxalate crystals

TABLE-1
2-θ AND d-VALUES

Pure cadmium oxalate		Cob. Doped cadmium oxalate	
Angle 2θ°	d-value (Å)	Angle 2θ°	d-value (Å)
14.152	6.25316	22.182	4.00428
15.912	5.56510	22.973	3.86820
19.294	4.59676	24.030	3.70037
20.045	4.42649	38.250	2.35172
24.944	3.56687	45.830	1.97835
28.187	3.16344	46.752	1.94147
31.826	2.80946	49.240	1.84902
34.082	2.62852	56.113	1.63775
40.077	2.24806	61.505	1.50646
42.656	2.11790	62.271	1.48976
57.423	1.60346	73.190	1.29211
69.891	1.34480	74.711	1.26953

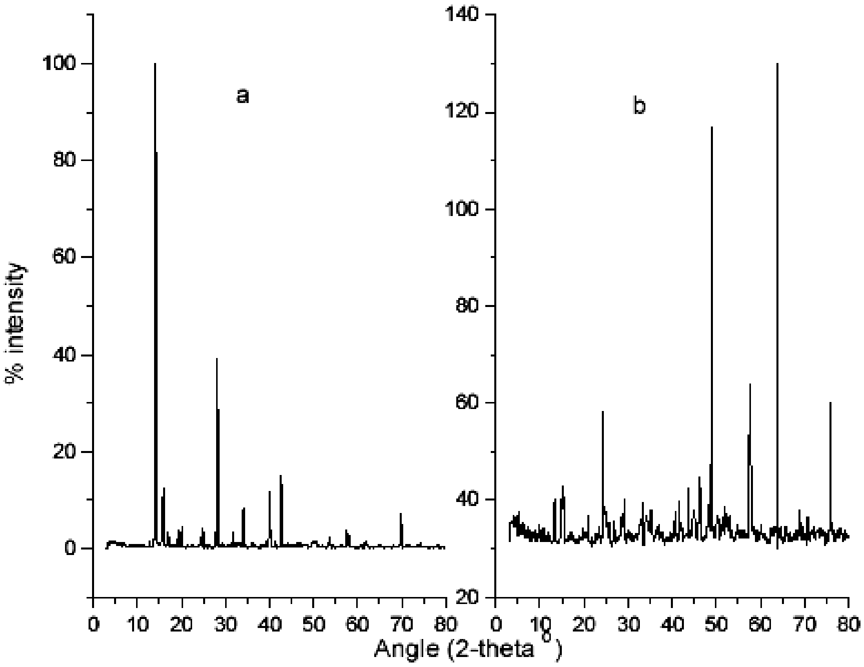


Fig. 2. XRD patterns (a) pure cadmium oxalate (b) cobalt doped cadmium oxalate

The thermal analysis was carried out on a Metlar TA 3000 system (heating rate 6 °C min^{-1}). The release of lattice water, CO and CO_2 at different temperatures are shown in TGA curve of both samples. The rate of loss of weight is explained by the curve DTG. The chemical changes during thermal analysis shown in the equation given below.

$MC_2O_4H_2O$ = MC_2O_4 + H_2O_4 (100-180 °C), water of crystallization evaporates;

MC_2O_4 = MCO_3 + CO (320-380 °C), CO exits out;

MCO_3 = MO + CO_2 (400-520 °C), CO_2 exits out. MO (M stands for Cd or Co-Cd) is stable above 520 °C.

The weight loss in the first step correspond to three molecules of water which confirmed the grown crystal to be cadmium oxalate trihydrate.

UV spectra: The UV absorption and reflection spectra of both pure cadmium oxalate and cobalt doped cadmium oxalate crystals were taken by Hitachi spectrophotometer model U-3400 at room temperature in the wavelength region 100-1000 nm. According to Tauc relation, the absorption coefficient for a direct band gap material is given by Tauc[9].

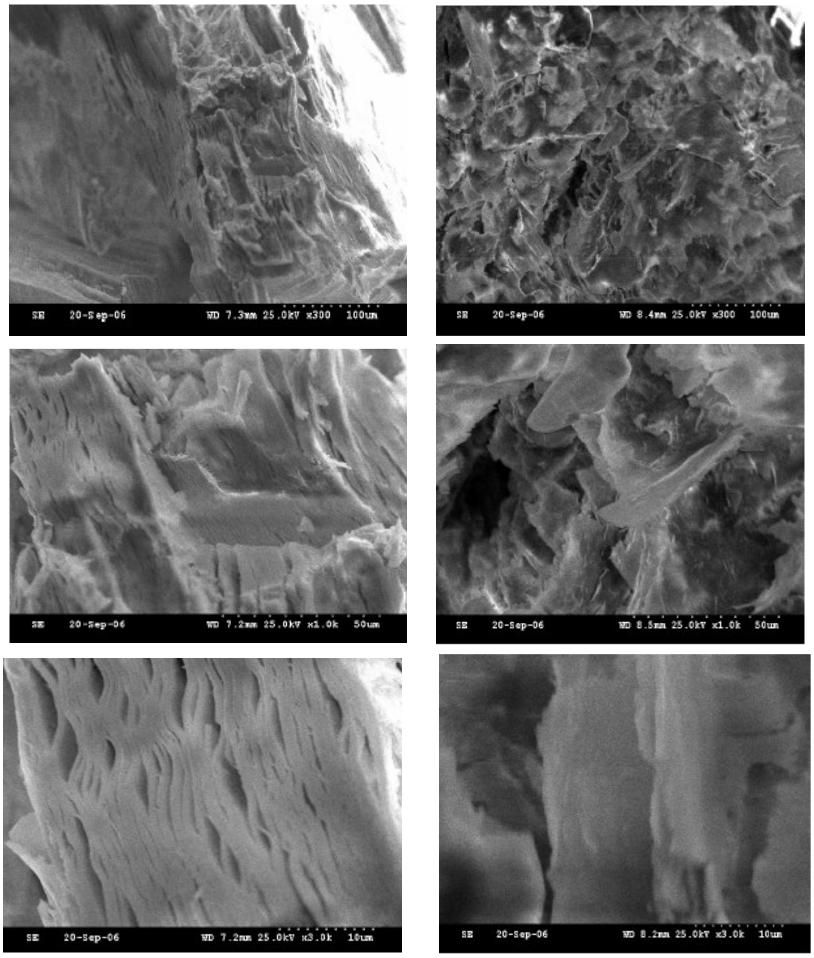
$$\alpha h\nu = A\ (h\nu - E_g)^{1/2}$$

where $\alpha h\nu$ is the photon energy, E_g the band gap energy and A is the constant which is different for different transitions. The absorption coefficient α may be written in terms of reflectance as:

$$2\alpha = \text{In}\ [(R_{max}-R_{min})/(R-R_{min})]$$

where R is the reflectance for any photon energy. The reflectance falls from R_{max} to R_{min} due to the absorption of light by the material.

Scanning electron micrographs: The SEM images of both pure cadmium oxalate and cobalt doped cadmium oxalate single crystals grown in silica gel are taken (Fig. 3). For each crystal, the images taken for three scales such as 100, 50 and 10 μm. In 10 μm measurement, the pure crystal surface seems to be a bundle of layers arranged one over the other. But in the case of cobalt doped crystal, surface looked like thick layers having few cavities. The cavities in the doped crystal are clear in 50 μm measurements.



(a) (b)

Fig. 3. SEM images (a) pure cadmium oxalate (b) cobalt doped cadmium oxalate

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