



# **MICROHARDNESS VARIATION OF COBALT DOPED CADMIUM OXALATE SINGLE CRYSTALS DUE TO DOPANT'S CONCENTRATION**

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## **ABSTRACT**

Pure and cobalt doped cadmium oxalate single crystals were grown by gel technique. These were characterized and undergone ICPAES and microhardness measurements. Characteristics such as powder XRD and FTIR are taken. The crystals are of few mm in size. XRD patterns of the samples reveal their crystalline nature. The FTIR spectrum shows the presence of water molecules and carboxylic acid. ICPAES measures the quantity of dopant in the pure crystal. The hardness measurement shows the variation of hardness values with load and dopant's concentration.

**Key words :** Silica gel., Gel growth, Nucleation, Cadmium oxalate crystals, Doping, ICPAES, Microhardness.

## **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<sup>1</sup>. Few mixed oxalate crystals were grown by gel technique<sup>2,3</sup>. Growth by hydro silica gel<sup>4</sup> 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<sup>5</sup> by adding impurities. Thermogravimetry of various oxalates have also been reported<sup>6</sup>. This paper presents growth, characteristics, ICPAES and microhardness measurement. In the present work, the molarity of pure crystal is 1 M while dopant's molarity varies from 0.1 M to 1.0 M.

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## EXPERIMENTAL

Sodium meta silicate gel (sp. gravity  $1.04 \text{ g cm}^{-3}$ ) was allowed to set in a coming glass tube after mixing with 1 M oxalic acid at pH 4. One week duration was 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 sample a mixture of 1 M cadmium chloride solution and 0.1 M cobalt chloride solution (1 : 1 in vol.) was added. The solution diffused into the gel as indicated by the Liesegang rings and their movements. Well formed colourless Cd and pinkish coloured Co-Cd oxalate single crystals of  $\sim 4 \times 3 \times 1 \text{ mm}^3$  size were obtained in about 25 days. The crystals were seen well inside the gel. The chemicals used were A. R. grade. The following chemical reaction was employed for the growth :  $\text{CdCl}_2 + \text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{CdC}_2\text{O}_4 + 2 \text{HCl}$ . Pinkish coloured Co-Cd oxalate single crystals of  $7 \times 2 \times 1 \text{ mm}^3$  were already obtained and its dielectric properties has been measured<sup>7</sup>. The presence of cadmium in pure crystal and cadmium and cobalt in doped crystal were studied using ICPAES analysis. The molarity of cobalt chloride solution (dopant) increased by 0.1 M, step by step until the molarity reaches 1 M. For each doping concentration, the ICPAES and microhardness measurements are taken.

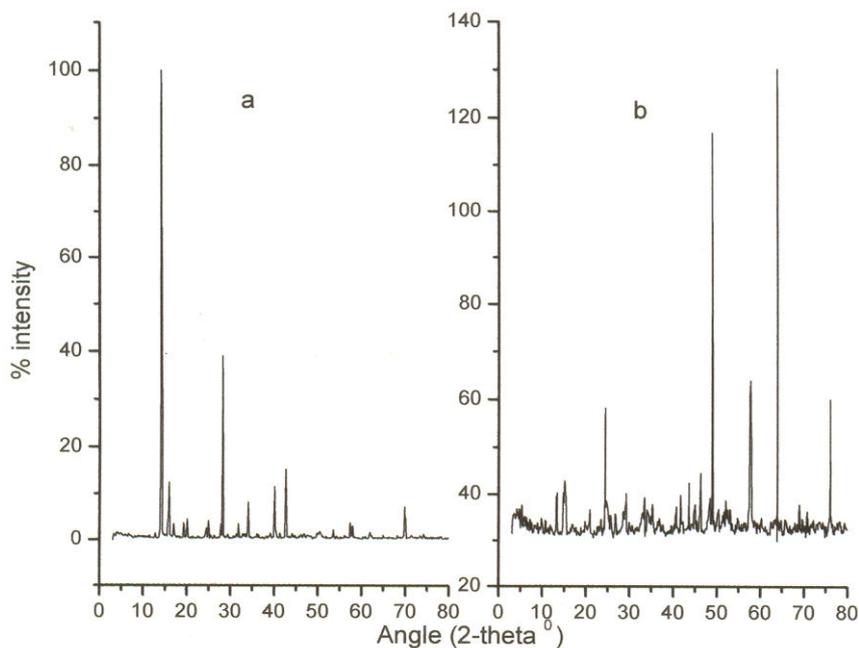
## RESULTS AND DISCUSSION

20 to 30 days were taken for the growth of crystals. The crystals are approximately 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 metasilicate gel impregnated with oxalic acid<sup>8</sup>. Cadmium / cobalt chloride solution and oxalic acid function respectively as the outer and inner reactants. For varying dopant's concentration, the molarity of cobalt chloride solution changed step by step from 0.1 M to 1 M. Variations on morphology, duration for growth of crystals and characteristics were not observed, but changes were seen in ICPAES and microhardness measurements. The following characteristic studies are carried out for crystal such as XRD and FTIR. The quantity of dopant present at different molarities in pure crystal was determined. The variation of microhardness due to dopant's concentration has also been studied.

### X-ray diffraction

The X-ray diffraction pattern of pure cadmium oxalate and cobalt (0.1 M) doped cadmium oxalate crystals are shown in Fig. 1. 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 was taken using Siemen X- ray

diffractometer (D 5000) having Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Powder X-ray diffraction method was used. Table 1 shows d-values for the prominent peaks of pure cadmium oxalate and cobalt (0.1 M) doped cadmium oxalate crystals. The variation in XRD spectrum due to the presence of cadmium (dopant) is clearly shown in the figure.



**Fig.1: XRD patterns ( a ) pure cadmium oxalate  
( b ) cobalt [ 0.1 M ] doped cadmium oxalate**

**Table 1. 2 theta and d-values**

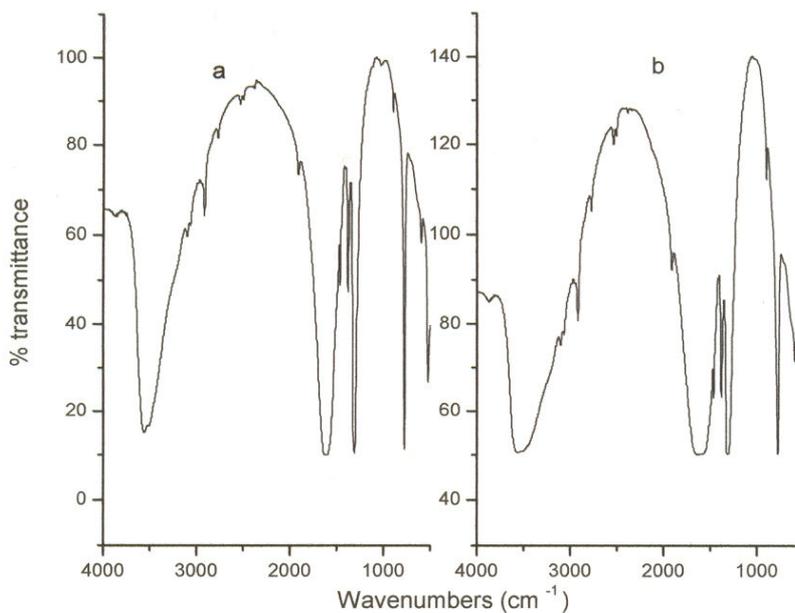
Pure cadmium oxalate		Cobalt doped cadmium oxalate	
Angle $2\theta^\circ$	d-value ( $\text{\AA}$ )	Angle $2\theta^\circ$	d-value ( $\text{\AA}$ )
14.152	6.25316	22.182	4.00428
15.912	5.56510	22.973	3.86820
19.294	4.59676	24.030	3.70037
20.045	4.42649	38.25	2.35172

Cont...

Pure cadmium oxalate		Cobalt doped cadmium oxalate	
Angle $2\theta^\circ$	d-value ( $\text{\AA}$ )	Angle $2\theta^\circ$	d-value ( $\text{\AA}$ )
24.944	3.56687	45.83	1.97835
28.187	3.16344	46.752	1.94147
31.826	2.80946	49.24	1.84902
34.082	2.62852	56.11	1.63775
40.077	2.24806	61.505	1.50646
42.656	2.11790	62.271	1.48976
57.423	1.60346	73.19	1.29211
69.891	1.34480	74.711	1.26953

## FTIR

Thermo Nicolet's Avtar 370 DTGS spectrometer was used for the study of FTIR spectrum of both the samples. KBr was used as the beam splitter and also as detector.



**Fig. 2: FTIR of samples ( a ) pure cadmium oxalate  
( b ) cobalt [0.1 M] doped cadmium oxalate**

Fig. 2 shows the spectra of samples. The peaks are identified in comparison with earlier reports<sup>9</sup>. The broad peak at 3400-3600  $\text{cm}^{-1}$  due to antisymmetric O-H stretching suggests the presence of water of crystallization in both the crystals. The broad peak around 1700  $\text{cm}^{-1}$  related to H-O-H bending also supports the presence of water. The well defined peak at 1300  $\text{cm}^{-1}$  reveals the presence of  $\text{CO}_2$  symmetric stretch, which support the presence of oxalate ions. FTIR spectra of cobalt doped cadmium oxalate crystal is almost same as that of pure crystal.

### ICPAES

The ICPAES measurement of the samples was carried out to determine the elemental concentration in the samples. Thermo Electron Corporation's IRIS INTREPID II XSP was used for ICPAES measurements. Table 2 shows molarity and elemental concentrations of cobalt. From the data, it is clear that the elemental concentrations of cobalt in the samples increases as the molarity was increased.

**Table 2. Elemental concentrations of cobalt in cobalt doped cadmium oxalate crystals**

<b>Trial</b>	<b>Molarity of cobalt in the samples</b>	<b>Elemental concentration of cobalt (ppm)</b>
1	0.1 M	178.6
2	0.2 M	342.8
3	0.3 M	725.6
4	0.4 M	900.9
5	0.5 M	1080.1
6	0.6 M	1262.9
7	0.7 M	1442.7
8	0.8 M	1611.9
9	0.9 M	1789.7
10	1.0 M	1957.5

### Microhardness

Microhardness values of cobalt doped cadmium oxalate crystals (at different molarities of cobalt) were measured using Vickers micro indentation hardness test (as per ASTM -E3 84-05) on Shimadzu HMV-2000. The samples are subjected for test loads 10

gf, 25 gf, 50 gf and 100 gf. Above 100 gf, cracks were initiated along and across the diagonals of the indentation mark. 14 s were taken for each trial at temperature 23.4°C. For each sample, 10 trials are done for each test load and the mean hardness value taken. The measurements are done at magnification 500 x. The chart given below (Table 3) shows the variation of microhardness values of the crystals due to doping concentrations.

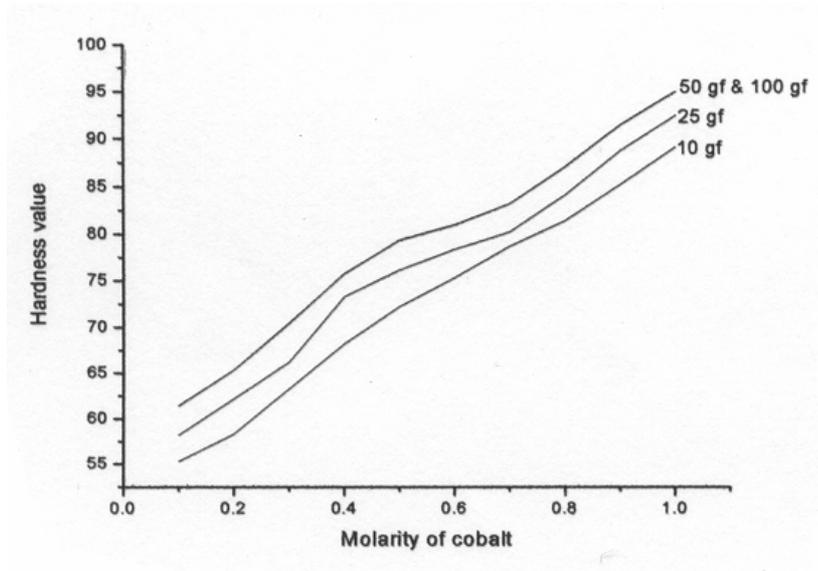
**Table 3. Microhardness values of cobalt doped cadmium oxalate crystals**

<b>Molarity of cobalt in the sample</b>	<b>Test load (gf)</b>	<b>Mean hardness value (Kg/mm<sup>-2</sup>)</b>
0.1 M	10	55.28
	25	58.21
	50	61.41
	100	61.43
0.2 M	10	58.31
	25	62.15
	50	65.32
	100	65.31
0.3 M	10	63.24
	25	66.17
	50	70.45
	100	70.41
0.4 M	10	68.17
	25	73.26
	50	75.69
	100	75.71
0.5 M	10	72.18
	25	76.09
	50	79.32
	100	79.31

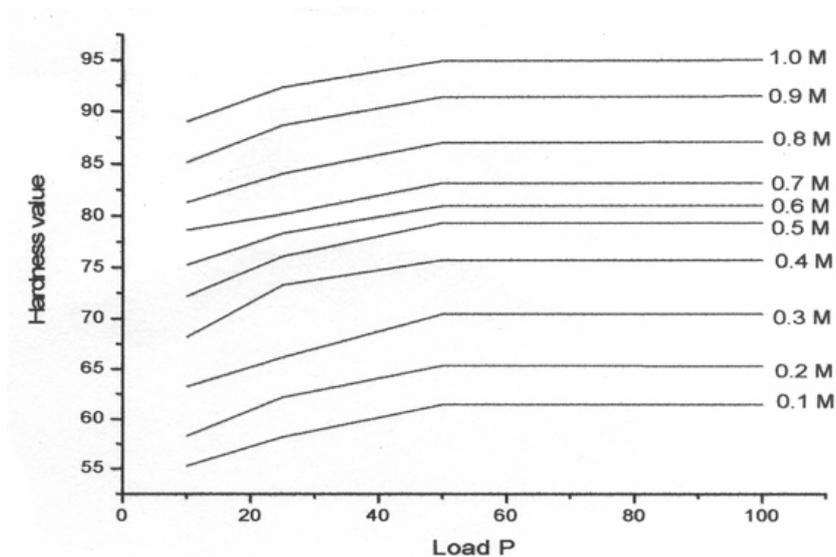
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Molarity of cobalt in the sample	Test load (gf)	Mean hardness value (Kg/mm <sup>-2</sup> )
0.6 M	10	75.25
	25	78.34
	50	80.92
	100	80.91
0.7 M	10	78.65
	25	80.15
	50	83.12
	100	83.11
0.8 M	10	81.31
	25	84.03
	50	86.95
	100	86.97
0.9 M	10	85.12
	25	88.65
	50	91.34
	100	91.35
1.0 M	10	89.01
	25	92.31
	50	94.85
	100	94.87

Variation of hardness with load is in increasing order and become steady above 50 gf. Also it is clear that the microhardness value of the crystals increases with dopant's molarity. These variations were studied earlier also<sup>10, 11</sup>. Fig. 3 shows the variation of microhardness with dopant's molarity while Fig.4 shows the microhardness variation with load. The hardness number was calculated using the relation ,  $H_V = r P/d^2$  , where P is the applied load , d is the length of longer diagonal of the indentation mark and r is a constant, which depends upon the geometry of the indenter.



**Fig. 4: Variation of microhardness with dopant's concentration**



**Fig. 5: Variation of microhardness with load molarity**

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