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Study of transition metal cobalt oxalate crystal in agar agar gel

S. U. Patil and R. T. Chaudhari

Physics Research Laboratory, Shri V. S. Naik,Arts, Commerce and Science College, Raver,,425508 India

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ABSTRACT

The transition metal oxalate crystals were grown in agar-agar gel. In the present investigation, the cobalt oxalate was grown by using gel techniques. Such grown crystals were found in different size and colour. The crystal was analysed by different techniques such as XRD, FTIR, TGA, SEM, and EDAX. The Surface morphology was studied by optical microscopy.

Keywords: Crystal growth, Agar gel, different analysing techniques, Optical Microscopy,

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INTRODUCTION

The transition metal oxalates has many applications in different fields. Recently it was reported that the transition metal oxysalts, such as carbonates and oxalates, [1-3] are directely used as the active electrode material.

Oxalates are considered to be useful precursors for preparing multicomponent oxides [4]. Also the oxalates containing different divalent cations can be obtained in a wide compositional range by the coprecipitation method,[5,6].

The transition metal cobalt oxalate is an interesting precursor, as it can be decomposed to metallic cobalt at relatively low temperatures. Dewei Wang et.al.[7] has synthesized cobalt oxalate and convert it into mesoporous Co3O4 nanostructures for application in supercapacitors. The cobalt oxalate crystals have been grown by the single diffusion and double diffusion techniques using silica gel and also studied as a precursor of Co3O4 nano particles[8].In the present study the cobalt oxalate crystals were grown in a agar-agar gel using single diffusion technique at an ambient temperature and their characterization by EDAX, powder XRD, FT-IR spectroscopy and TGA.The work was already published by the authors[9].The crystals were analyzed using various Characterization techniques. The physical properties and surface morphology were studied under the high resolution microscope and the scanning electron microscopic technique. Using the analyzing technique XRD, crystalline nature was confirmed, while determination of various elements in the sample was carried out by EDAX. Different functional groups were found by using FTIR, while thermal study was carried out by using TGA analysis.

MATERIALS AND METHODS

The single diffusion technique was employed for the growthof cobalt oxalate crystal using AR grade material. Solution of 0.75 M cobalt chloride reactant was taken in a test tube and 0.5% hot agar agar gel was poured along the wall. Afterseting the gel, 1M solution of second reactant oxalic acid was gently poured over set gel. After about 45 days the crystal are harvested. The growth progression and crystals grown are shown in fig 1 and fig 2.

fig 1. Growth of cobalt oxalate crystal

fig 2. Cobalt oxalate crystal

RESULTS AND DISCUSSION

3.1. X-Ray diffraction analysis

The X-ray diffractogram pattern for cobalt oxalate crystal is shown in Figure 3 . The crystalline phases and d-values obtained from the XRD pattern have been compared with JCPDS data. The powder X-ray diffraction pattern of cobalt oxalate are found to be closely matched to the earlier reported data (JCPDS No. 037-0719). The unit cell parameters (‘a’ = 5.39800 Å, ‘b’ = 5.03000 Å, and ‘c’ = 5.73500Å) are close to the reported cell parameters of $CoC_2O_4.2H_2O$, which can be indexed to the monoclinic phase[10]. Table 1 gives the position, d-values, and matching peaks of the crystals, however Figure 4 shows plot identified phases of cobalt oxalate crystal. Thus, the XRD result confirmed the crystalline nature of cobalt oxalate crystal.

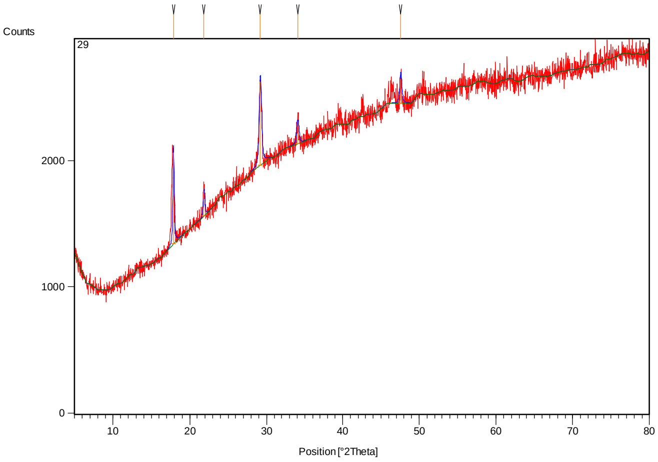


Figure 3: Powder diffractogram of cobalt oxalate crystals

Table 1 : The position, d-values, and matching peaks of the cobalt oxalate crystals

Pos. [°2Th.]	d-spacing [Å]	Matched by	hkl
29.2075	3.05514	025-0250; 037-0719	1 0 1
34.0621	2.62999	025-0250; 048-1068; 037-0719	2 0 0
47.5397	1.91111	025-0250; 048-1068; 037-0719	3 0 -1

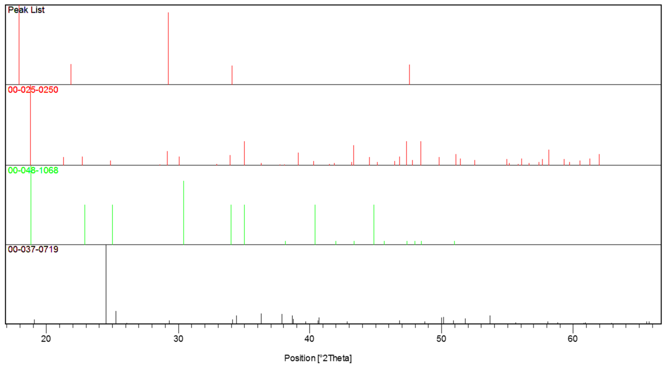


Figure 4: Plot of identified phases of cobalt oxalate crystals

3.2. FT-IR spectral study

FTIR spectra of cobalt oxalate crystals is shown in Figure 5. The spectrum shows various frequencies of vibrational modes which confirm the presence of oxalate in the crystal.

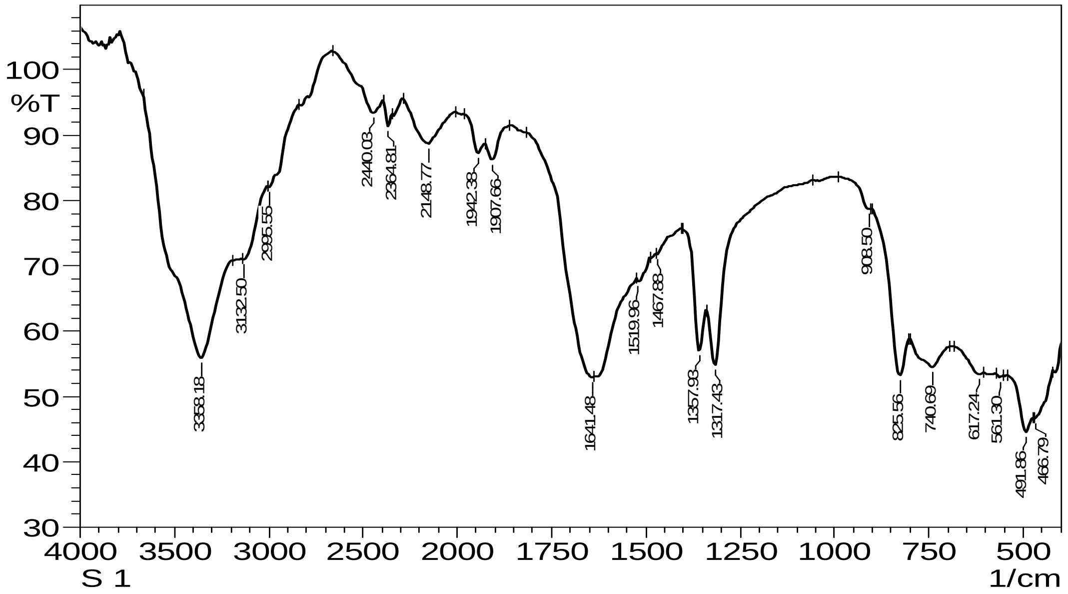


Fig.5. FTIR spectra of cobalt oxalate crystal

The sharp peak at 3358.18 cm^{-1}is attributed to the stretching of O−H group, indicating the presence of water of crystallization or water of hydration [7,10]. However the peak at 1641. 48 cm^{-1} correspond to C=O carbonyl stretch vibration[07], while two identical sharp peaks around 1357.93 and 1317.43 cm^{-1} are correspond to asymmetric and symmetric stretch of C–O respectively presence of bridging oxalates with all four oxygen atoms coordinated to the metal atoms. [7,12]. Moreover, a peak at 825 cm^{-1} belongs to asymmetric vibration of O–C–O [7]. The sharp peak at 491.86 cm^{-1} confirmed the presence of Co–O metal oxygen bond [7, 12-14]. Thus the FTIR spectroscopy confirmed the growth of cobalt oxalate crystals are due to the presence of water of crystallization, C=O, C–O, O-C-O and M-O bonds. The observed vibrational frequencies and their tentative assignments are listed in Table 2.

Table 2: Tentative assignments of vibrational frequencies

Sr. No.	**Absorption bands (cm-1)**	**Interpretations**
1	3358.18	Stretching of O−H group
2	1641. 48	Carbonyl stretch vibration C=O
3	1357.93	Asymmetric stretch of C–O
4	1317.43	Symmetric stretch of C–O
5	825.56	Asymmetric vibration of O–C–O
6	491.86	Metal–oxygen stretching

3.3. TGA study

Thermogravimetric analysis (TGA) was carried out to investigate the thermal behavior of the cobalt oxalate. The result of TGA study has been shown in Fig.6(a). The TGA curve of the cobalt oxalate shows that there are two distinct weight loss steps. In first step, the weight loss of 18.607% can be observed at the temperature range from150 to 210°C; this is according to the theoretical value 19.67% [7,15], due to loss of two moles of water.

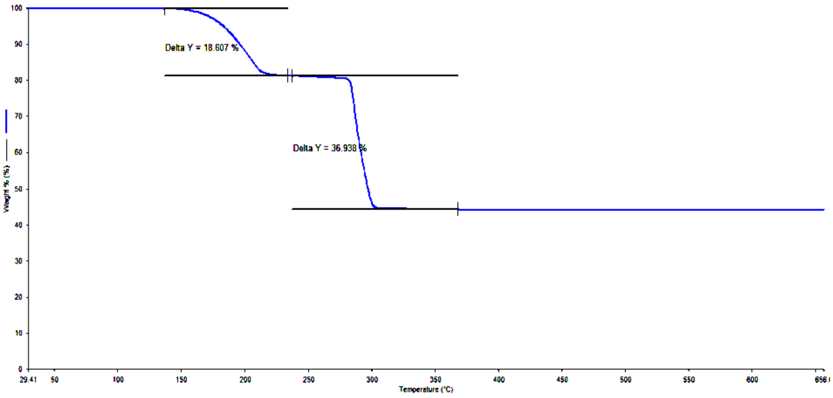


Fig.6(a) TGA for cobalt oxalate

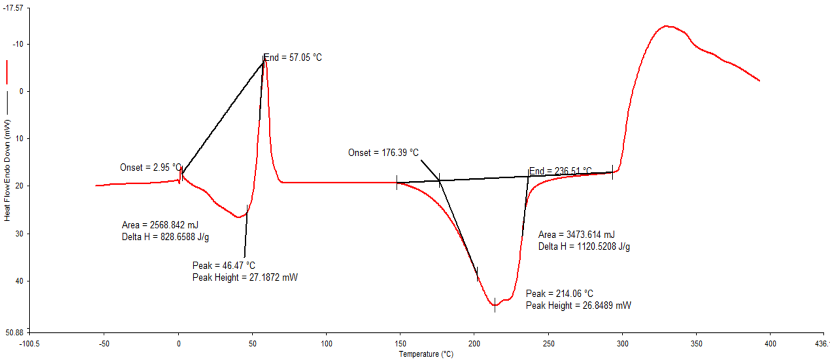


Fig.6(b)DSC for cobalt oxalate

The following reaction is expected during the dehydration of cobalt oxalate crystals,

$$\mathbf{CoC_2O_4 \cdot 2H_2O(s) \rightarrow CoC_2O_4(s) + 2H_2O\ (g) \uparrow}$$

In second step, the weight loss of 36.93% can be observed at the temperature range from210 to 330°C. This weight loss in second step may be attributed to the decomposition of the anhydrous cobalt oxalate to cobalt oxide, which agrees with the theoretical value [07, 15, 16]. The decomposition reaction in this step can be written as,

$$\mathbf{3CoC_2O_4(s) + 2O_2 \rightarrow Co_3O_4(s) + 6CO_2\ (g) \uparrow}$$

Figure 6(b) shows the corresponding DSC curve associated with these processes. It is an endothermic peak at 214.06°C with the area 3473.614mJ.It is important to observe that the absence of any additional peak on TG and DTA curves, indicates the high purity of the cobalt oxalate [15].

3.4. Morphology study

3.4.1 Optical microscopy

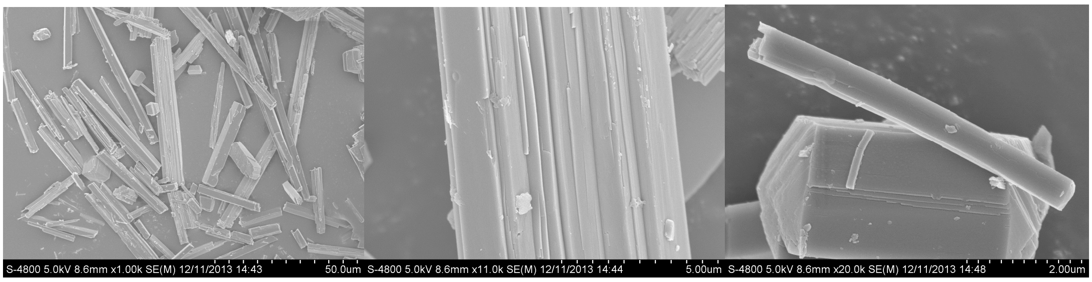
The grown sample was observed under the optical microscope. It was observe that, the growth of sample is in a form of needles originating from centre point and spread equally in all directions as shown in figure 7(a). While, figure 7(b) shows the portion of the sample which likes in the shape of needles braided together.

Fig 7.a. Needle shaped Sample spreading in all directions

Fig 7.a. Sample like braided Needles

3.4.2 SEM:

The morphology and particle sizes were observed by scanning electron microscopy. Figure 8 shows typical SEM images of the as-prepared cobalt oxalate at resolution 50,5and 2µm respectively.



(a)Sample resolution 50 µm (b)Sample resolution 5 µm (c)Sample resolution 2 µm

Fig.8. SEM images of cobalt oxalate

The as-obtained products were in needle and rod-like morphologies with a diameter of about 50 µm as shown in fig.8 (a) [7]. Figure 8(b)shows, the sample was composed of many rectangular sheets approximately greater than 5 µm in length and of the thickness more than 5µm.However in the high magnification of the sample as shown in figure 8(c), it revealed that, the rods are actually the bundle of rectangular plates those are in hexagonal shape, which were stacked in a parallel fashion.[7,11,15]

4.0. EDAX study:

The amount of carbon, oxygen and cobalt present in grown sample was determined by EDAX, which was found to be 22.23 at % C,48.02 at % O and 28.37 at % Co.Table 3 shows the Edax Analysis of cobalt oxalate crystal.

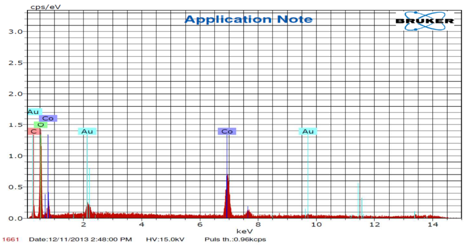


Fig.9.EDAX of a cobalt oxalate sample

Table 3:Edax Analysis of cobalt oxalate crystal

```
El AN Series unn.C norm.C Atom. C Error (1 Sigma)
[wt.%] [wt.%][at.%] [wt.%]
-----------------------------------------------------
C  6  K-series 5.16   8.97 22.23  1.39
O  8  K-series 14.85 25.80 48.02  2.48
Co 27 K-series 32.32 56.14 28.37  1.14
Au 79 M-series 5.23   9.09 1.37  0.30
-----------------------------------------------------
Total: 57.56  100.00100.00
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CONCLUSION

Transition metal cobalt (II) oxalate crystal was grown by gel method using agar agar gel in well size and shape. The surface morphology was studied using SEM and high resolution electron microscope. Different functional groups were studied by FTIR shows the metal bond and different vibrations in the sample. XRD powder diffraction patterns and analysis shows the crystalline nature of crystal.. TGA studies revealed that the crystals have high purity. EDAX studied the composition of sample.

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