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Thermal and Morphological Study of Transition Metal Cobalt Oxalate Crystal Grown By Agar-Agar Gel Technique

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ABSTRACT

In this article, we have reported fabrication of various morphological of cobalt oxalate. Cobalt oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of cobalt oxalate crystals to spherulites growth was demonstrated. Also Liesegang ring are observed. The cobalt oxalate preparation method was played crucial role on the crystal structure and its morphology. The optimum growth conditions cobalt oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by TGA, DTA and EDAX.

Keywords: Crystal growth, cobalt oxalate, TGA, DTA and EDAX.

Introduction:

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. Crystals are used in semiconductor physics, engineering, as electro-optic devices etc., so there is an increasing demand for crystal [1-5]. For years, Natural specimens were the only source of large, well-formed crystals. The growth of crystals generally occurs by means of following sequence of process. Diffusion of the molecules of the crystallizing substance through the surrounding environment. Diffusion of these molecules over the surface of the crystal to special sites on the surface. Today almost all naturally occurring crystals of interest have been synthesized successfully in the laboratory [6-9]. It is now possible only by crystal growth techniques.

Materials and Methods

Materials used to grow the cobalt oxalate crystals are cobalt chloride, oxalic acid, and agar-agar gel. All the chemicals used for the experiment were used without any further purification. Sodium silicate glass test-tubes were used as crystallizing vessels. The test-tubes were filled with the first reactant (cobalt chloride) of desired volume and morality. The second reactant, oxalic acid having a concentration range of 0.5 to 1.5 M, was poured along the walls of the test-tube into the set-gel, and allowed to diffuse into the gel medium. The open end of the tube was closed with cotton plugs and kept undisturbed. The said procedure was carried out at room temperature. The ions of the supernatant solution reacted with ions of the first reactant via capillaries formed in gel medium. After six to seven days, nucleation kick-started at the gel-solution interface. The chemical reaction that occurred between the two reactants is given as follows:

$$CoCl_2 + H_2C_2\,O_4 \longrightarrow CoC_2O_4 + 2HCL$$

The diamond-shaped, spherulites, opaque crystals were obtained in the test-tube. The crystals were harvested by washing them carefully with acetone and collected for further characterization. Table 1 shows the optimized crystal growth parameters for the cobalt oxalate crystals.

Table 1 shows the Optimum condition of cobalt oxalate crystal

Sr.No	Condition Single Diffusion	Condition Single Diffusion
1	Percentage of gel	2.0 %
2	Concentration of cobalt chloride	1.0M
3	Concentration of oxalic acid	1.0M
4	Volume of cobalt chloride	5.0 ml
5	Volume of oxalic acid	15 ml
6	Gel setting period	34 Hours
7	Gel aging period	4 days

Liesegang rings - are a phenomenon seen in many, if not most, chemical systems undergoing a precipitation reaction under certain conditions of concentration and in the absence of convection. Rings are formed when weakly soluble salt are produced from reaction of two soluble substances, one of which is dissolved in a gel medium [10]. The phenomenon is most commonly seen as rings in a Petri dish or bands in a test tube; however, more complex patterns have been observed, such as dislocations of the ring structure in a Petri dish, helices', and Saturn rings in a test tube [11]. Despite continuous investigation since rediscovery of the rings in 1896, the mechanism for the formation of Liesegang rings is still unclear.


(a)


(b)

Fig. 1(a) Shows the spherulites cobalt oxalate crystals (b) Shows the formation of Liesegang rings

Result and Discussion-

Thermogravimetric Analysis (TGA) of Cobalt Oxalate- The thermogram of cobalt oxalate crystal were obtained with the help of SDT Q600 V20.9 Build 20. TGA/DTA/DSC thermal analyser available at Materials Characterization Laboratory Department of Materials Science and Engineering, Yonsei University,Room No.B307,Engineering Hall 2,50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea. The TGA curve of cobalt oxalate agar-agar gel grown crystal is as shown in fig (2), the percentage of the weight loss in the different stages of decomposition of cobalt oxalate are presented in the table (2) . There is good agreement between the observed and calculated weight. The four stages of decomposition are described as below: In the first stage decomposition occurs in the temperature range 30^0C to 177^0C in which weight loss of 17.46% agrees very well with the calculated weight loss 17.58%. Thus it is clear that the crystals are hydrate and the weight loss calculation clearly indicate that cobalt oxalate crystals have nine water molecule as water of crystallization. It is notice that the sample losses water of hydration and becomes anhydrous at 177^0C.

In the second stage of decomposition in the temperature range 200^0C to 247^0C, the total weight loss 3.411% is seen which is due to the loss 3C and $3H_2O$ this is well agreement with calculated weight loss of 3.50%. Then an anhydrous cobalt decomposes into cobalt oxalate.

In the third stage of decomposition total weight loss 36.88% was observed in the temperature range 247^{0}C to 260^{0}C which corresponds to the loss of 2CO. This weight loss agrees very well with the calculated weight loss 37.00%. Thus cobalt oxalate further decomposes into cobalt carbonate.

Finally in the temperature range 892^{0}C to 930^{0}C, total weight loss of 2.538% was obtained. This loss is attributed to the loss of CO_2. This is in well agreement with the calculated weight loss of 2.8%. Thus the cobalt carbonate finally turns into cobalt oxide at 930^{0}C. Which is confirmed by residual weight up to the end of analysis 2.538%. This is in good agreement with calculated residual weight of 2.80%.[12-14]

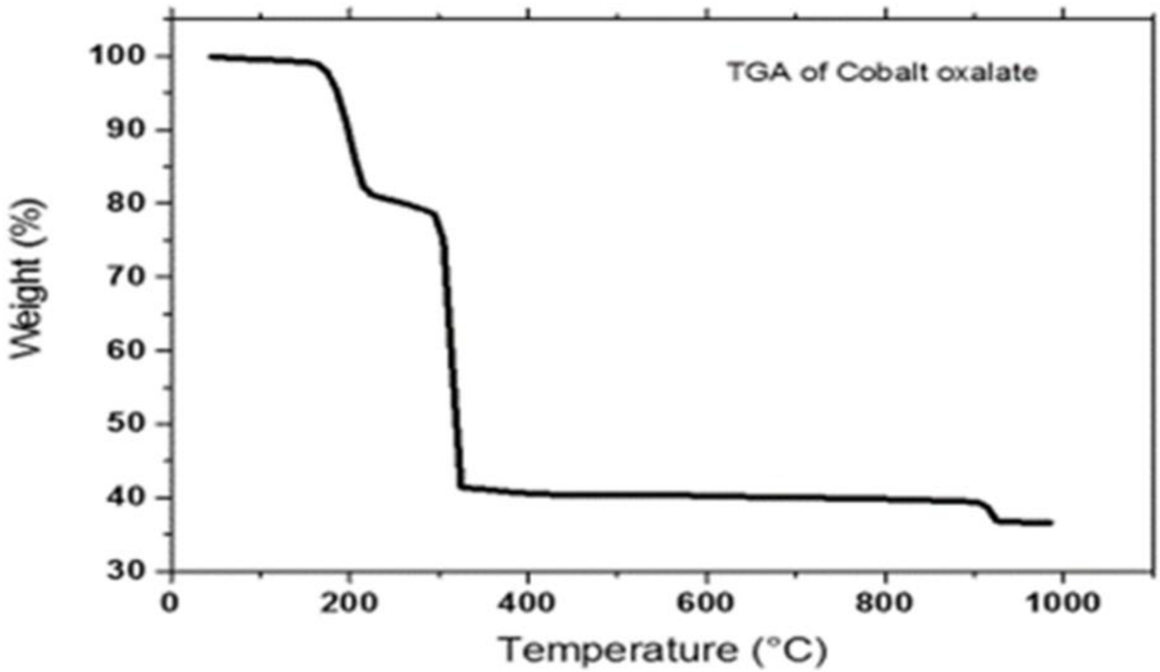

Fig.2 Shows the TGA Curve of Cobalt oxalate crystal grown by agar-agar gel technique

Table 2 Summarized data of TGA results of decomposition process of cobalt oxalate crystals

Stage	**Temperature range ^{0}C**	**Observed Weight loss %**	**Calculated Weight loss %**	**Loss of Molecule in stage**
I	30-177^{0}C	17.46%	17.58%	$9H_2O$
II	200-247^{0}C	3.41%	3.50%	3C and $3H_2O$
III	247-260^{0}C	36.88%	37.00%	2CO
IV	892-930^{0}C	2.538%	2.80%	CO_2

Differential Thermal Analysis (DTA) –

The DTA curve for cobalt oxalate agar- agar gel grown crystal is as shown in figure(3) and the DTA data collected from this curve is tabulated in the table(3). In DTA curve we observe two endothermic peak at 208.25^{0}C and 919^{0}C and one exothermic peak at 310^{0}C are due to decomposition of hydrated cobalt oxalate into anhydrous cobalt oxalate. In the first stage of decomposition, peak at 208.25^{0}C is attributed to loss of first

$4H_2O$ molecules immediately followed by another endothermic peak at 919^{0}C which corresponds $2H_2O$ molecules. The endothermic peaks observed in the DTA curve corresponds to the total weight loss of Nine water molecule in TGA curve [15-17].

Table 3 DTA data of Cobalt oxalate

Peaks recorded	Nature
208.25^{0}C	Endothermic
919^{0}C	Endothermic
310^{0}C	Exothermic

The exothermic peak at 310^{0}C due to the decomposition of anhydrous cobalt oxalate into cobalt oxalate. The exothermic peak attributed to the loss of 4C molecule and endothermic at 208.25^{0}C is attributed to the loss of 3 water molecules. The endothermic peak at 919^{0}C is due to the decomposition of cobalt oxalate carbonate to cobalt oxide which is attributed to the loss of $2CO_2$.

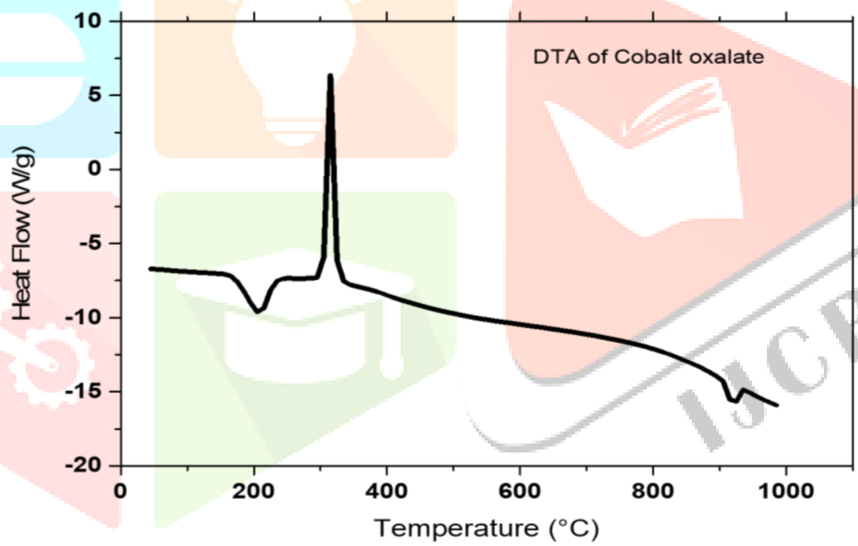

Figure 1 DTA curve for Cobalt oxalate

Energy Dispersive Analysis by X-rays (EDAX) –

The chemical composition of as grown crystals is analyzed by Energy Dispersive X-ray Analysis (EDX). Fig. 4 shows the EDX spectrum which confirms the presence of expected elements O,C and Cu.The stoichiometric composition was computed using experimental and theoretical results of EDX. Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of cobalt oxalate and is also called as elemental analysis. It conclude that the (weight & atomic %) of copper (Cu) in the grown crystal measured by EDAX are very close with the values calculated from the molecular formula.[18-22].

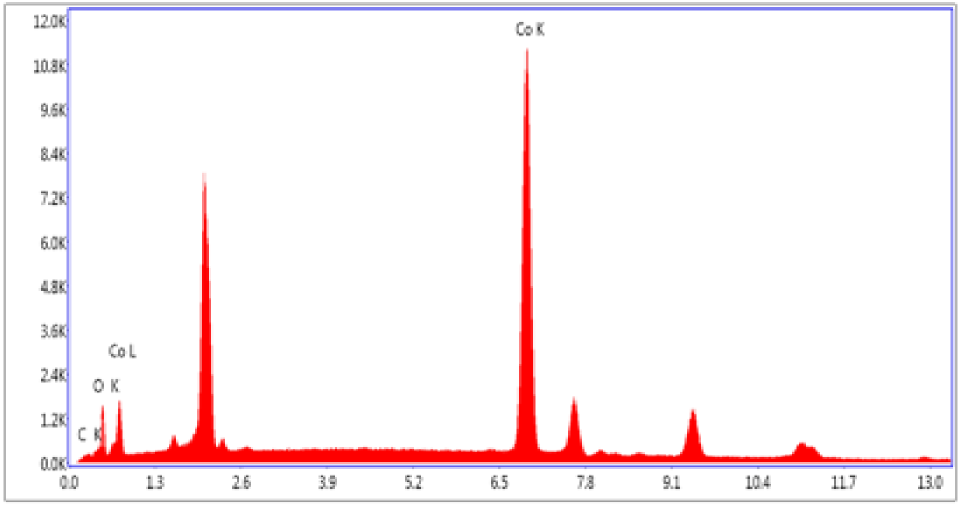

Figure 2EDAX of Cobalt oxalate

Table 4 EDAX of cobalt oxalate

Element	Weight%	Atomic%	Net.Int	Error	%	K ratio	Z	R	A	F
Ck	2.22	9.46	44.68	19.14	0.01	0.05	1.33	0.84	0.21	1.00
Ok	2.41	7.71	227.93	10.39	0.01	0.05	1.28	0.86	0.42	1.00
Cobalt	95.37	82.83	6779.47	1.88	0.97	0.80	0.98	1.01	1.0	1.03

Conclusions –

The present work reports the growth and characterization of cobalt oxalate single crystals. We have demonstrated the formation of cobalt oxalate single crystals in agar-agar gels. Cobalt oxalates exhibits star shaped, opaque and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of cobalt oxalate, both reactants –cobalt chloride and oxalic acid were interchanged. With cobalt chloride incorporated gels result only fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of cobalt oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of cobalt oxalate.

Conclusions-

Transition metal cobalt (II) oxalate crystal was grown by gel method using agar agar gel in well size and shape.Red –pink colour crystal were observed. In contrast bigger and better shape of red pink block crystal of cobalt oxalate observed, however, longer growth time was needed to grow the crystal.

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