Physical and Morphological Study of Barium Oxalate Crystals Grown by Agar-Agar Gel Method

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ABSTRACT

Barium oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of barium oxalate crystals to cylindrical growth was demonstrated. The optimum growth conditions barium 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, DSC and EDAX.

Keywords: Crystal growth, Barium oxalate, TGA, DTA, DSC, and EDAX.

Introduction

The growth of crystal occurs not only in the crust of Earth or in laboratory but also in a living body. Many crystals, particularly, bio-materials and proteins, cause various ailments and health related problems. The urinary stones are usually composed of either pure or mixed crystals of calcium oxalate, brushite, struvite, and hydroxyapatite and carbonate apatite [1]. Arthropathies, i.e., bone and joint diseases, are caused by crystals such as hydroxyapatite, calcium pyrophosphate and monosodium urate monohydrate [2]. There are other crystals which play important role in various ailments, for instance, f.c.c. type ferritin crystals in development of cataract [3] and cholesterol crystals for cardiovascular diseases and gall stones [4]. This bio-crystallization occurring in human body causes suffering and it is not desirable to occur. This has been discussed in detail by the predecessors of the present author [5-7]. There are several micro-organisms which synthesize crystals, for example, magneto-tactic bacteria synthesizing magnetite [8], chrysophytes [9] diatoms and act in opoda synthesizing siliconous materials and S. layer bacteria synthesizing gypsum and calcium carbonate surface layers [10]. Calcite crystals are found in mollusk shells [11] and as a component in gall stones [12]. The earlier crystal growth study was divided into two parts :(1) The study of the equilibrium between the crystal and surrounding medium(2) The study of the kinetics of growth.

Experimental

Experimental procedure 5 gm of agar-agar powder was dissolved in to hot double distilled water mixed with 0.5 M to 1 M barium chloride solution was incorporated then again the mixture was stirred to make homogenous mixture. The crystallizing vessel were used essentially consist of standard glass tube having inner diameter 2.5 cm and the length 25 cm. Gelling mixture poured in glass test tubes. These tubes were hermitically sealed to prevent evaporation and contamination of the exposed surface by dust particles of atmosphere or atmospheric

impurities and were kept undisturbed. Usually in 3 to 4 days the gel was to be set which depends on the environmental temperature. It was observed that the mixture in a glass tube was initially transparent and slowly turned light white. The water slowly evaporated and gel was completely set. After ensuring firm gel setting, it was kept for aging for 3 to 4 days. After that 0.5 M to 1 M solution of oxalic acid was added as a supernatant over the set get. Nucleation was observed after 5 to 6 days and crystals started to grow. White color, larger size, transparent and shining crystals were obtained in the gel, as shown in fig.1, Optimum condition tabulated in table 1, [13].

Table 1 Optimum conditions for barium oxalate crystal grown by agar-agar gel method

Concentration of agar-agar gel	5 %
Concentration of reactant, strontium chloride	1M
Concentration of supernatant, oxalic acid	1 M
Room temperature	27^0C
Gel aging period	4 days
Growth period	25 - 40 days
Quality of crystals	White colour, larger size (1mm × 1mm) transparent, shining crystals

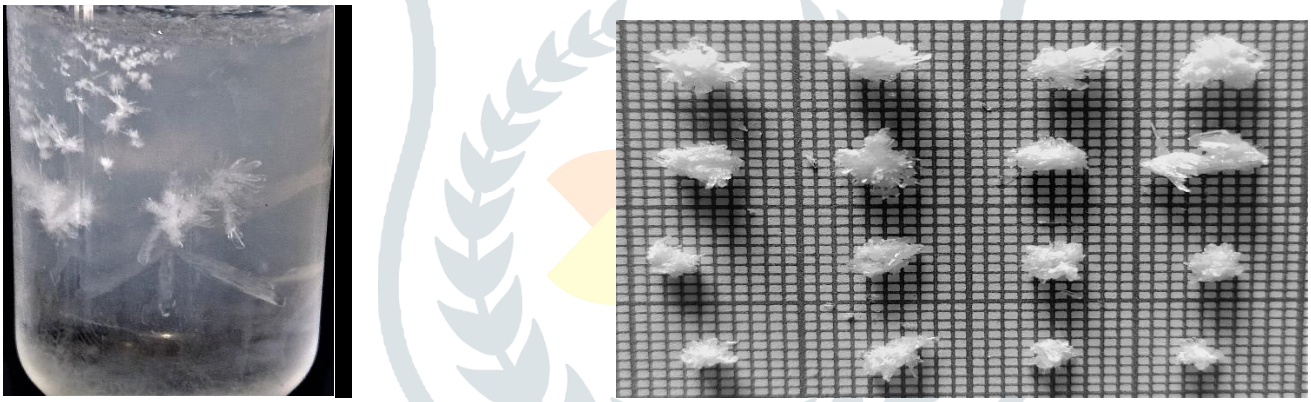

Fig.1 (a) Barium crystal inside the test tube (b) Opaque and shiny crystals

Result and Discussion-

Thermo-Gravimetric Analysis (TGA)

TGA was carried out at Department of Physics, Shivaji University Kolhapur, TGA curve for barium oxalate is shown in figuer.2. From the thermo gram of barium oxalate one can observe that

i) The compound is stable up to 50^0C.

ii) 5.165% weight loss in temperature range 50^0C. To 172^0C may be due to dehydration of water molecule and up to 172^0C there is no further loss of weight.

iii) 25.68% weight loss in temperature range 172^0C to 277^0C from the dehydrated compound corresponds to loss of CO.

iv) 36.68% weight loss in temperature range 277^0C to 435^0C corresponds to loss of CO_2.

v) 13.45% weight loss in temperature range 435^0C to 478^0C.

v) The residue remains stable from 478^0C and decompose the material. [14-16].

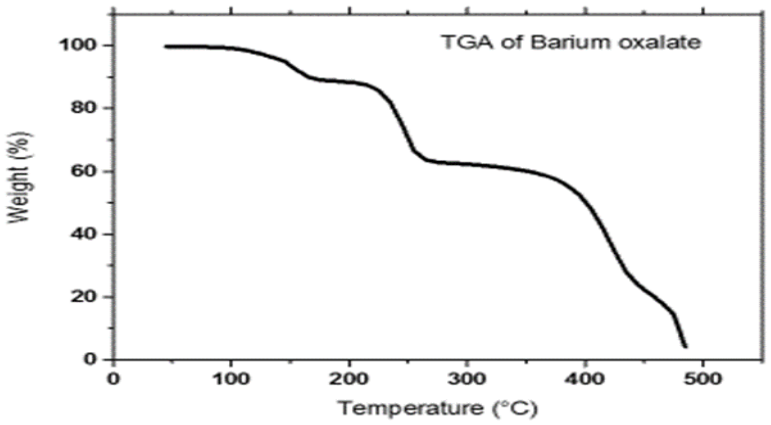

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Figure 2 TGA of Barium oxalate crystal grown by agar-agar gel

TGA data indicates that the grown crystals contains water molecule,

Table 2 TGA Data of Barium oxalate

Stage	Temperature range	Observed % weight loss	Calculated % weight loss	Loss of molecule in stage
I	50^0C-172^0C	5.165%	5.045%	H_2O
II	172^0C-277^0C	25.68%	25.8%	It may be CO
III	277^0C-435^0C	36.68%	35.99%	CO_2
IV	435^0C-478^0C	13.45%	13.56%	-

Differential Thermal Analysis (DTA)

DTA was carried out at Department of Physics, Shivaji University Kolhapur.DTA curve for barium oxalate is shown in figure3. From the thermo gram of barium oxalate one can observe that.

In DTA curve of barium oxalate by agar-agar gel at 37.51^0C an endothermic peak is observed due to the loss of bulk of water of crystallization. The decomposition of oxalate is observed at the onset due to complete dehydration. In DTA curve the exothermic peaks at $153.^0$C to 154.54^0C shows the decomposition of oxalate. Loss of weight at the temperature range $153.^0$C relates to the loss of water of crystallization which is endothermic in character.

Loss of weight at the temperature 250.07^0C endothermic peak is observed that means the weight loss with respect to temperature of the grown crystals was further supported by

DTA results. DTA data is shown in table- 3

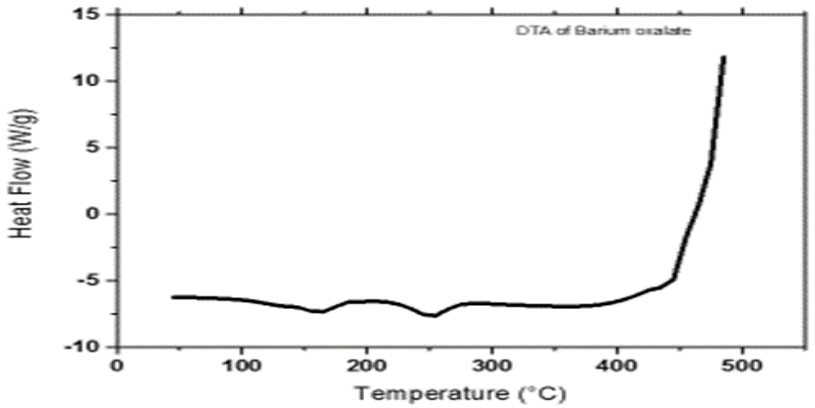


Figure 3 DTA of Barium oxalate

Table no.3 DTA data of barium oxalate

Peak recorded	Peak height	Nature	ΔH(J/gm)
37.51^{0}C	-0.600	Endothermic	-0.6406
154.54^{0}c	-0.5	Exothermic	-0.5344
250.07^{0}c	-0.4	Endothermic	-0.4613

Differential Scanning Calorimeter (DSC)

DSC was carried out at Department of Physics, Shivaji University Kolhapur, The DSC thermogram was recorded in the temperature range from 25^{0}C to 450^{0}C.Microcrystalline (powdered) samples of barium oxalate crystals were taken for DSC studies and the weight of the sample 8.5230mg.The sample was hold for 10 min in air to evaporate water due to moisture and then heated from 25^{0}C to 450^{0}C.at the rate 10c/min in Air .After reaching the temperature of 450^{0}C,the sample was hold for I minute at 450^{0}C and then again cooled from 450^{0}C to 25^{0}C at the rate of 10C/min in Air.

The DSC curve for barium oxalate gel grown crystal shown in figure 4. And the DSC data collected from this curve is tabulated in the table 4.

Step-I

i) The initiation temperature is 225^{0}C and equilibrium temperature 277^{0}C.At 225^{0}C (initiation temperature) initiation of phase change start & is completed at peak endo-down temperature of 250.07^{0}C(transition temperature).The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 277^{0}C.The peak appeared in the DSC curve at 154.54^{0}C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous barium oxalate. This is the good agreement with the TGA curve,

ii) Area under the curve is 5707.384 mJ.

iii) Heat of transisiton ΔH i.e. enthalpy change of transisiton 517.56 J/g which 0.51756kJ/mole. Since molecular weight is 1g/mole, $\Delta H_{tr} = \Delta H_f$ i.e. heat of phase transformation is also 0.5756 kJ/mole, where ΔHf is enthalpy change of new phase transformation or it is called heat of phase formation.

Step-II

i) The initiation temperature is 430^0C and equilibrium temperature is 450^0C.At 430^0C (initiation temperature) initiation of phase change starts and is completed at peak endo- down temperature of 438.76^0C (transition temperature).The temperature at which the sample and the reference come to the thermal equilibrium diffusion appears to be 450^0C.The further phase transition occurs at temperature 438.76^0C due to the loss of carbon and H_2O and formation of stable barium oxalate. This is good agreement with TGA Curve.

ii) Area under the curve is 232.43mJ.

iii) Heat of transition ΔH i.e. enthalpy change of transition 21.99J/g which is 0.02199KJ/mole. Since molecular weight is 1 g/mole, Hence ΔHtr = ΔHf i.e. heat of phase transformation is also 0.02199KJ/mole. Where ΔHf enthalpy change of new phase transformation or it is called heat of phase formation. DSC data is shown in table- 4.

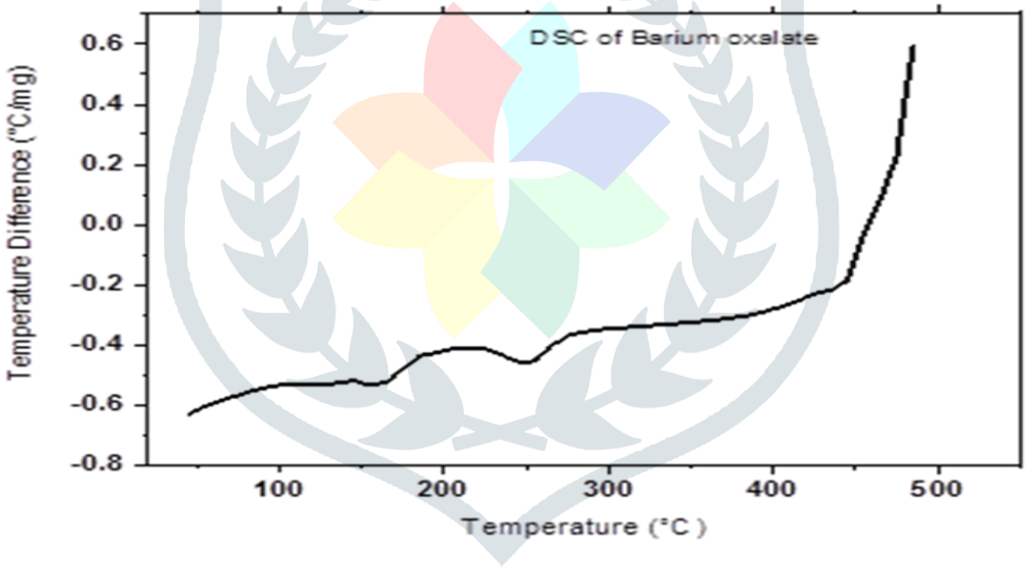


Figure 4 DSC curve for Barium oxalate

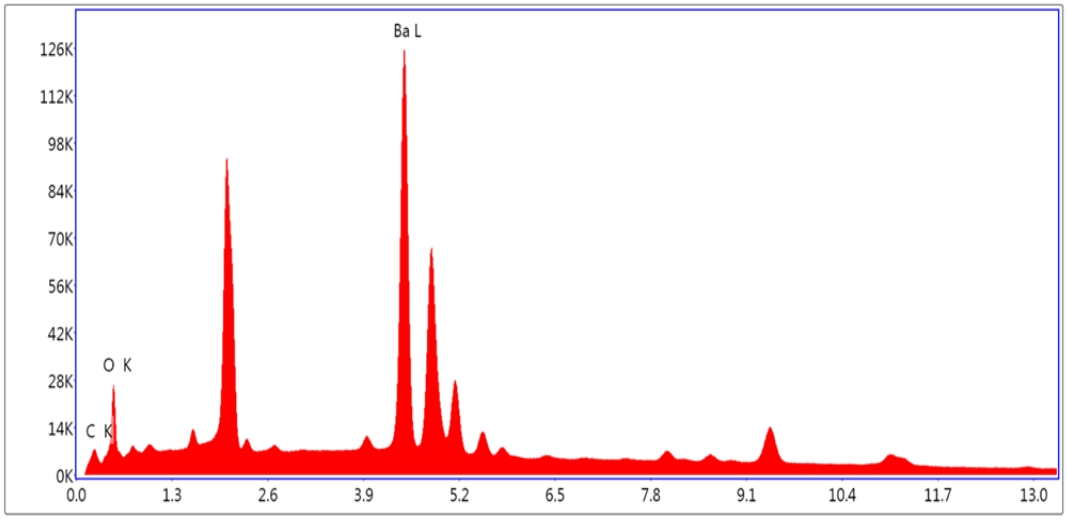
DSC data is shown in table- 4

Sample	Weight of the sample	Stage	Change in the enthalpy(ΔH)	Transition temperature (Tr)
Barium oxalate	0.8523gm	I	0.51756KJ/mole	250.07^0C
		II	0.02199KJ/mole	438.76^0C

Energy Dispersive Analysis by X-rays (EDAX) –

Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of barium oxalate and is also called as elemental analysis. Fig 5& Table No 5 shows, in present work elemental analysis of gel grown barium oxalate crystals was Department of Physics, Shivaji University Kolhapur. 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.[17-20]



eZAF smaryt quant Results

Element	Weight%	Atomic%	Net.Int	Error	%	K ratio	Z	R	A	F
Ck	7.36	34.64	443.18	7.82	0.05	0.05	1.47	0.75	0.47	1.00
Ok	8.71	30.80	991.30	7.87	0.05	0.05	1.42	0.77	0.39	1.00
Barium	83.93	34.56	5594.20	2.05	0.80	0.80	0.91	1.07	1.03	1.03

Conclusions —

The present work reports the growth and characterization of barium oxalate single crystals. We have demonstrated the formation of barium oxalate single crystals in agar-agar gels. Barium oxalates exhibits micro-rod-like and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of barium oxalate, both reactants –barium chloride and oxalic acid were interchanged. With barium 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 barium 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 barium oxalate.

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