JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

# PHYSICAL CHARACTERIZATION OF MANGANESE OXALATE CRYSTAL GROWTH BY AGAR - AGAR GEL METHOD

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***Abstract:*** Single crystals of manganese oxalate were synthesized by gel method using agar- agar gel media at normal temperature. The optimum growth conditions manganese oxalate was established by varying gel parameter such as concentration of supernatant, aging period, percentage of gel, reversing reaction. Using such parameter nucleation was controlled and found the required condition to well defined morphology grown crystals. Thermal properties of the crystals were studied by TGA, DTA and DSC was discussed. The elemental analysis has been carried out by EDAX.

***Keywords*** - Crystal growth, Gel Technique, Thermal analysis, EDAX.

## 1. INTRODUCTION

The word crystal has a perfect meaning in material science and solid-state physics. Based on arrangement of atom, ion and molecule solid state material classified into three type a) Single crystal b) polycrystalline c) amorphous. Single crystal is one of the types of solid-state physics. Importance of single crystal in material science due to single crystal having uniform, continues and highly order structure. The single crystals are the backbone of modern technology. The impact that highly demand of single crystal visible in industries like amplifier, transducer, semiconductor, ferrites, infra rays, non-liner optics, piezoelectric, photosensitive material, microelectronic and microprocessor [1]. The gel technique is simple as well as adorable technique for growing single crystal under controlled growth and room temperature. Gel technique is most effective, selective, low-cost material and made up easily available. Due solubility of water [2] crystal growth in the gel is superior, attractive, and easy technique for growing single crystal transition metal oxalate [3] and metal oxalate [4]. In the various filed transition metal oxalate are valuable and having many important uses and applications. Many research grown the crystal by using silica gel [5-10] and very rare research use agar -agar gel to grown the crystal [11-13].

Mostly work on manganese oxalate growth reported by silica gel [14-17] and very rarely study of manganese oxalate crystal growth in agar-agar gel [18]. The manganese oxalate has been playing a vital role in industrial application. These material shows a significant impact on paint as well as cloths. The manganese oxalate used as semiconductor photosensitive material. Thus, we reported in the present paper to grown and discuss the effect of different gel parameter on manganese oxalate crystal growth in agar-agar gel by using single diffusion method. The grown manganese oxalate crystals were spherulitic, spherical irregular, granular, well-shaped and white in colour.

## 2. EXPERIMENTAL WORK

A glass beaker 250ml and single glass tube having 15 cm and 2.5 diameter has been taken and cleaned with acetone and rinsed with double distilled water which remove the organic and inorganic present moisture. Manganese chloride ($Mncl_2$), Oxalic acid ($H_2C_2O_4$) and agar- agar powder were used as chemical compound which were AR grade. The manganese chloride solution prepared by 12.35gm ($Mncl_2$), dissolving into 100ml distilled water constant stirring and kept in dark and cool place. A single glass test tube was filled by the manganese chloride as first reactant with different volume and molarity. Agar gel prepared by mixture of agar -agar powder into double distilled water boiling water, prepared hot agar gel transfer into test tube which was filed by manganese chloride. Mixture kept in cool and dry place yield perfect gel set. Oxalic acid used as second reactant prepared by 9.003gm($H_2C_2O_4$) added into 100ml double distilled water.

After setting gel the prepared oxalic acid poured into test tube slowly with desire volume and molarity. By using cotton open end of test tube was closed. After 6-7 days tiny seed crystal with good transparency were obtained due to spontaneous nucleation. After 8-week nucleation process was completed and large size of milky manganese oxalate crystal were obtained. The grown crystals were separated from gel in the test tube, washed with acetone and dried. As grown crystals were collected and observed.

The following reaction is expected to take place giving required compound. The optimum condition for growing manganese oxalate crystals is shown in table 1

$$MnCl_2 + H_2C_2O_4 \longrightarrow MnC_2O_4 + 2HCL$$

| Crystallization parameter | Values |
|---|---|
| **Molarity of Manganese chloride** | 1M |
| **Molarity of oxalic acid** | 1M |
| **Percentage of gel** | 1% |
| **Aging period** | 2 days |
| **Crystal maturity period** | 56 days |
| **Temperature** | Room temperature |

**Table 1: Optimized growth parameters of the manganese oxalate crystals**

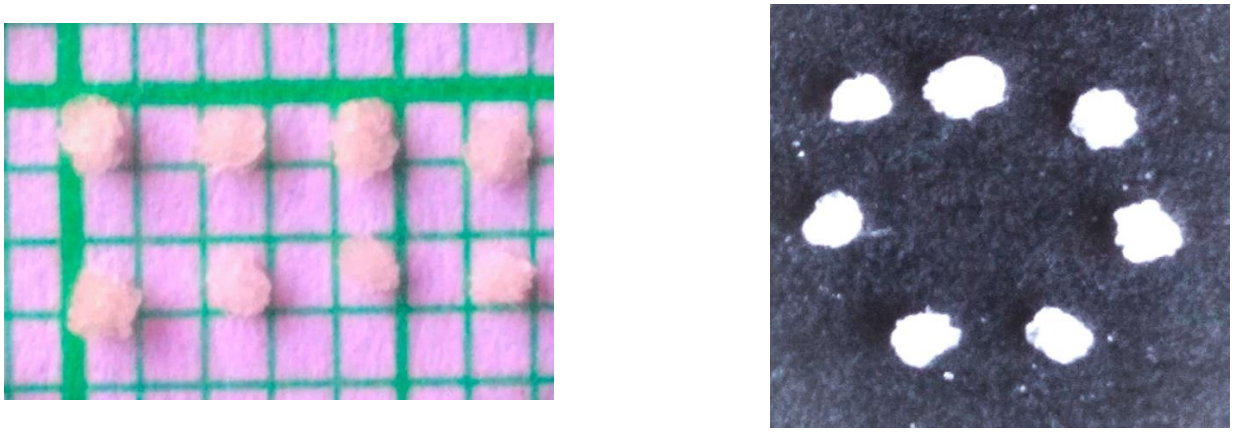
## 3. RESULTS AND DISCUSSION

To set the optimum condition for growing crystals. The manganese oxalate crystal growing in a test tube was observed. The effect of different gel parameter like concentration of reactant, percentage of gel, reversing reactant and gel setting and aging period was investigated**.** The concentration of manganese chloride changes from 0.2M to 2.5M and other parameter such as concentration of second reactant, percentage of gel, gel setting and aging period kept constant at room temperature. Controlled growth nucleation was seen in the test tube. Better quality of growth crystals was obtained at 1M than other concentration as shown in figure 1. As the concentration increases the number of growth crystals decreases, they are observed to accumulate on the surface of gel.

To investigation the effect of various percentage of gel on the growth of manganese oxalate crystal. Percentages of gel commuted 0.5% to 2% and other gel parameter kept constant at normal temperature. It was found that, as the percentage of agar gel was increased, the number of crystal beads increased but the crystal lustre decreased. At 1% of agar gel shows better result than other. The aging period was 48 hours, it was observed that, nucleation was started readily at the interstitial and inside test tube [19]. In the present work figure.1 shows growth of manganese oxalate crystals in test tube and figure.2 shows illustrating varied morphology of manganese oxalate crystal. The shape of these crystal is dependent on the types of molecular bonds between the atom as well as on condition under which they formed [20-21]. The grown crystals were spherical irregular, blocky, granular, spheroidal, crumb remarkable heavier and better quality than that obtained by other technique.

(a) (b) (c)

**Figure 1. effect on growth of manganese oxalate crystal in different concentration of manganese chloride (a) growth in 0.5M (b) growth in 1.0M (c) growth in 2M.**



(a) (b)

**Figure 2. grown manganese oxalate crystal (a) good size crystal (b) different in morphology**

## 4. CHARACTERIZATION

### 4.1. Thermal Analysis

Recrystallized alumina sample holder was used and the heating rate was $10^0$C/min. Thermograms were recorded in the temperature range from $30^0$C to $900^0$C.The sample was hold for 1.0min at $300^0$C to evaporate water due to moisture and then heated from $30^0$C to $900^0$C at $10^0$C/min. Manganese oxalate crystal powder under nitrogen atmosphere was taken as sample for thermal studied. The sample weight for TGA/DTA was 22.021mg.

### 4.1.1 Thermogravimetry Analysis (TGA)

The thermal stability of grown crystal and the number of water molecule associated with grown crystals determine by thermogravimetric analysis. Figure 3 shows TGA curve for manganese oxalate crystal. The thermogram of manganese oxalate one can observed that, the compound is stable up to $34.51^0$C and 2.40% loss in weight may be dehydration of water molecule in temperature range $45^0$C to $115^0$C, the observed weight loss in the range nearly agreed with calculate weight loss 5.00% and decomposition continues in this manner. In the next stage observed weight loss in temperature range $120^0$C to $170^0$C is 18.92% which agreed with calculated weight loss 18.42%, this weight loss attributed to loss of CO and decomposition is in continues manner. Decomposition of next stage occur in $340^0$C to $424^0$C temperature range in which observed weight loss of 34.10% nearly agree with calculated weight loss 30.00%. This weight loss indicated to loss of $CO_2$ and decomposition is in continuous manner. The remaining product finally turn into residue MnO (manganese oxide) is conformed at $550^0$C.The compound remains stable up to $889^0$C. The observed residue weight is 44.68% which is closely agreement with calculated residue weight 46.71. This confirms the present of manganese in the grown crystal. Thermal behavior in term of scheme may be explain as below [22].

$$MnC_2O_4\,0.5\,H_2O \xrightarrow{45^0C - 115^0C} MnC_2O_4 + 0.5\,H_2O,$$

$$MnC_2O_4 \xrightarrow{120^0C - 170^0C} MnCO_3 + CO,$$

$$MnCO_3 \xrightarrow{340^0C - 424^0C} MnO + CO_2$$

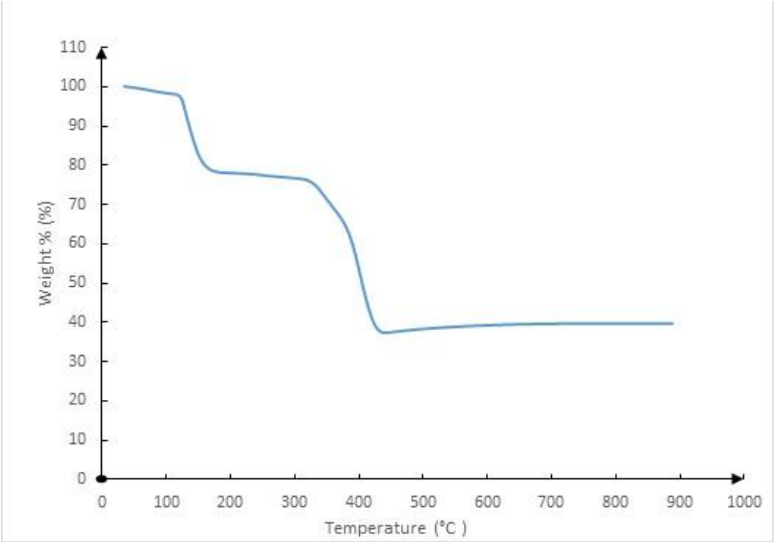



**Figure. 3. TGA curve of manganese oxalate**

**4.1.2 Differential Thermal Analysis (DTA)**

The loss of molecule can be determined by using DTA analysis. DTA Spectrum for gel grown manganese oxalate crystal is shown in figure 4 and collected DTA data from this curve is tabulated in the table 2. In the first stage an endothermic peak observed due to loss bulk of water of crystallization at $145^0$C, another endothermic peak at $408^0$C represent the decomposition of manganese oxalate. The endothermic peak studied in DTA treatment corresponds to the total weight loss of water molecule in TGA curve. TGA and DTA were carried out at National Chemical Laboratory, Pune.

**Table 2. DTA data of manganese oxalate**

| Stage | Peak Record | Peak Height | Nature | ΔH (J/g) |
|---|---|---|---|---|
| 1 | 145.55°C | -55.42% | Endothermic | -551.667 |
| 2 | 408.67°C | -18.17% | Endothermic | -247.85 |

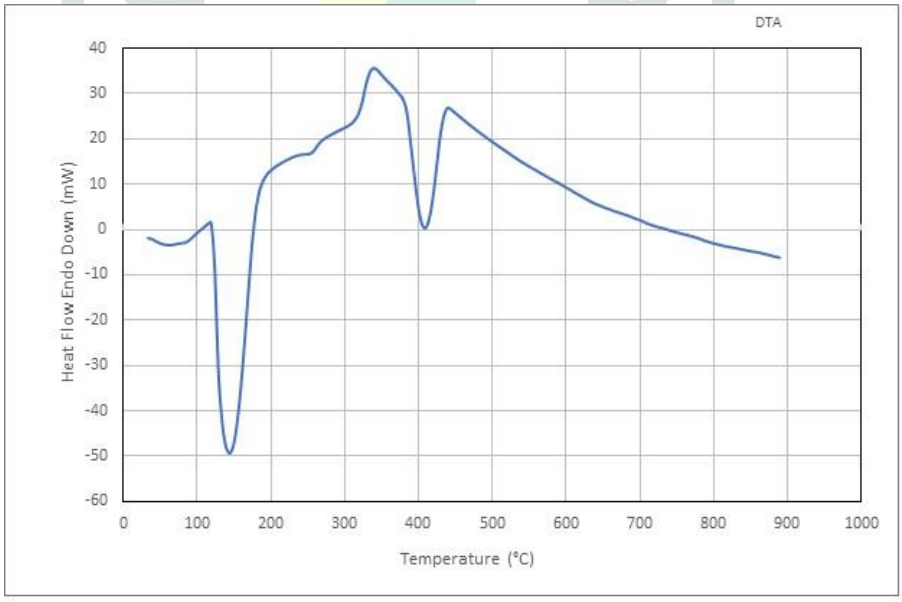



**Figure. 4. DTA curve of manganese oxalate**

### 4.1.3 Differential Scanning Calorimeter (DSC)

DSC was carried out at KBCNMU Jalgaon. The 9.00 mg weight of powder of manganese oxalate crystal was taken for DSC analysis. The DSC analysis of grown crystal was recorded between $30^0$C to $300^0$C the figure 5 represented DSC curve for manganese oxalate crystal. From the DSC curve confirmed the existence of endothermic dip peak at $151^0$C result in the formation manganese oxide this is good agree with DTA curve. Heat of transition $\Delta H$ i.e enthalpy change transition 583 J/g observed in temperature range between $130^0$C to $160^0$C.

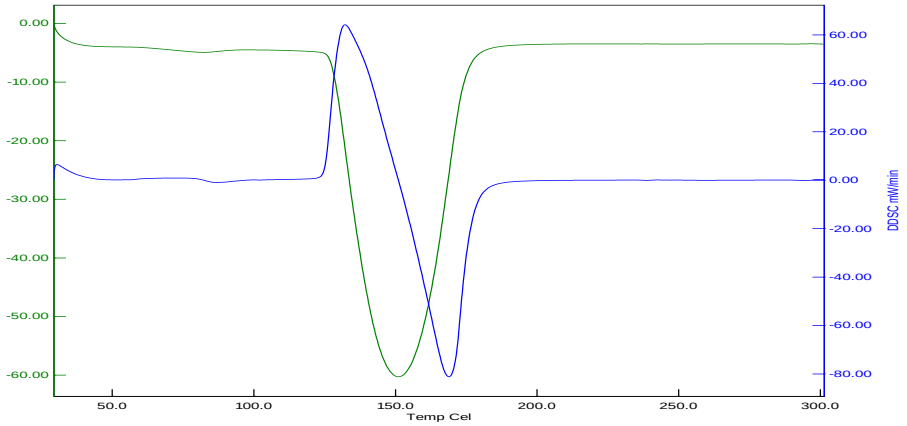



**Figure. 5. DSC curve of manganese oxalate**

### 4.2 ENERGY DISPERSIVE ANALYSIS BY X-RAY(EDAX)

Energy Dispersive analysis by X-Ray (EDAX) is used for the qualitative analysis. Elemental analysis of manganese oxalate crystal carried out at CRYSTA PEAK SOLUTION LAB, Pune which standard less at 10 eV energy show the results. Figure 6 shows elemental analysis spectrum of manganese oxalate crystal and observed elemental analysis data as shown in table 3. The peak ranging from 5.5 KeV to 6.2 KeV clearly indicates the presence of manganese in the sample. The relative concentration of manganese is observed as 43.04%. EDAX investigated that sample crystal show presence of manganese.

**Table 3. EDAX data of manganese oxalate**

| Sr.No | Element | Shell | Wt. % | At. % |
|---|---|---|---|---|
| 1 | O | k | 56.96 | 81.96 |
| 2 | Mn | k | 43.04 | 18.04 |

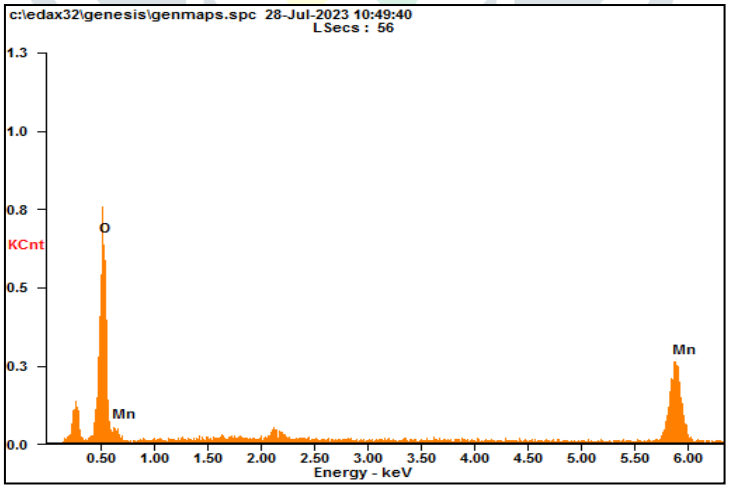



**Figure. 6. EDAX curve of manganese oxalate**

### 5. Conclusion

Single crystal of manganese oxalate crystals was successfully grown by using single diffusion technique in agar -agar gel. White colour with average size of $2mm^3$ were obtained during a period of 8 weeks at room temperature by applying different parameter such as variation of concentration of reactants, changes of percentage of gel, aging period and reversing reactant. The incorporation of Mn in the manganese oxalate crystals has been confirmed by EDAX. Thermal stability was studied by TGA, DTA and DSC analysis.

**Acknowledgment**

The author is very much thankful to Dr. S. J. Nandre, Department of Physics, Uttamrao Patil Arts and Science College, Dahiwel, (Dhule), M.S. for his keen interest and valuable suggestion. Principal Dr. R. R. Ahire, Department of Physics, S. G. P. Arts, Commerce and Science Senior College, Sakri,(Dhule), M.S. for providing laboratory facilities and also to Director, NCL, Pune and Mr. Satish Bagal, CRYSTA PEAK SOLUTION LAB, Pune and KBCNMU Jalgaon for providing characterization facilities.

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