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Optical and Thermal Studies on Strontium Doped Cadmium Tartrate Oxalate Single Crystals by Sol Gel Technique

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Abstract: This paper looks at the applications of sol-gel deposition technique to crystals growth. Sol gel technique which is one of the oldest methods of crystal growth. A single test tube technique coupled with gel again conferred maximum size crystals by controlled the nucleation rate. It was found that the P^H and age of gel greatly influenced the crystal quality, their size and transparency. In the gel preparation process sodium meta silicate (Na_2SiO_3) is mixed with the mixed solution of oxalic acid ($C_2H_2O_4$) and tartaric acid ($C_4H_6O_6$) in the desired mole fraction. The harvested crystals were characterized by X- ray powder Diffractogram, Fourier Transform Infrared Spectroscopy, quantitative elemental analysis of EDAX and Scanning Electron Microscope. Powder XRD results indicates the polycrystalline nature of this materials. FTIR for these crystals show all the bands expected from the metal tartrate oxalate with water of crystallization. Further the presence of cadmium, carbon and oxygen is confirmed by EDAX.
***Keywords*:** Gel growth, Strontium doped Cadmium tartrate oxalate, XRD, FTIR, EDAX, TGA and SEM.

1. Introduction

In recent years crystal growth in gel medium has attracted the attention of many investigators [1-5]. Scientifically and technologically crystal growth and characterization have became an interesting research area in the past decades. All basic solid materials are made up of single crystals and they are backbone of the modern technology. The influence of single crystal is noticed in the semiconductors, optics and acoustics, in various medical applications and in jewellery industries [6-9]. Cadmium Tartrate crystals, $CdC_4H_4O_6$, $3H_2O$, is isostructural with other elctroseramic divalent metal ions. Some divalent metal ion tartrates are exhibiting non-linear optical and spectral characteristics and hence are used in transducers and many linear and non-linear mechanical devices [10-13].

Oxalate crystals have attracted the attention of many researchers due to their interesting physical properties and their suitability in preparing ceramic superconductor and solid solution [14-17]. The formations of solid solutions of some multi-metal oxalate have been discussed in detail by schuele [18] and fischer [19].

2. Materials and Methods

All chemicals used such as oxalic acid, tartaric acid, sodium metasilicate , strontium chloride and cadmium chloride were of AR grade to avoid impurity accumulations. Strontium doped Cadmium tartrate oxalate crystals were grown from free solution of oxalic acid, tartaric acid, strontium chloride and cadmium chloride. Silica gel were prepared by adding oxalic acid (1M) and tartaric acid (1M) mixture to sodium meta silicate (water glass) solution of specific gravity 1.04 drop by drop till the p^H of the gel adjusted to 3.5, 4.0 and 4.5. Continuous stirring is needed to avoid excessive local ion concentration, which may cause premature local gelling and make final solution inhomogeneous. The solution with the desired value of p^H is transferred to

several glass tubes. The gel found to set in 30min to 24 hours, depending upon its P^H and the environmental temperature. Once gelled, feed solution of aqueous strontium chloride and cadmium chloride of concentration 1.5M was carefully placed with the help of a pipette over the set gel in order to avoid the surface damage and breakage of the gel. The cd^{2+} ions diffuses slowly through narrow pores of the gel to react with the oxalate and tartrate ions, giving rise to the formation of single crystals.

After harvesting the fully grown Strontium doped Cadmium tartrate oxalate crystals, structural characterization was performed using X-ray powder diffraction technique. XRD patterns were obtained using a Philips analytical X-ray diffractometer with cu Kα(λ=1.5406Å) radiation. The FTIR spectra were recorded for the crystals in the wave number range of 400-40000cm^{-1} using bruker vector 22 spectrometer using KBr pellet technique.

3. Results And Discussion

3.1. Growth kinetics

The crystal size as a function of time was noted every day and it was observed that the crystal size gradually increases with time and finally the growth rate ceased after a period of 240 hrs as shown in Fig.1.This is mainly due to the decrease of solute concentration of feed solution and non-availability of the ions in the gel after a period of 10 days. The nucleation rate of strontium doped cadmium oxalate tartrate crystals grown for three different pH values were recorded and their variations. It is evident that the number of crystals increases as the growth period increases are shown in Fig 2. This is only due to the inpregmentation of the outer reagent which forms more number of crystals as time advances. Further, on decreasing the P^H values from 4.5to3.5, the nucleation rate is considerably reduced. Also it was observed that the lowest p^H value limit is 3.5, below which the crystal formation is absolutely not possible.

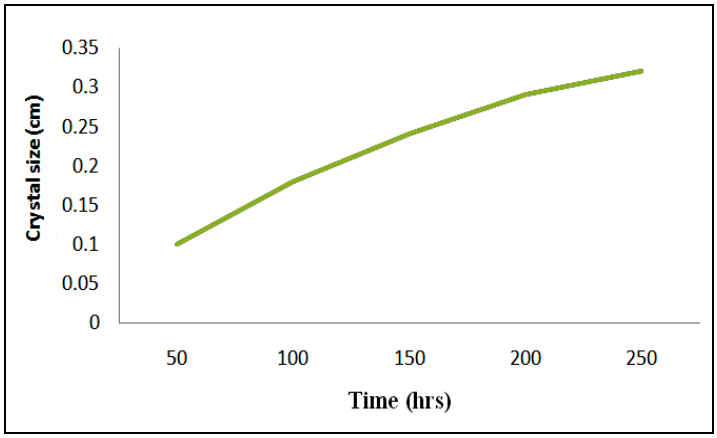


Fig.1. Crystal size variation with time.

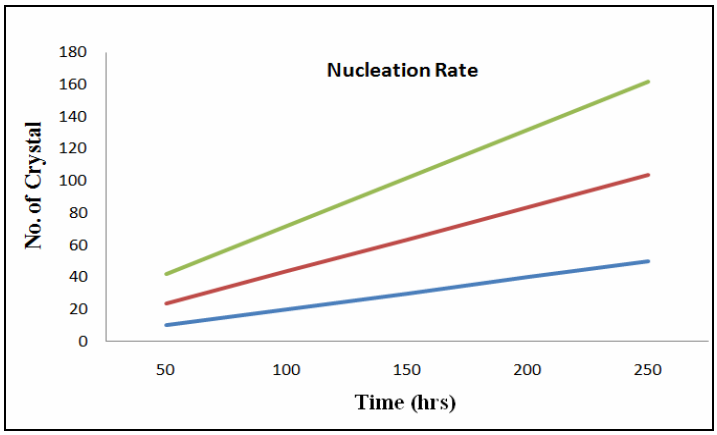


Fig 2 .Time vs. No. of crystals.

The size and parameters of single strontium doped cadmium tartrate oxalate crystal grown in silica gel. The crystal size as a function of time was noted every day. It was observed that the crystal Size gradually increases with time.

Fig.3. Shows photo graph of prepared strontium doped cadmium tartrate oxalate crystal.

Table-1: Optimized growth parameters of crystals.

S. No.	Various process parameters	Values
1.	Density of Na_2SiO_3	1.04 g/cm^3
2.	Concentration of oxalic acid	1M
3.	Concentration of tartaric acid	1M
4.	Concentration of cadmium chloride	1.5M
5.	Concentration of Strontium chloride	1.5M
6.	Gel setting period	10h
7.	Gel aging	3 weeks
8.	Period of growth	30days
9.	Temperature	Room temperature

3.2. X-Ray Diffraction Analysis

The crystal structure of a sample compound was studied by powder X-ray diffraction method. The X-ray diffraction was recorded using Miniflex-Rigaku model Japan with CuKα radiation of wavelength λ=1.54056Å. The recorded diffraction pattern of the strontium doped cadmium oxalate tartrate crystals is shown in the figure.

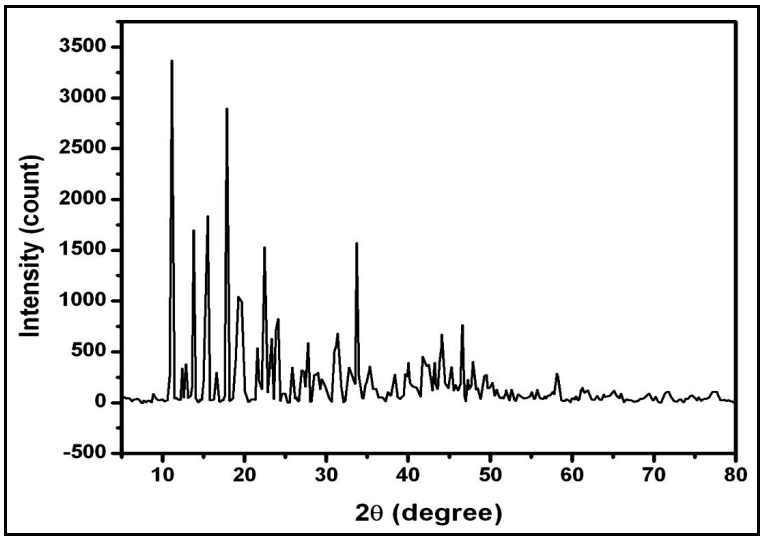


Fig.4. Powder diffraction pattern of strontium doped cadmium oxalate tartrate crystal.

3.2.1. Determination of Grain size from XRD spectra

From the XRD pattern, it is observed that, each peak has got a finite width. The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using the formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where, β is full with of half maxima in radian and D is grain size of the crystal.

$$D = \frac{0.9 \times 1.54056}{0.182 \times \cos(17.865)}$$

= 8.0042Å

The calculated average grain size is 0.80042 nm. The analysis of different diffraction peaks indicates the formation of system .The diffraction peaks at 2θ value were measured very carefully and converted into d value using the Bragg's equation putting n=1. The size of the crystal is very small compared to the Cadmium Tartrate Oxalate Single Crystals (2.40268nm) [20]**.** This variation in size explains the influence of addition of Strontium on the size of the crystal.

3.3. FTIR spectrum analysis

IR spectroscopy is very helpful for the identification of a compound [21, 22]. The spectrum is shown in Figure 5. Strong and very broad band appeared at 3459.95cm^{-1} which is attributed to O-H stretching vibration. Very intense but broad band appeared at 1612.44cm^{-1} which may be due to O-H bending vibration [23]. The sample that has oxalate $(C_2O_4)_2$ ion is supported by the broad peak merged in the strong broad band in the region 1612.44cm^{-1}, which is attributed to the asymmetric stretch of CO_2 [24]. And the well-pronounced sharp peak at 1310.94cm^{-1} and a weak but sharp peak at 1310.36cm^{-1} correspond to the CO_2 symmetric stretching. The strong and very sharp band which observed at 774.54cm^{-1} is due to the combined effect of in-plane deformation of CO_2 and the presence of a metal-oxygen bond. A moderate sharp band appeared at 526.74cm^{-1} which might be due to CO_2 wagging.

The presence of band at 3493.22 cm^{-1}for pure and 3459.95 cm^{-1} for strontium doped indicates the presence of water of hydration in both the crystals. The peaks corresponding to other functional groups are also present in both the cases. As seen from the spectrum, a slight shift is observed in some of the characteristically vibration frequency in case of the strontium doped cadmium tartrate oxalate Crystals.

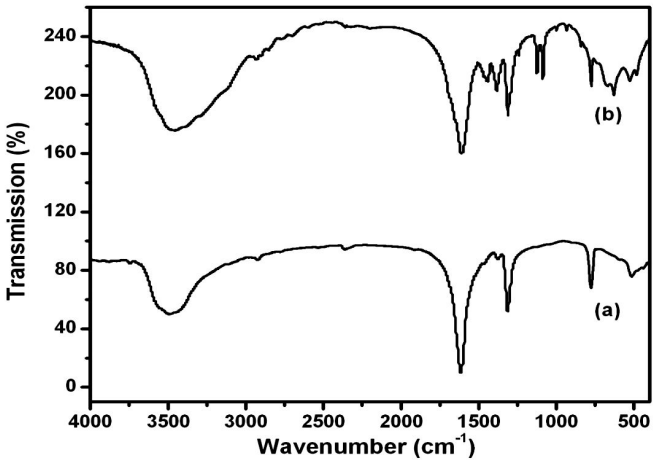


Fig.5. FT-IR Spectrum (a) Cadmium tartrate oxalate crystals and (b) Strontium doped Cadmium tartrate oxalate crystals.

3.4. EDAX

In order to confirm the presence of cadmium and strontium, quantitative elemental analysis were performed on the application of EDAX. The EDAX spectra shown in figure 6 reveals prominent Peaks due to cd Lα, CKα and

OKα. This confirms the formation of cadmium tartrate oxalate Crystals. The weight [%] and atomic weight [%] calculated from the peaks height further confirms the expected proportion of carbon, oxygen and cadmium crystals.

Table-2: EDAX data

Elements	(keV)	Mass%	Atom%	K
C K	0.277	14.36	29.18	2.5867
O K	0.525	38.07	58.06	1
Sr L	1.806	39.61	11.03	3.1824
Cd L	3.133	7.96	1.73	3.7857
Total		100	100	

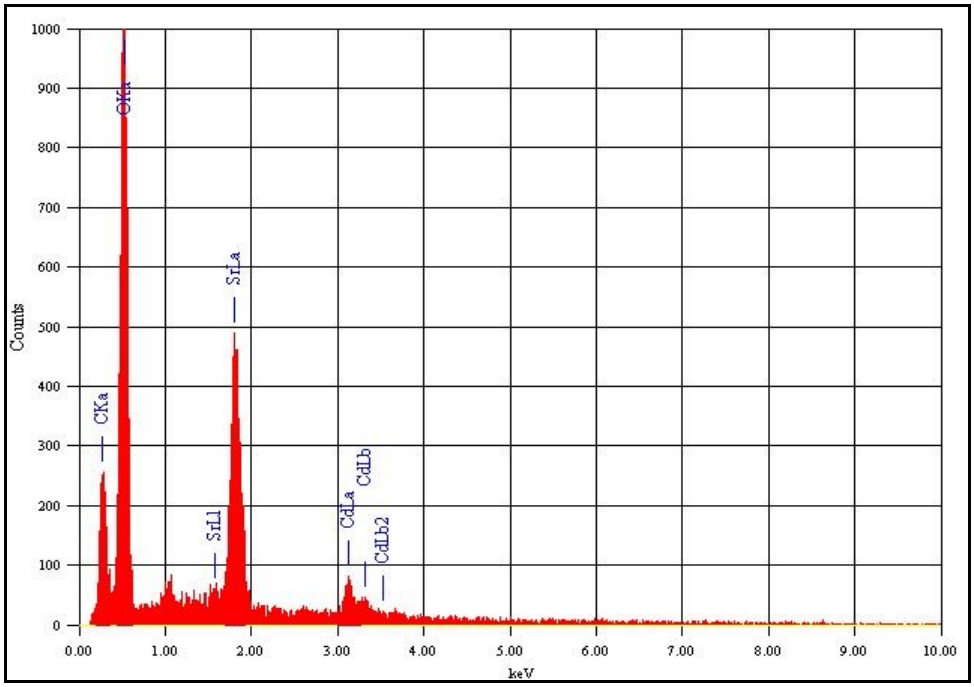


Fig.6. EDAX analysis for strontium doped cadmium oxalate tartrate crystal.

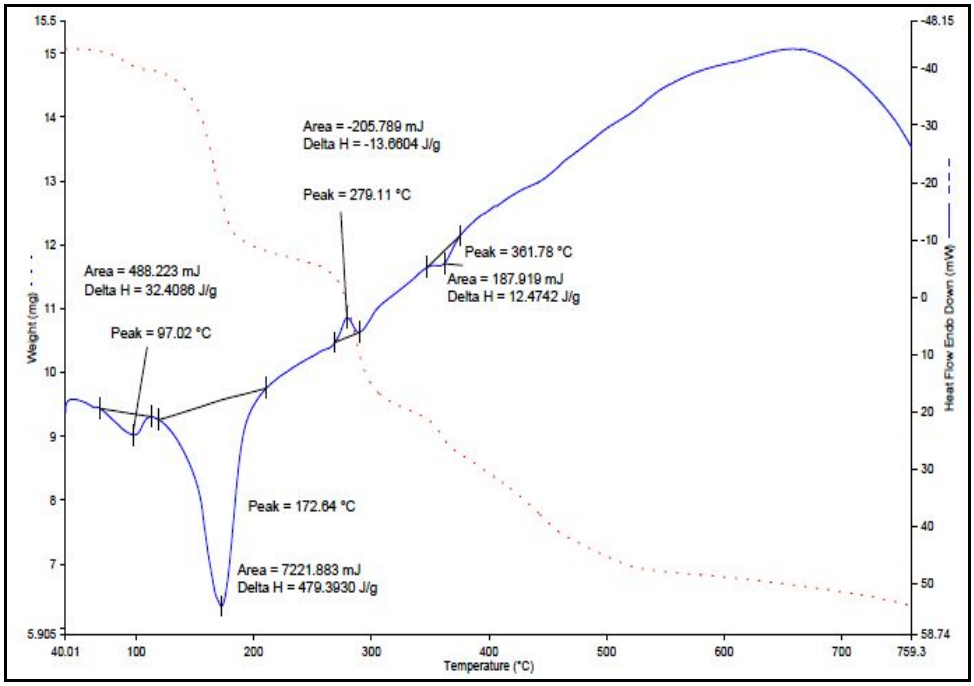
3.5. Thermal Analysis

Thermo gravimetric analysis (TGA), Differential thermal analysis (DTA), techniques are widely used for thermal studies of organic and inorganic compounds. Modern commercial thermo balances with variable heating rates, variable gaseous media, with vacuum or high-pressure facilities, and with continuous recording facilities eliminated satisfactorily the possible sources of errors in thermal studies of samples under study. As a result, numbers of possible analytical precipitates are mentioned in the literature. Thermal studies on oxalate tatrate crystals grown by gel method were reported by many investigators [25-28]. Thermal studies on strontium doped cadmium oxalate tartrate crystals grown by gel method using Cadmium format mixed with acid as the supernatant solution was reported [29]. Thermal studies on pure gel grown oxalate tartrate crystal grown by gel method using Cadmium Chloride as supernatant was reported [30]. The thermal decomposition study of Cadmium oxalate tartrate involves simultaneous TGA, DTA of the compound under ambient conditions. At the temperature range 120 to 180°C there is a change in mass occurred on the TG curve.

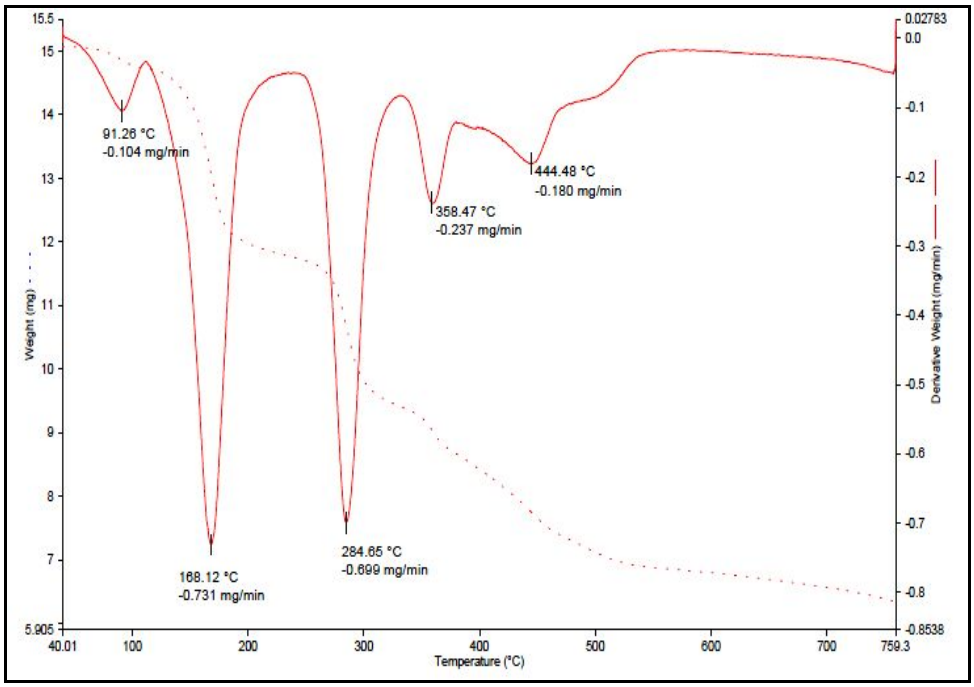
TG, DTG and DTA curves for strontium doped cadmium oxalate tartrate crystal at a heating rate of 10^0C/min shows in Fig.7 (a-b). Its weight is found to be lost continuously as a function of the temperature applied. The overall decomposition process is clearly seen to be divided into three consecutive stages described as follows.

In the first stage of decomposition, in fact, the dehydration, which begins at 82.5^{0}C and continue up to, or terminates at, 185.1°C . The net weight loss (2.6%) as observed between 82.5°C and 185.1°C corresponds to loss of the water molecules, suggesting that the grown crystals were initially trihydrated. The coordinated molecules of water lost during this stage leads to the formation of anhydrous strontium doped cadmium oxalate

tartrate. The second stage of decomposition sets in at around 185.1°C and is completed at around 274.3°C; this stage of reaction corresponds numerically to 0.9% of the total weight loss. Then, in the third stage of decomposition, which seemingly occurs in the temperature interval of 273.4°C –301.6°C, the complex is decomplexed to form strontium doped cadmium oxalate tartrate as the second intermediate product. This is of course confirmed by the fact that 1.65% of the total mass is found to have been lost. DTA shows an endotherm at 168.12°C corresponding to DTG peak at 172.64°C with a shoulder in DTG at about 180^0C. Simultaneous loss of $6H_2O$ and 2C can be confirmed from the peak is observed in DTG curve at 284.65°C and 358.47°C since only one peak is observed in DTG curve corresponding to two peaks in DTA curve. The decomposition in the temperature range between 400 and 490°C, the material losses 3CO molecule leading to the formation of carbonate [31].



(a)



(b)

Fig.7. (a) TG and DTG Profile (b) TG and DTA Profile.

3.6. Surface analysis (SEM)

In order to study the surface feature of the grown crystal, scanning electron microscopic studies of strontium doped cadmium oxalate tartrate crystals were performed. Fig. 8 shows different type of morphologies exhibited by crystals as seen under scanning electron microscope. The various types of morphologies include spherulites, platelets, cuboids, and coalesced crystals. The feature of same crystal under scanning electron microscope at higher magnification showing crystal surface along with some gel inclusions, which means that crystals were not properly cleaned while taking out from the crystallizer.

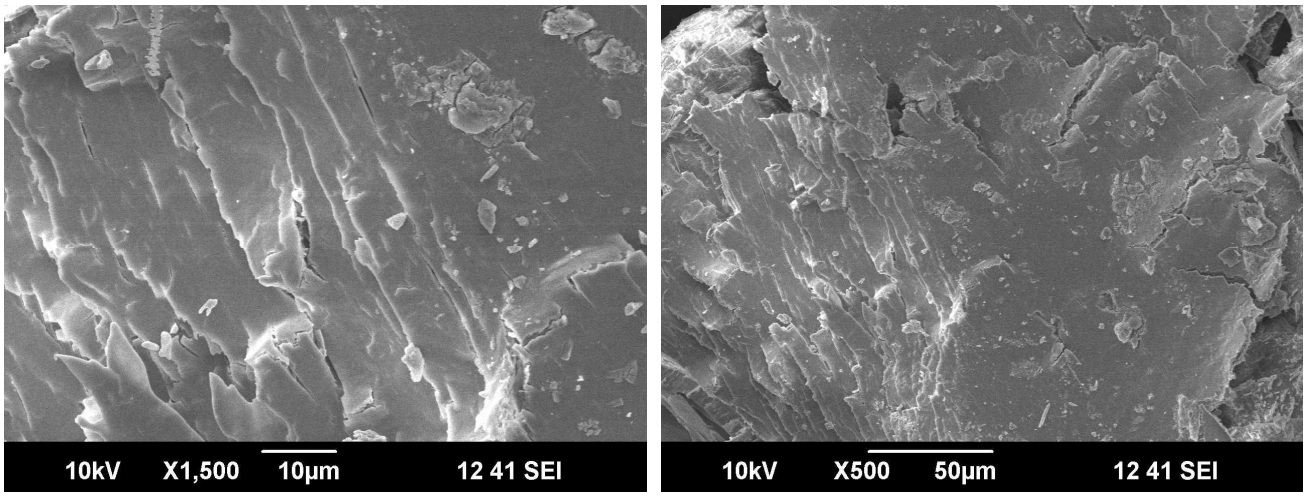


Fig.8. SEM image of strontium doped cadmium oxalate tartrate crystals.

4. Conclusion

Different habits of strontium doped cadmium oxalate tartrate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants, concentration of impurities etc. It was found that well-developed single crystals of strontium doped cadmium oxalate tartrate are obtained at 1M concentration of feed solution in the pH range 4 to 5 of the gel. The thermal behaviour of the material reveals that decomposition takes place through many stages.

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