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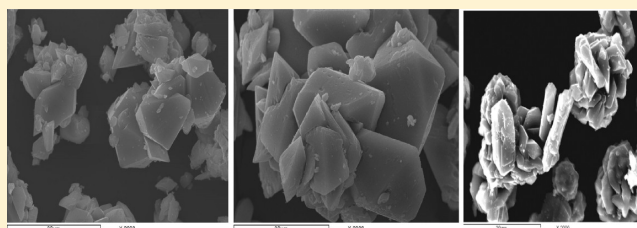
Crystal Nucleation of Nano Crystallite Strontium Malonate without and with Additives

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ABSTRACT: A basic study was carried out to understand the crystallization of nano crystallite strontium malonate without and with addition of sodium dodecyl sulfate surfactant (SDS) or poly ethylene glycol (PEG). Induction time was measured under different supersaturations ranging from 2.6 to 4.3 using conductivity method. The induction time was estimated from the time vs conductivity of the solution. The results show that, the induction time decreases exponentially with increasing the supersaturation. On the other hand, the induction time is decreased with addition of SDS or PEG. Using an equation that relates induction times and supersaturation ratios, free energy barrier, and critical nuclei radius were calculated. The results revealed that decrease of free energy barrier and critical nuclei radius as supersaturation increased and by addition of SDS or PEG. In addition, the calculated surface energy of strontium malonate crystals was decreased from 6.0 to 5.7 and 5.5 mJ/m² with SDS and PEG, respectively. In addition, the precipitated crystals are agglomerated as shown using scanning electron microscopy (SEM) investigation. In addition, the crystallite sizes of the formed crystals without and with SDS or PEG are 244, 222 and 121 nm, respectively.



Without Additives With SDS Surfactant With PEG Polymer

SEM Photomicrographs of Strontium Malonate without and with Additives at 4.3 Supersaturation and 2000X Magnifications

INTRODUCTION

Alkaline earth metals and alkali metals are almost invariably found in an oxidized state as a component of metallo-organic salts due to the highly reactive nature of such elements. Salts of such metal-ions are widely distributed throughout nature. Strontium is one of the less common of these elements but is an important component of some salts because of the beneficial actions of strontium in biological systems.¹

Salts of alkaline earth metal and alkali metal compounds are used in a great number of industrial processes and in production of food products, medical products, pharmaceutical ingredients, vitamins, and other health related products, products for personal care, as well as for a number of industrial products, such as fertilizers, building materials, catalysts, ceramics, glass, iron and steel manufacture and in a great number of other products.¹

It is well established that strontium stimulates the formation of bone volume,² and strontium is the only trace metal of bone that can be positively correlated with compression strength of bone.³ After four weeks of treatment of strontium malonate, strontium level increased.⁴ This drug (strontium malonate) labeled NB S101 for trials, is a dual-acting bone agent has a demonstrated ability to decrease resorption of bone while maintaining formation of new bone; it was taken on a once daily tablet.⁵

Strontium malonate and other strontium salts find immense applications in the medical field especially for treatment of rheumatic and arthritic disorders.⁶ Recently, the binding

modes of strontium cations with carboxylate and dicarboxylate anions have special interest because of the significance of such interactions in the blood and bone proteins.⁶

Induction time method has been used to measure nucleation kinetics as compared to metastable zone widths method.⁷ Organic additives play an important role in crystallization. They alter the surface properties of the crystals. In addition, the additives change nucleation, growth, shape of the crystals and their agglomeration or dispersion behavior. Surfactants can either enhance or retard crystallization. The reported mechanism for enhancing growth of crystals is surfactant increase the localized supersaturation around the crystals. So, faster growth will occur.^{8–14}

The main objective of this work is to study the crystal nucleation of strontium malonate and the effect of additives, such as sodium dodecyl sulfate (SDS) or polyethylene glycol (PEG) on the induction time and nucleation of the formed crystals in aqueous medium. Calculations of surface energy, nucleation rate, free energy, and critical nucleus size with and without additives are another objective of this study.

EXPERIMENTAL SECTION

Apparatus and Instruments. Strontium malonate crystals were identified by X-ray diffraction (XRD) on a Bruker axis D8

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diffractometer using Cu K α ($\lambda = 1.5406$) radiation and secondary monochromator in the range 2θ from 5° to 70° , CMRDI. The strontium malonate particles morphologies were investigated by scanning electron microscope (SEM, JSM-5400), CMRDI. Thermal analysis of strontium malonate crystals were made in the temperature range 10 – 1000°C with a heating rate of $10^\circ\text{C}/\text{minute}$ using NETZSCH STA 409 C/CD apparatus under helium gas atmosphere, CMRDI. Chemical analysis and EDX analysis of strontium malonate crystals were made by Vario EL III, Germany, Cairo University, and scanning electron microscope (EDX, JSM-5400), CMRDI. Fourier transmission infrared spectrometer (FT-IR) of strontium malonate crystals was made by JASCO-Japan, Model 4100, Cairo University.

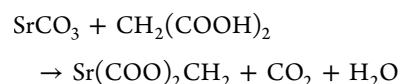
The primary nucleation of strontium malonate with and without additives was followed by conductivity measurement by using a Cond 315i/SET conductimeter, CMRDI.

Chemicals and Solutions. Pure chemicals including malonic acid [$\text{CH}_2(\text{COOH})_2$] from MERCK Company and strontium carbonate anhydrous [SrCO_3] from Oxford Company are used for this study. In addition, SDS (sodium dodecyl sulfate) surfactant [$\text{C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$] and PEG (poly ethylene glycol) polymer [$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$] from Fisher Scientific Company and Fluka Company are used. The primary nucleation of strontium malonate with and without additives was followed by conductivity measurement.

Preparation of Strontium Malonate. Malonic acid solution (90 mL) of concentration (1.25–2.5%) with 10 mL of water or water/additive solution was added in 500-mL beaker and heated to 45°C using a water bath. Then, the SrCO_3 (90 mL) of concentration (2.1–3.55%) of deionized water of the same temperature was added simultaneously with 10 mL of water or water/additive solution of the same temperature. The reaction was kept at 45°C with constant agitation. The conductivity of the resulting solution was measured on line at different time intervals during the course of the reaction. So, there is no time delay between the sampling and measurement. A graph of time versus conductivity was plotted. The time corresponding to the point of intersection of the two asymptotic lines represents the induction time.

RESULTS AND DISCUSSION

Strontium malonate was prepared according to the following reaction equation:



The strontium malonate crystals grow at 45°C in malonic acid and strontium carbonate solution with and without additive. The experiments were performed at different supersaturation.

The absolute supersaturation was used instead of supersaturation ratio. Generally, there are 3 methods for expression of supersaturation namely absolute supersaturation, relative supersaturation or supersaturation ratio.¹⁵ These definitions of supersaturation assume an ideal solution with an activity coefficient of 1. It is common practice to ignore activity coefficients in most cases and employ concentrations in expressions of supersaturation, refer to the reference.¹⁵ The supersaturation (S) was calculated¹⁶ as follows:

$$\text{supersaturation } (S) = c - c^*$$

where c is strontium malonate concentration (%) and c^* is strontium malonate (solute) solubility under the applied conditions, which is equal to $0.141 \text{ g}/100 \text{ mL}$ water or 0.141% .¹⁷

The results of induction time measurements are presented in Table (1).

Effect of Supersaturation on Induction Time with and without Additives. Effects of crystallization times on

Table 1. Effect of Additives on the Induction Time (t) of Strontium Malonate (At Different Supersaturation)

item	supersaturation			
	4.3	3.4	3.0	2.6
	t^a	t	t	t
without additives	8.2 ± 0.3	16.8 ± 0.5	18.2 ± 0.7	37.0 ± 1.2
with 100 ppm SDS surfactant	6.4 ± 0.2	9.6 ± 0.3	12.8 ± 0.5	22.0 ± 0.7
with 100 ppm PEG polymer	7.6 ± 0.3	11.2 ± 0.3	12.0 ± 0.5	14.4 ± 0.5

^aIn minutes.

conductivity at different supersaturations with and without additive are studied. Example of the results is given in Figure 1.

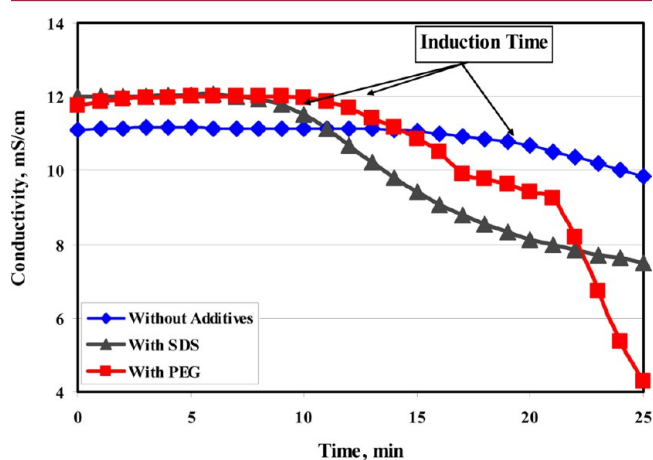


Figure 1. Effect of crystallization time on conductivity at supersaturation 3.4 with and without additives.

The conductivity of malonic acid solution of 2% concentration, strontium carbonate suspension of 2.8% concentration, SDS solution, PEG solution, and bidistilled water are 8.6, 7.25, 3.3, 0.5, and 0.25 mS/cm, respectively. So the initial conductivity of baseline is lower than that with additive solution as shown in (Figure 1).

Moreover, induction times were determined at different supersaturation with and without additives and given in Table (1). These results confirm that 100 ppm SDS surfactant or 100 ppm PEG polymer consistently decrease the induction time to a lower degree than the baseline at all the studied supersaturation. In all these cases, as the supersaturation has increased, the induction time is decreased.

Correlation between Supersaturation and Induction Time. Surface Energy (γ) Calculation. The surface energy (interfacial tension) between the crystals and the aqueous solution is a fundamental parameter for understanding the rate of both nucleation and crystal growth. On the basis of the classic homogeneous nucleation theory, the induction time can be related to the supersaturation using the following correlation:^{18,19}

$$\log(t_{\text{ind}}) = A + \frac{B}{T^3(\log^2 S)}$$

where A is an empirical constant (dimensionless), T is the absolute temperature (K), and B depends on the number of variables and is given by

$$B = \frac{\beta \gamma^3 V_m^2 N_A f(\theta)}{(2.3R)^3}$$

where β is a geometric (shape) factor of $16\pi/3$ for the spherical nucleus, $f(\theta)$ is a correction factor, when purely homogeneous nucleation takes place $f(\theta) = 1$ and when heterogeneous nucleation occurs $f(\theta) = 0.01$, V_m is the molar volume ($141.5 \text{ cm}^3 \text{ mol}^{-1}$, which is calculated by molecular weight/density (density was experimentally determined) = $189.6/1.34$), R is the gas constant ($\text{J/mol}\cdot\text{K}$), γ is the surface energy (J/m^2), and N_A is the Avogadro's number (mol^{-1}). Plotting of $\log t_{\text{ind}}$ against $1/[\log^2 S]$ over a range of high supersaturation ratios (2.6–4.3) for a fixed temperature gives a straight line with slope (B), relative to homogeneous nucleation. As a matter of fact, the change of nucleation mechanism produces change in the slope of B .^{17,18}

Relation between \log induction time and $1/\log^2$ supersaturation with and without 100 ppm additive is given in Figure (2). The calculated surface energies are 6.0, 5.7, and 4.5 mJ/m^2

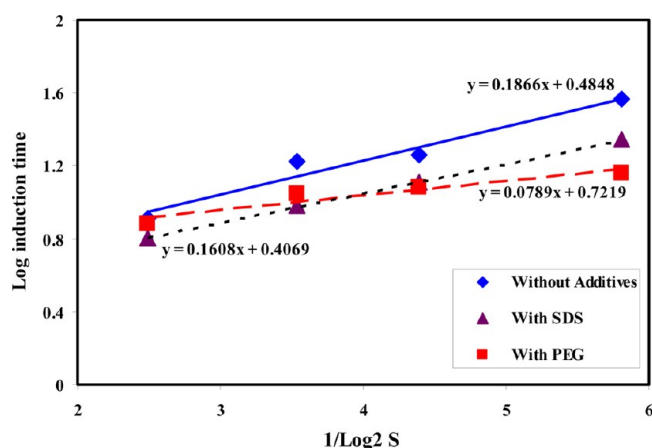


Figure 2. Relation between \log induction time and $1/\log^2$ supersaturation with and without additives.

without, with SDS or PEG, respectively. It is clear that, the surface energy is decreased with addition of SDS or PEG. Decreasing the surface energy leads to increasing the nucleation rate of strontium malonate crystals.^{8,20} Generally, the surface energy for more soluble salts is less than that for less or sparingly soluble salts^{8,20} as shown by the following calculations.

Calculation of Nucleation Rate (J_s), Free Energy Change (ΔG_{cr}), and Critical Nucleus Radius (r). On the basis of classic homogeneous nucleation, it can easily calculate the nucleation rate, i.e., the number of nuclei formed per unit time per volume by applying the following relation:¹⁵

$$J_s = F \exp \left[\frac{-\beta \gamma^3 V_m^2 N_A f(\theta)}{(RT)^3 \ln^2 S} \right]$$

where J_s is the nucleation rate and F is a frequency constant and is known as the pre-exponential factor and has a theoretical value of $10^{30} \text{ nuclei/cm}^3 \cdot \text{sec}$.¹⁸ By known the surface energy of strontium malonate crystals (γ), it can easily determine the nucleation rate with and without additive. The difficulty with applying the above equation is that it predicts the nucleation rate only at high supersaturation.¹⁴ So, it is applied at supersaturation ranged from 2.6 to 4.3. The free energy change

ΔG_{cr} for the formation of critical nucleus size can be calculated from the following Arrhenius type equation:^{15, 21}

$$J_s = F \exp \left[-\Delta G_{\text{cr}}/KT \right]$$

where K is Boltzmann constant and T is the absolute temperature.

By known the free energy change (ΔG_{cr}), the radius of the critical nucleus (r) can be calculated from the following equation:

$$\Delta G_{\text{cr}} = 4/3\pi r^2 \gamma$$

The number of molecules in the critical nucleus can be calculated as the following equation:²²

$$i = 4\pi r^3 N_A / 3V_m$$

Table 2 and Figures 3 and 4 show nucleation rate, free energy change for formation of critical nucleus size and radius of

Table 2. Effect of Additives on Nucleation Rate, Free Energy Change for Formation of Critical Nucleus Size of Strontium Malonate Crystals (At Different Supersaturations)

supersaturation	nucleation rate, nuclei/cm ³ ·s × 10 ²⁹			free energy change for formation of critical nucleus size $\Delta G_{\text{cr}} \times 10^{-21}$, J		
	without additives	with SDS	with PEG	without additives	with SDS	with PEG
2.6	0.8	1.2	3.5	10.9	9.4	4.6
3.0	1.5	2.0	4.5	8.2	7.1	3.5
3.4	2.4	2.9	5.4	6.3	5.5	2.7
4.3	3.4	4.0	6.4	4.7	4.0	2.0

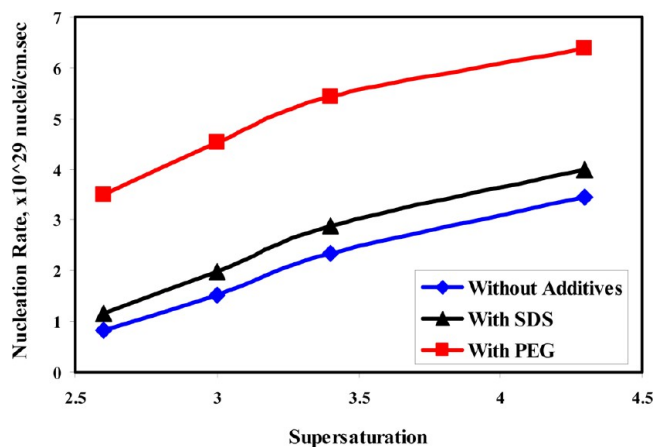


Figure 3. Effect of supersaturation on the nucleation rate with and without additives.

critical nucleus of strontium malonate crystals with and without additive at supersaturation ranged from 2.6 to 4.3. It is clear that, the nucleation rate is increased with increasing supersaturation with and without additives Figure (3). Moreover, addition of SDS surfactant or PEG polymer increases the nucleation rate at all the studied supersaturation compared with the baseline (without additives). High nucleation rate means that a high number of formed nuclei are obtained. These nuclei have relatively lower chance to grow to large crystals compared to lower number of formed nuclei grows under the same conditions. The nucleation rates at supersaturation of 3.4 are 2.4×10^{29} , 2.9×10^{29} , and $5.4 \times 10^{29} \text{ nuclei/cm}^3 \cdot \text{s}$ without and

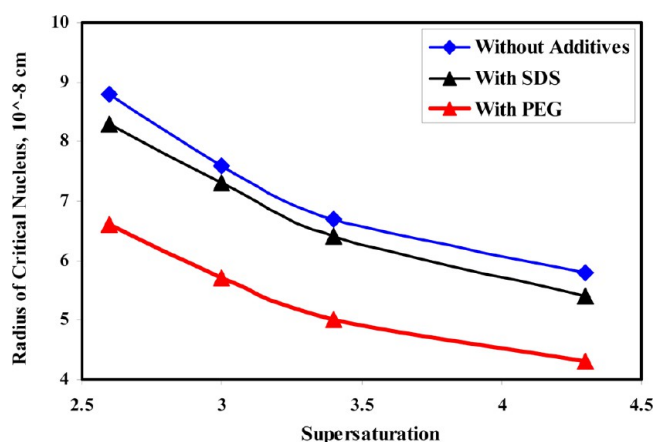


Figure 4. Effect of supersaturation on the radius of nucleus with and without additives.

with 100 ppm SDS or 100 ppm PEG polymer addition, respectively.

The free energy change for formation of critical nucleus is decreased with increasing the supersaturation. It is also decreased with addition of additives. In parallel, the radius of critical nucleus is decreased with increasing the supersaturation or with addition of additives (Figure 4 and Table 3).

Table 3. Effect of Additives on Radius of Critical Nucleus and Number of Molecules in the Critical Nucleus (At Different Supersaturation)

supersaturation	radius of critical nucleus, cm $\times 10^{-8}$			number of molecules in the critical nucleus		
	without additives	with SDS	with PEG	without additives	with SDS	with PEG
2.6	8.8	8.3	6.6	12	11	5
3.0	7.6	7.3	5.7	8	7	4
3.4	6.7	6.4	5.0	6	5	3
4.3	5.8	5.4	4.3	4	3	2

Characterization of Strontium Malonate. XRD Analysis of Strontium Malonate. Strontium malonate with and without additives was characterized using XRD. The results of XRD analysis is given in Figure 5. The results show that the sample is strontium malonate single phase, and there is no difference between single-phase produced with and without SDS or PEG additives.

SEM Photomicrographs of Strontium Malonate. SEM photomicrographs of the strontium malonate crystals produced at supersaturation of 4.3 with and without additives are shown in Figure 6. SEM investigation show that strontium malonate crystals have larger agglomerated particle size with SDS surfactant (10–40 μm) compared to baseline (5–20 μm). The reason for agglomerates formation is not fully understood. Moreover, strontium malonate crystals have tabular structure of 2–20 μm diameter size with PEG polymer. EDX analysis and C, H elemental analysis was carried out for the crystals and given in Figure 7 and Table 4. The results show that there is a reasonable agreement between the values obtained experimentally using EDX and C, H chemical analysis with the calculated on the basis of proposed elemental composition of the material $\text{SrC}_3\text{H}_2\text{O}_4$.

TG and DTG Analysis of Strontium Malonate. Thermal analysis of strontium malonate crystals were made in the

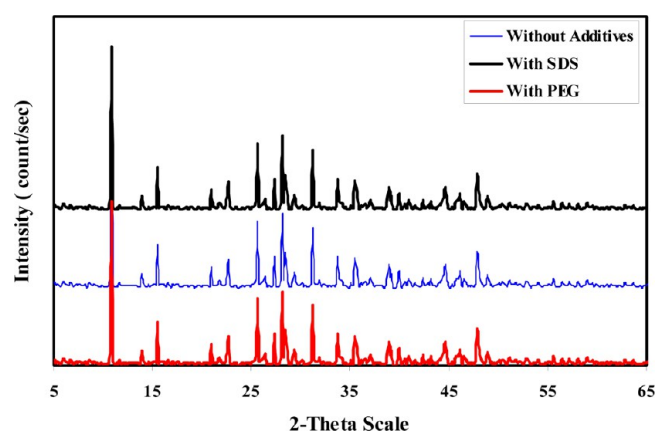
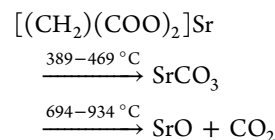


Figure 5. XRD pattern of strontium malonate with and without additives.

temperature range 10–1000 $^{\circ}\text{C}$. The decrease of weight by temperature is shown in the thermo gravimetric (TG) curve in Figure 8, while the differential thermal gravimetric analysis (DTA) results are given in Figure 8. From TG Curve, the total weight loss % or total mass change in the strontium malonate crystals is about 43.28%. Moreover, the TG curve exhibits mass losses in two stages which indicate that the decomposition takes place continuously. It is seen that the TG curve shows a plateau up to 389 $^{\circ}\text{C}$ suggesting that the compound is thermally stable up to a temperature of 389 $^{\circ}\text{C}$. After this temperature, the curve describes a mass loss of 15.38% in the temperature range of 389–469. These results are in good agreement with published data of thermal decomposition of calcium malonate.²³ This mass loss is attributed to the decomposition of the sample to give SrCO_3 as a residue by losing elements of the organic moiety in one step as calcium malonate.²³ The SrCO_3 formed after decomposition remains stable up to 694 $^{\circ}\text{C}$. In the temperature range of 694–934 $^{\circ}\text{C}$, the TG curve shows a mass loss of 28.0%. This stage indicates the thermal decomposition of the SrCO_3 to strontium oxide (SrO). The observed mass loss of 28.0% is in close agreement with the formation of SrO as the final product as calcium malonate.²³

The weight loss observed in the all temperature regions is 43.28%, and the weight of $\text{SrO} = 100 - 43.28 = 56.72\%$. The following chemical reaction occurs during thermal treatment as calcium malonate:²³



The DTA curve (Figure 8) of strontium malonate showed two major peaks in the curve. The first peak corresponds to the endothermic decomposition of the malonate to SrCO_3 at 400 $^{\circ}\text{C}$. The second peak shows the decomposition of SrCO_3 to SrO at temperature up to 919 $^{\circ}\text{C}$. These results confirm that SrCO_3 is the only residue left after the decomposition of strontium malonate as calcium malonate.²³ In addition, SrO is the only residue left after the decomposition of strontium carbonate.

FT-IR Spectrum of Strontium Malonate. FT-IR spectrum of strontium malonate crystals is given in Figure (9). In the range 400–4000 cm^{-1} . The frequencies observed in the region of 3013–2310 cm^{-1} are assigned to stretching vibration of CH

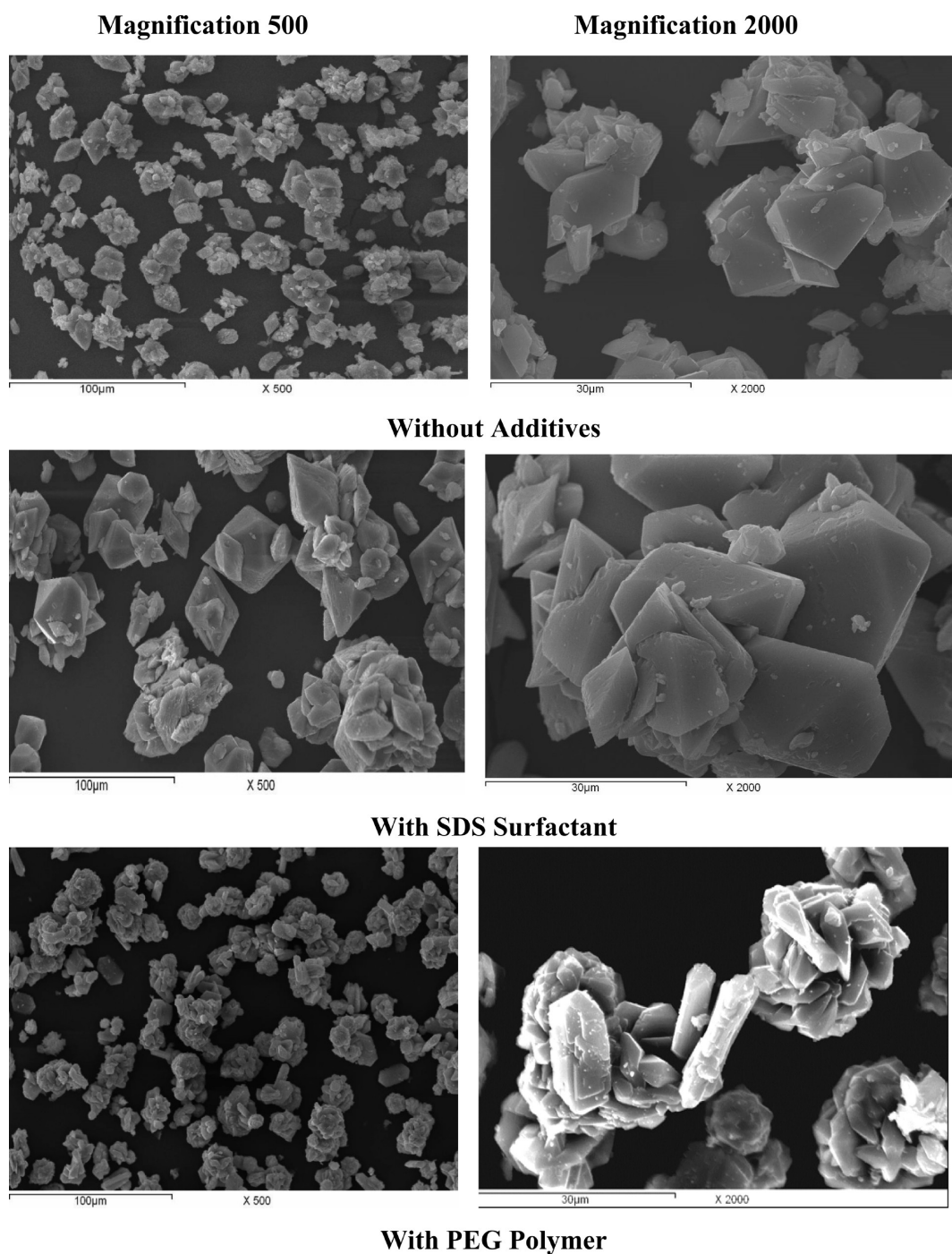


Figure 6. SEM photomicrographs of strontium malonate without and with additives at 4.3 supersaturation and different magnifications.

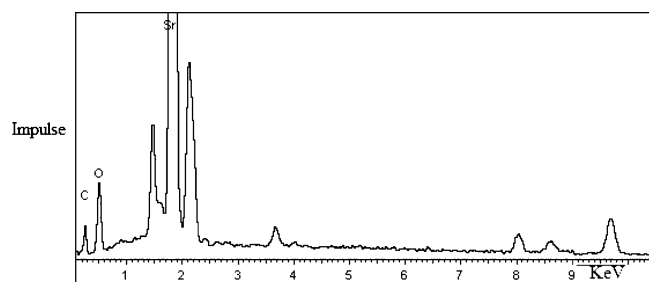


Figure 7. EDX spectrum of strontium malonate.

Table 4. Assignment of Some Selected FT-IR Wave Numbers of Strontium Malonate

IR, cm^{-1} (strontium malonate)	assignment of peaks	IR, cm^{-1} (pure malonic acid)
3013.2	$\nu\text{C-H}$	
1589.0	$\nu_{\text{as}}(\text{C=O})$	1720
1352.8	$\nu_{\text{s}}(\text{C=O})$	
947.8	$\nu\text{C-C}$	

group. The peaks appeared at $1589.06\text{--}1325\text{ cm}^{-1}$ are assigned to asymmetric $(\text{COO})_{\text{as}}$ stretch of coordinated carboxyl group and the absorption at 1352.8 cm^{-1} is due to $(\text{COO})_{\text{s}}$ symmetric

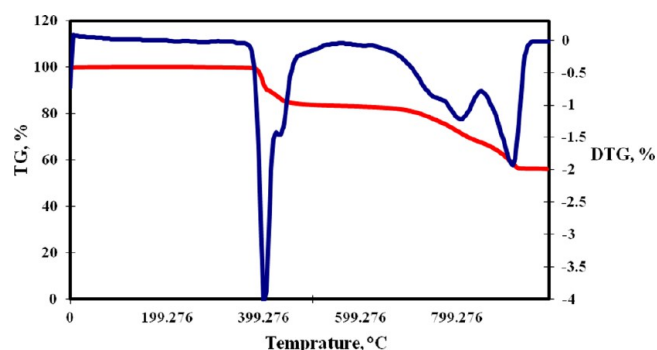


Figure 8. TG and DTA curve of strontium malonate.

vibration. The values of $\Delta\nu$ ($\nu_{as} - \nu_s$) for the material are 140 and 237 cm^{-1} . These high values of $\Delta\nu$ suggest bidentate chelating due to confinement of interaction with both oxygen atoms of carboxylate group. The peak of (C=O) of pure malonic acid appears at 1720 cm^{-1} .²³ The (C=O) stretching frequency has shifted from 1720 to 1589 cm^{-1} . The value of $\Delta\nu$ ($\nu_{free} - \nu_{complex}$) is 131 cm^{-1} . The frequency shifted to lower frequency by 131 cm^{-1} because of the oxygen atom of carboxyl group has coordinated with Sr^{2+} .²⁴ The obtained spectrum of strontium malonate crystals (Figure 9) shows a strong peak at 1165.76 cm^{-1} because of the asymmetric vibration (C–C)_{as} and another strong peak at 947.84 cm^{-1} because of the symmetric vibration of (C–C)_s. Thus IR spectrum of strontium malonate confirms the presence of malonate ligands.²⁵ The assignment of some selected absorption bands/peaks as observed in FT-IR spectrum is shown in Table 5.

CONCLUSIONS

Crystallization of strontium malonate without and with additives such as sodium dodecyl sulfate (SDS) surfactant or poly ethylene glycol (PEG) polymer are studied. The results indicate that (1) SDS or PEG decrease the induction time at all the supersaturations studied due to decreases the regular crystal

Table 5. Chemical Composition of Strontium Malonate

element	EADX results	theoretical results	C, H chemical analysis
C	22.3	18.9	21.7
O	31.5	33.7	
Sr	46.2	46.2	
H		1.1	1.4
total	100.0	100.0	

growth, (2) surface energy is decreased in the presence of SDS or PEG compared with the baseline, (3) nucleation rate is increased in the presence of SDS or PEG compared with the baseline, (4) the critical nucleus diameter and hence size is smaller in the presence of SDS or PEG, and (5) crystallite size is smaller in the presence of SDS or PEG.

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Notes

The authors declare no competing financial interest.

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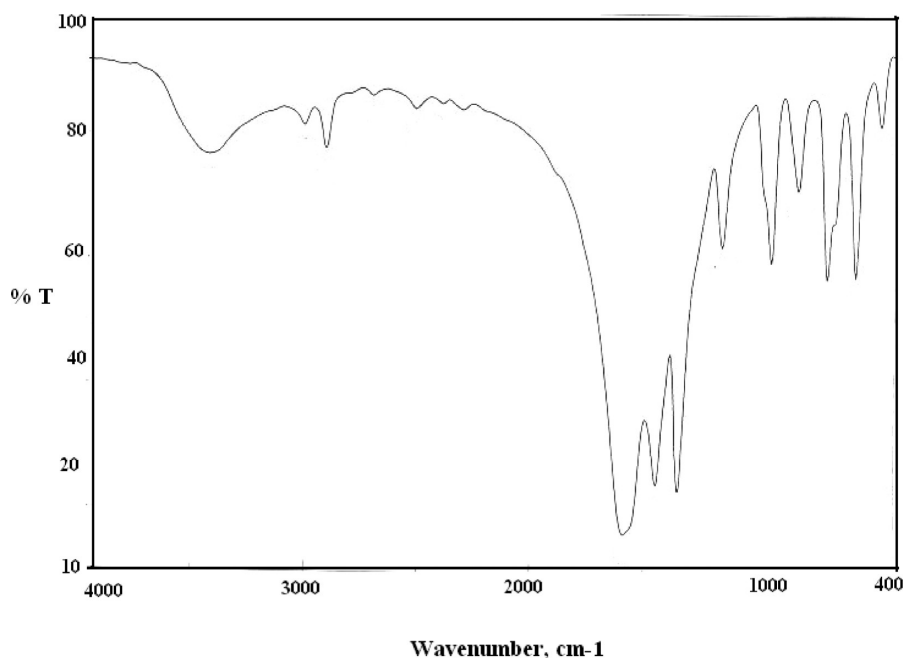


Figure 9. FT-IR Spectrum of Strontium Malonate.

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