Growth aspects of barium oxalate monohydrate single crystals in gel medium

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Single crystals of barium oxalate monohydrate ($BaC_2O_4.H_2O$, BOM) were grown in pure form by controlled diffusion of Ba^{2+} using the gel technique at different temperatures. Starting from aqueous Ba^{2+} chloride ($BaCl_2$) and acetic acid ($C_2H_2O_4$) in gel, this method offers a low-cost and an easiest alternative to other preparation methods for the production of barium oxalate bulky single crystals. The optimal conditions for the growth of BOM crystals in silica gel were found by investigating different growth parameters such as gel pH, gel aging and crystallization temperature. Irrespective of all such crystallization environments, growth rate of the crystals were initially less and then exhibited supersaturation effect leading to non-linearity. Gel aging and temperature has profound effect on nucleation density that resulted less number of crystals of maximum size in the gel matrix. Perfect single crystals were grown on gels of higher pH. The macropore morphology and porosity was controlled by changing age of the gel. It has been found that temperature has a fabulous effect in controlling the nucleation density by altering the supersaturation conditions for the formation of critical nuclei. The entire growth kinetics informed that the grown crystals were derived by the one dimensional diffusion controlled process.

1 Introduction

In this day and age, the availability of high-quality single crystals for many device characterizations is essential in several fields of materials science. For most of the investigations, best crystallization conditions for a specific system have been focused to attain huge single crystals by minimizing convection phenomena. Growing crystals in low gravity conditions, keeping unidirectional transport of the molecules and a controlled growth in porous network are the essential conditions to have better crystallization. Growth of pure and bulk crystals from gel is an inexpensive and simple technique that satisfies all these required conditions for crystallization [1,2]. In this technique, the gel works as a porous network that permits only the vertical transportation of the ions. Moreover, gel medium provides chemical species for the formation of crystals by keeping the diffusional path invariable all over the experiment. Consequently, gel technique has become more popular and has been used by several investigators [3-5].

Most oxalate compounds have shown to exhibit interesting applications such as precipitation agent [6], precursor for superconductive oxides [7], nano particles synthesis [8,9], magnetic and luminescent devices [10-12]. In addition, microporous oxalate materials have open-framework structure and are layered with honey-comb like apertures [13]. Oxalate ions $(C_2O_4)^{2-}$ are therefore engaged in constructing a large variety of molecular structures and frameworks by incorporating suitable metal ions in the crystal lattice. It can act as monodentate, bidentate, tridentate or tetradentate donor ligand and can form with metal centers, chains, layers

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or three-dimensional networks. Combined with the presence of water molecules that directly linked to the metal ions or weakly bonded to the framework, leads to a very large variety of structural architectures in one, two or three dimensions [14,15]. Moreover, by adopting thermal decompositions on mixed oxalates, variety of other compounds can be synthesized. Barium titanate is a well known compound that can be easily decomposed from its oxalate phase and form solid solutions [7]. Among the metallic ions studied, Ba^{2+} and Cd^{2+} ions have attracted a great deal of interest because it has rather simple chemistry and coordination geometry [16,17]. The thermal decomposition of various forms of barium oxalate has been extensively discussed by many research groups [18-20]. Barium oxalate has been reported to exist in two distinct forms; the neutral barium oxalate with various hydrated forms, and the acid salt of barium oxalate. However, detailed growth kinetics has not been discussed so far. The present paper gives an exhaust study on the growth kinetics of the monohydrated barium oxalate crystals ($BaC_2O_4.H_2O$).

2 Experimental

Reagent grade Sodium metasilicate ($Na_2SiO_3.9H_2O$, Merck), barium chloride ($BaCl_2.2H_2O$, Sigma) and acetic acid ($C_2H_2O_4$, Sigma) were used as obtained for the growth of barium oxalate crystals. Deionized water purified and filtered through a 0.25 μm pore size membrane was used for the preparation of all solutions. Silica hydrogels were prepared from a pure sodium metasilicate solution of density 1.04 g/ml by acidification with 1M acetic acid using the following equation:

$$V_{sms} = \frac{V_m \ (0.04)}{\rho_{sms} - \rho_w} ,$$ (1)

where V_{sms} is the volume of the sodium metasilicate stock solution to be taken, V_m is the volume to be measured, ρ_{sms} is the density of the sodium metasilicate solution and ρ_w is the density of water at room temperature.

After preparing sodium metasilicate solution of known density, titration plots were drawn in order to get gels of different pH for determining the gelling time and the reproducibility in the experiments. The resulting solution is then allowed to set in tubes of internal diameter 2.5 cm and length 20 cm. The set gel of the desired pH was then permitted to age for a specific time. In our experiment, gel aging for a period of 24, 48 and 72 hours have been attempted. This was followed by pouring upper reagent (1.5 M aqueous solution of barium chloride) along the sides of the tube to ensure no breakage on the gel surface. Ions in the supernatant solution (Ba^{2+}) diffused into the gel and its controlled reaction with the oxalate ions (C_2O_4)$^{2-}$ in the gel matrix resulted in the growth of barium oxalate crystals. The expected chemical reaction that led to the growth of barium oxalate is:

$$BaCl_2 + C_2H_2O_4 \rightarrow BaC_2O_4 + 2HCl$$ (2)

Crystals were appeared near the gel-solution interface within a day and prominent at the middle of the gel column within 2 days. Barium oxalate crystals were harvested after 10 days by removing the crystal disc along with the residue of gel and placed it inside water. After stirring lightly, the gel residues floated on the solution surface were removed by decantation. After three washings, the barium oxalate crystals were separated by filtration. After drying, the crystals were stored in a moist free atmosphere. Fully grown needle shaped crystals appearing inside the gel column and the harvested crystals are shown figure 1.

The density 'D' of the grown crystals was calculated using the formula [21]:

$$D = \frac{FW \ * \ Z \ * \ 1.66}{V} \ g/cm^3,$$ (3)

where, V is the volume of the unit cell in $Å^3$, FW is the formula weight, and Z is the number of formula units in a unit cell. With $Z = 4$ [22], the calculated density value of the barium oxalate crystal (3.483 g/cm^3) is almost equal to the reported bulk value [23].

BOM crystals were grown for various deposition conditions to have better crystallinity and perfection. From the repeated trials and measurements, optimized crystallization parameters for the growth of barium oxalate crystal are given in table 1.

During the growth of BOM crystals, their growth kinetics including crystal size and nucleation rate variations were studied with respect to gel pH, gel aging and crystallization temperature. The temperature of the growth environment was changed by immersing the crystallizer in a constant temperature bath. Powder XRD pattern of the samples were recorded to confirm the phase purity of the grown crystal. Obtained crystal data are: monoclinic, a = 8.703(4) Å, b = 7.971(2) Å, c = 6.868(7) Å, β = 99.64°, V = 469.72 Å^3 and space group P2$_1$/c with Z = 4. Observed values are in agreement with the previously reported standard values [23].

Table 1 Optimized growth parameters

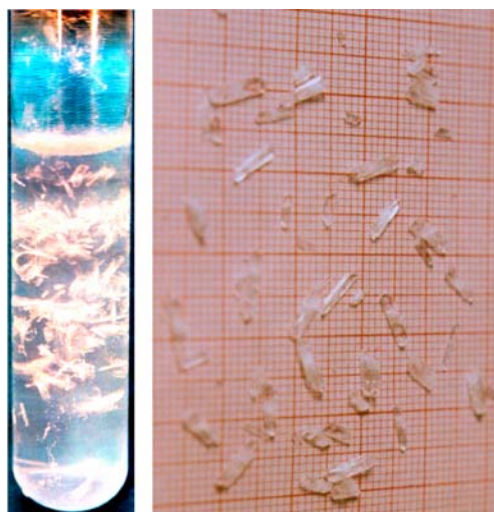| Crystallization parameter	Values
Crystallization temperature	30 – 50°C
Specific gravity of gel	1.04
Molarity of oxalic acid in gel	1 M
pH of gel	3.5-4.5
Setting time	1-2 days
Molarity of supernatant solution	1.5 M
Gel aging	1-3 weeks
Nucleation period	1-2 days
Maturity period	10 days
Shape of the crystal	Needle
Maximum crystal size	1.11 cm

Fig. 1 Barium oxalate crystals grown at the optimized conditions. (Online color at www.crt-journal.org)
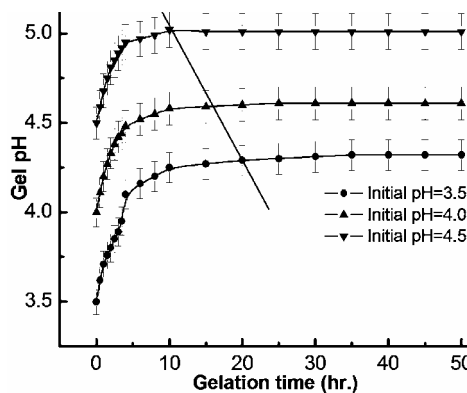

Fig. 2 Gelation time variations in gels of different pH at 30°C.

3   Results and discussion

Growth kinetics of barium oxalate crystals   The effect of various growth parameters such as gel pH, gel age and temperature on growth rate, and nucleation rate as measured by the total number of crystals that appear in the gel column were investigated by conducting separate experiments. Growth observations along with the variations in crystal counts are discussed with proper evidences and interpretations.

Gel and gelation time   Gel is a two component porous flexible polymer network soaking with water molecules. Gelation process, structuring polymeric cluster over the entire volume of the solution is different for physical gels and chemical gels. Chemical gel such as silica gel is obtained from the formation of strong bonds at moderate temperatures and has high efficiency for growing macromolecular compounds [24,25]. On building three dimensional solid polymeric phase during gelation, leave more number of pores filled with liquid phase that are useful for the controlled migration of ions and small clusters in one dimension leading to the formation of single crystals. The gelation period, time to stick to the crystal growth cell walls and resist flowing, depends on many parameters such as gel pH, temperature, concentration of species in solution, etc.

There are many methods of determining the gelation time of different types of gels. In one such method, the time taken is measured when the solution is fixed on the walls of the container during the polymerization process. After gelation, the entire amount of water is encapsulated in the porous polymer network and usually the gel does not pour. Also due to the cross linkage of the macromolecules that arises from the polymeric reaction, there is reduction in the pore size, which expels water form the pores, another indication of the closure of gelation period. However, the time required for gelation is very sensitive to initial pH of the gel. During gelation, there is continuous variation in gel pH due to expel of water from the cross linkages and therefore pH variation is stabilized only after completion of the gelation process. This is the easiest method of monitoring gelation period. In the present study, silica gel was prepared by neutralizing sodium metasilicate solution (specific gravity = 1.04) with 1M oxalic acid. The different solutions of initial pH 3.5, 4.0 and 4.5 were prepared and their gelation time as a function of pH variation is shown in figure 2.

It is observed from the plot that the gelation time is higher for low pH gel than that of high pH gels. The gelation time of the gel prepared for the initial pH value of 3.5 is more than 20 hours. Comparatively, high pH gels take lesser time to complete polymerization reactions, 15 hours. for gels of 4 pH and 10 hours. for 4.5 pH gels. This is because of the polymerization reaction that is slow in low pH alkaline solutions. However in high pH gels, the cross linkages are modified and the gel become more and more hard leading to retardation of free motion of the ions, which is essential for the controlled growth of the crystals.

Growth observations Migration of Ba^{2+} cations from the supernatant solution reacts with $C_2O_4^{2-}$ anions present in the gel and formulate the barium oxalate crystals. The incubation time required to visualize the first crystal varied from many hours to days depending up the concentration of the species and the pH of the gel. The minimum value of pH for which crystals of barium oxalate crystallized was 3.5. In the pH range studied, grown crystals attain spherulitic morphology. Spherulites are spherical aggregates of crystallites. They are radially oriented microcrystals arranged at non-crystallographic angles within a spherical envelop. In the case of barium oxalate, spherulite is described as needles fanning out from the centre with extensive branching as seen in figure 1. These spherulites grow from a single crystal nucleus in a direction perpendicular to c-axis lying in the plane of the crystal [26], since they have low solubility in water. Spherulitic crystallization may also be due to crystalline fibers growing radially from a common centre or a nucleus [27]. The occurrence of secondary nucleation at the growth front has also been emphasized [28]. However, Liesegang ring formation is not observed in all the gel pH studied. At the gel-solution interface, chances are more for nucleation resulting large umber of crystals and less spacing between crystals which minimizes the size of the crystals. At the bottom of the growth vessel, the density of nucleation was highly controlled and isolated nucleation sites were observed as seen in figure 1. As metal ions take more time to diffused deep into the gel, the number of crystals was decreased, resulted larger crystals with definite morphology. These crystals continued to grow for about 10 days and growth tapered off afterwards.

Nucleation and growth of BOM The growth of crystals from solution is known to be affected by mass transport processes. When mass transfer resistances are strong, changes in the hydrodynamic conditions of the solution have a direct impact on the crystallization kinetics. Such variations in crystal size as a function of time was noted during the growth of barium oxalate crystals in three gels of different pH. Crystal size variations are illustrated in figure 3.
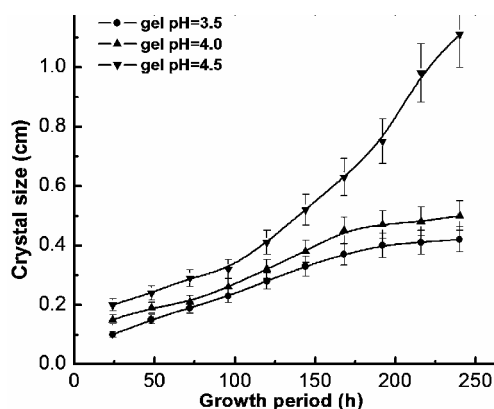

Fig. 3 Crystal size variations as a function of growth time.
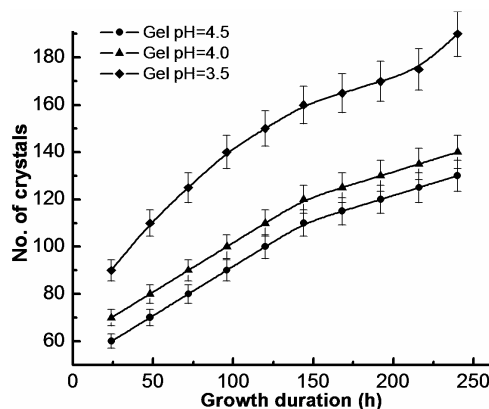

Fig. 4 Variation of nucleation density with growth duration.

In low pH gels, the growth rate is less and it leads to saturation due to increased nucleation density. The radius of pore in high pH gel is small which in turn reduces the migration of the species resulting bigger crystals at locations far from the gel-solution interface. The growth pattern of the curve obeys the equation,

$$L = \left(k \ t \right)^{\frac{1}{2}},\tag{4}$$

where, L, length of the crystal (cm), t, time of growth (h), 'k', Growth rate constant (cm^2/h.).

It represents a portion of a parabola, which is the characteristic of a one dimensional diffusion control process. However at the early stages of growth in optimized pH, a departure in linearity is observed. This may be due to transient period during which the steady state concentration transfer are established. The linear parabolic middle region reveals the supersaturation of the species needed for the growth process. The self sufficient supply of the required species results in the formation of highly perfect single crystals that confirms the constant surface supersaturation hypothesis [29]. During the final growth stage, the curve deviates from its linearity due to the shortage of the available solute for the formation of the required compound.

Nucleation rate Nucleation rate was estimated during the growth of the BOM crystals in three gels of different pH (3.5, 4.0 and 4.5). Gel pH has direct impact on nucleation kinetics that drastically changes the nucleation rate of the crystals. This variation is attributed to the variation in pore size of the gel matrix that controls the velocity of ions and the number of nuclei obtained all over the crystallization phenomena. Fig. 4 shows the variation of nucleation density of the barium oxalate crystals during the growth period of the first 10 days.

Gels with more acidic pH show more number of nucleation sites. Consequently, it is possible to say that gels with acidic pH have a more homogeneous porous size distribution [30]. Further in homogeneous nucleation, molecules come together and form a stable nucleus that grows in size to form critical nucleation that obeys the homogeneous nucleation theory. However in high pH gels, there is an exponential drop in the nucleation density that can be explained with nucleation rate (N) and supersaturation (S) [31].

$$N \ = \ N_0 \ \exp[-\delta\Omega^2\gamma^3 / k^3 T^3 (\ln S)^2],\tag{5}$$

where, δ is the shape factor, Ω is the volume of one growth unit in the nucleus, γ is the nucleus solution interfacial tension, k is the Boltzmann constant, T is the temperature in Kelvin and S is the supersaturation ratio ($S = C_0/C$, C_0 is the equilibrium solution concentration which is related to the solubility product and C is the solution concentration).

According to the nucleation theory, the amount of work that has to be done to form a critical nucleus is 'W' given by [32]:

$$W \ = \ 16\pi\Omega^2\gamma^3 / 3(kT \ln \ S)^2 .\tag{6}$$

The nucleation probability P is related to W and is given by [1],

$$P \propto \exp[-W/kT]\tag{7}$$

$$P \propto \exp[-16\pi\Omega^2\gamma^3 / 3k^3 T^3 (\ln \ S)^2] .\tag{8}$$

In the present study, growth is confined to one medium and therefore the interfacial tension 'γ' has no influence on the probability of nucleation. Also under isothermal growth conditions, the probability of nucleus formation depends only on supersaturation and therefore,

$$P \ = \ \exp[b/(\ln \ S)^2] .\tag{9}$$

Supersaturation depends mainly on the concentration of reactants and the diffusion rate of reactants in the gel medium. Since the concentration of the over head solution is kept constant in the study, diffusion rate depends only on the gel structure of the medium, which in turn depends on gel pH and gel age. This case favors the controlled growth of crystals in high pH gels and therefore, the number of crystals in the gel column increases as shown in figure 4. Increase in supersaturation leading to an increased number of crystals has been reported for the growth of tetragonal lysozyme crystals [32]. Gel pH thus has a profound influence on the gel structure and in turn on porous size. Moreover, gel structure has the property of cross linkage and becomes rigid in high pH gels leading to hinder the free motion of the ions, which is the main reason for the decrease of nucleation sites. It is also observed that the nucleation rate increases rapidly during the early stages of observation and

then it ceases at the end stages and move towards saturation. At this stage, the non-availability of chemical species tends to reduce/hamper the creation of new nucleation centers.

Nucleation control using gel aging Control of nucleation is of great importance because crystals that grow in any particular gel system compete with one another for solute. The competition reduces their size, perfection, and purity. If suppression has not been sufficient, various sol-gel parameters such as gel density, concentration of reactants, gel pH, intermediate neutral gel column, and concentration programming have been varied to grow good quality single crystals. By adopting gel-aging technique, the nucleation sites can be controlled by placing an overhead solution after a predefined period above the set gel. Gels of fixed pH 4.5 were prepared with 1 M sodium metasilicate and 1 M oxalic acid and allowed to set in a number of test tubes. The gels were allowed to age for different periods (1-3 weeks) before pouring 20ml of supernatant reactant of molarity 1.5 M. The variations of crystal count in gels of different age are shown graphically in figure 5.

As seen, the nucleation rate decreases as the age of the gel and pH are increased. This may be due to syneresis, during which the pore size gets reduced further so that less amount of reactant is transported through the gel for the formation of crystals that leads to controlled growth with less number of nucleation sites. These results are identical to the report previously concluded by H. K. Henisch [1,2] that the gel concentration and the gel age both have the effect of decreasing the average pore size of the silica gel. In the present study, purity of the crystal is retained only by adopting the gel-aging technique and by optimizing the pH of the gel to 4.5.
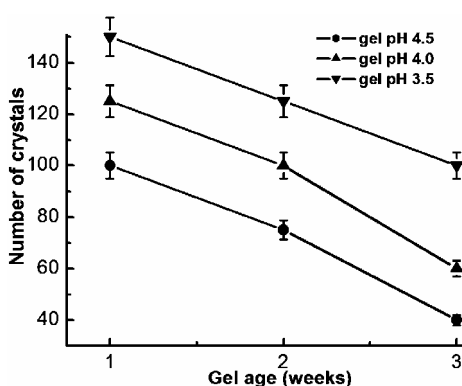

Fig. 5 Variation of crystal count with gel aging in three gels of different pH.
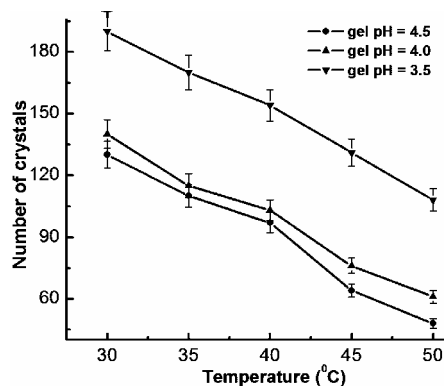

Fig. 6 Variation of crystal numbers with crystallization temperatures.

Nucleation rate and temperature Quality of the crystal can be increased by limiting the number of nucleation centers in the gel matrix. In addition to gel aging, steps have been taken to control the number of crystals by considering the temperature of the growth medium. The gelation and crystallization temperatures were kept constant at various temperatures ranging from 30 to 50°C in steps of 5 K. Temperature variations were set up by placing the crystallizer in a constant temperature bath, whose temperature variations can be adjusted to an accuracy of ± 0.1 K. High resolution traveling microscope was engaged for the measurements of the nucleation rate for the entire growth period of about 10 days. Observed variations are shown in figure 6 during the growth of the barium oxalate crystals in three different pH values studied.

It is observed that the nucleation rate decreases with increasing the crystallization temperatures. The decrease in number of crystals with temperature may be due to many of the associated crystallization parameter, like supersaturation, radius of the critical nuclei and the energy formation of critical nuclei. In the present study, nucleation is homogeneous without any impurities as revealed by the XRD measurements. According to the homogeneous nucleation theories, a stable nucleus with critical radius is expected to form due to recombination of ions and molecules. After attaining a critical radius, the crystal continues to grow if sufficient solute is available. Formation of critical nucleus needs supersaturation which is related to temperature as given according to Gibbs-Thompson [33,34] is:

$$\log S = \frac{2M\sigma}{RT\rho_c}, \tag{10}$$

where, M is the molecular weight of the solute, σ is the surface energy per unit area, R is the gas constant, T is the temperature, and ρ_c is the critical density. It is evident from equ. 10 that the supersaturation decreases with

rise in temperature. As supersaturation decreases, there is a decrease in nucleation density as evidenced from the experimental results. Moreover, as temperature increases there is a possibility of increase in solubility of the crystal nucleus in water which is available in the pores between the polymerized cross linkages in the gel. The solubility crisis also favors decrease in crystal count on increasing the temperature of the growth environment.

4   Conclusion

A systematic study has been carried out to understand the influence of various parameters on the growth mechanism of single crystals of barium oxalate. The growth kinetic studies reveal the dependence of nucleation density and ultimate size of crystals on diffusion rate of ionic species. Moreover, the transport of ions depends on the polymerized cross linkages on the gel matrix. Observed results show that the Gel pH and gel age are the prominent factors in deciding the gel structure. The decrease in nucleation density or number of nuclei in higher gel pH and aged gel has been explained as due to the decrease in pore size that diminishes the ion transport for the formation of nucleation. Effect of crystallization temperature on nucleation has been explained on the basis of supersaturation. As the temperature is increased, the nucleation density decreases due to decrease in supersaturation. The solubility of the nucleation center also increases with temperature. The overall optimized conditions for the growth of barium oxalate crystals have been found out and the gel method can be adopted to grow technologically important crystals like PbS, CdS, ZnS, etc.

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