

## Crystal Growth and Characterization of Carbonates of Calcium, Barium, and Strontium in Gel Media

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**Abstract.** The single crystals of calcium carbonate (calcite), barium carbonate and strontium carbonate have been grown in sodium meta silicate gel using the single and double diffusion methods at room temperature. The X-ray Laue-technique is used to characterize the gel grown calcium carbonate crystal. It has been observed that the gel medium prevents the turbulence and helps the formation of good crystals. Further, the varying density of gel can control nucleation and the growth at each stage that may be observed in a transparent medium. The general chemical reaction is taken in this case.

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### 1 Introduction

The solids are characterized by nearly perfect periodicity of atomic structure. The geometric regularity of atomic structure provides a simple picture of a crystal and helps a lot in gaining the knowledge of the physical properties of the solid [1,2]. In a crystalline solid, the atoms are arranged in a regular manner, *i.e.* the atomic array is periodic. Each atom is at regular intervals along arrays in all directions of the crystal. The crystalline solid has directional properties, which are also called isotropic or anisotropic substances accordingly [3-5].

The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds. Gel-growth is an alternative technique to solution-growth with controlled diffusion and the growth process is free from convection. The growth of single crystals in gel is a self-purifying process, free from thermal strains which is common in crystals grown from melt [6]. The gel method has also been applied to the study of crystal formation in human system, such as cholesterol stones, sex hormones, *etc.*

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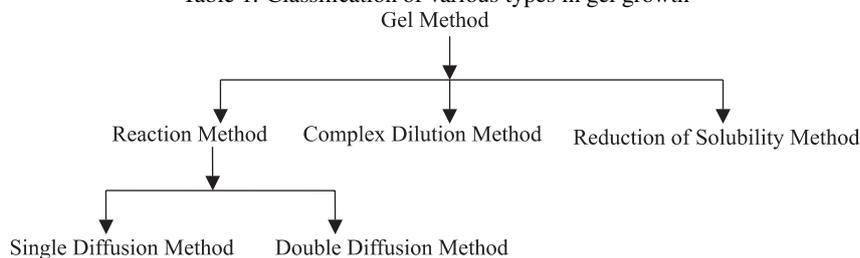
Crystals play major role in biology also. Most of the living beings form crystals. In human body, there are many minerals, which present in dissolved form. The body fluids contain minerals at various levels of saturation. When the body fluids get supersaturated with minerals, crystallization takes place. These crystals have both beneficial, as well as pathological effects on humans. The major beneficial role of mineralization is formation of bones and teeth, which consist of oriented microcrystals of hydroxyapatite. Our sense of balance and acceleration is dependent upon small calcium carbonate (calcite) crystals present in the inner ear. The pathological effects result in the crystal deposition diseases. The increasing incidence of crystal deposition diseases, such as heart disease, gout, gallstones, urinary stones *etc.*, among population has resulted in an extensive research on this. Gallstones consist mainly of cholesterol with some quantities of calcium phosphates and calcium carbonates. The clusters of small crystals formed in the urinary system give rise to urinary (renal) calculi, which consist primarily of different forms of calcium, such as calcium oxalates, calcium phosphates *etc.*

The crystallization experiments that are intended to understand different problems should be carried out in a gelatinous medium rather than solutions or suspensions. Thus, gel-growth seems to be an ideal medium to study the crystallization of biomolecules as its viscous nature provides simulation of biological fluids in which it grows. Many theories have been pronounced to explain the mechanism of the stone formation and growth [7]. However, none has satisfactorily accounted for all aspects of crystallization problems.

One of the main problems is in determining whether nucleation is essentially homogeneous and takes place spontaneously from highly supersaturated fluids or whether it is heterogeneous and is initiated by some other agent, such as trace elements (Ba, Sr, Pb, Mg, Zn, *etc.*). It has been suggested that some trace elements enhance the growth rate of deposits of crystalline compounds and their high concentration in body fluids and tissues may be significant in this respect. The quantitative determination of the trace elements in the calculi and in the surrounding body fluids is essential for the understanding of etiology of the crystal deposition diseases.

The principal aim in this area is to identify the mechanism of crystal growth in conditions prevalent in biological systems, and to devise means of inhibiting the unwanted crystal growth. In the present investigation reaction method is used to prepare the gel-grown crystals. The various classification of gel method is shown in Table 1. The author's interest is to grow the single crystals (*i.e.*, calcium carbonate  $\text{CaCO}_3$  and barium carbonate  $\text{BaCO}_3$ , strontium carbonate  $\text{SrCO}_3$ ) in sodium meta silicate ( $\text{Na}_2\text{SiO}_3$ ) gel because the sodium meta silicate medium permits the reactants to diffuse at a controlled rate.

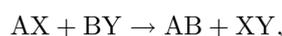
Table 1. Classification of various types in gel growth



## 2 Experimental

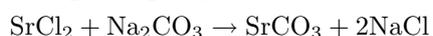
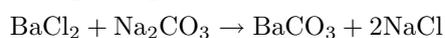
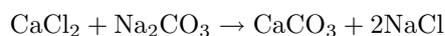
### (A) Materials and Methods

The solutions of two suitable compounds give rise to the required insoluble crystalline substances by mere chemical reaction between them. They are allowed to diffuse into the gel medium and to react chemically as follows:



where AX and BY are the solutions of two compounds, which on reaction give rise to the insoluble substances AB and also the waste product XY being highly soluble in water [8-10].

The reaction taken is



$\text{BaCO}_3$  crystals are grown by using  $\text{K}_2\text{CO}_3$  also.

### (B) Advantages of Silica Gel

Even though crystals can be grown in a variety of gels, the general observation is that silica gel is the best to grow, which can be regarded as a loosely interlinked polymer. Better crystallinity of products is the main advantage. It does not need any heating effects. There is no need of additional acid as well as alcoholic substances. It is comparatively cheap and best also.

### (C) Preparation of Gel

The gel is a two-component system with highly viscous, semi-solid in nature and having the fine pores through which diffusion takes place. The gelling process

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takes a definite amount of time that varies from minutes to days depending upon the nature of material and its temperature. The gelling time is always approximate in case of silica gel and the mechanical properties of fully developed gels are found to vary widely depending on the density and prescribed conditions during the gelling process.

In the present work, the various concentrations of gel solutions are used with acetic acid as pH reducing agents. The pH values of sodium meta silicate ( $\text{Na}_2\text{SiO}_3$ ) solution having densities 1.04 and 1.05 gm/cc are reduced individually using acetic acid. It is observed that the pH values in the range of 6-7 are showing good results. It is true that the gelation depends on pH of the gel solution. Further, the growth of crystal depends on the structure of the gel medium, which is indirectly related with the width of the pores, the rate of diffusion and temperature.

#### **(D) Growth of $\text{CaCO}_3$ , $\text{BaCO}_3$ , and $\text{SrCO}_3$ Crystals by Single Diffusion Method**

In this method, one of the components  $\text{Na}_2\text{CO}_3$  (inner reactant) of 0.1N, which is highly soluble in water and chemically inactive with the gel, is impregnated in the gel solution of 20 ml having the density 1.05gm/cc. The pH value is adjusted to 6.0 using acetic acid. After the gelation, the other component  $\text{CaCl}_2$  (outer reactant) of 0.1N is taken over the set gel. This solution on diffusion through gel medium reacts with the inner reactant and the nucleation process is taken nearly three days. The growth process of  $\text{CaCO}_3$  crystals is ceased after three weeks. At the same time, during the chemical reactions, other compound  $\text{NaCl}$ , which is highly soluble in water and it dissolve in water present in the hydro gel medium. The grown calcium carbonate crystals are shown in Figure 1. For the growth of  $\text{BaCO}_3$  crystals, gel solution of density 1.05 gm/cc and the pH of 7.0 with 0.1N  $\text{Na}_2\text{CO}_3$  have been taken. After gelation, the outer reactant  $\text{BaCl}_2$  of 0.1N is poured over the set gel. The nucleation starts within two days. The growth process of  $\text{BaCO}_3$  crystals is ceased after three weeks. For  $\text{SrCO}_3$  crystals, the gel solution of 1.05 gm/cc with the pH value of 8 provides the suitable condition for the nucleation. 0.1N of  $\text{SrCl}_2$  solution is poured over the set gel. The nucleation process took nearly four days. The growth process is very slow and less numbers of triangular crystals have been formed. The growth process is ceased after three weeks. The gel grown  $\text{SrCO}_3$  crystals are shown in Figure 2.

#### **(E) Growth of $\text{CaCO}_3$ , $\text{BaCO}_3$ Crystals by Double Diffusion Method**

A gel solution of 40 ml having the specific gravity 1.05 gm/cc is adjusted to a pH value about 7, using acetic acid into the U-tube. Further, 0.1N solution of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  are poured over the two limbs of U tube to form  $\text{CaCO}_3$  crystals. The two components can meet each other at the common region of

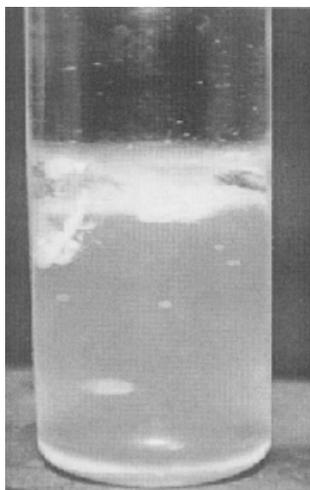


Figure 1. The gel grown  $\text{CaCO}_3$  crystals by single diffusion (test tube) method

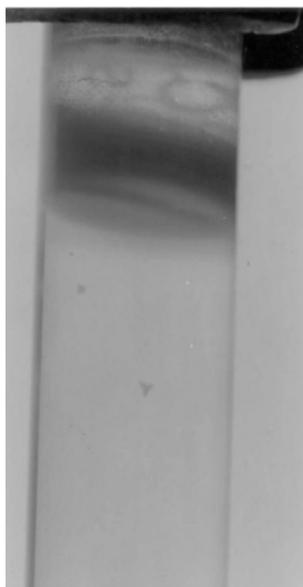


Figure 2. The gel grown  $\text{SrCO}_3$  crystals by single diffusion (test tube) method

the gel medium because of diffusion, normally, the bent portion of the U tube. They react chemically without vigorous chemical effects allowing the formation of  $\text{CaCO}_3$  crystals in gel. The nucleation starts after three days and the crystallization is ceased after two weeks. The same condition is followed for  $\text{BaCO}_3$  crystals too, instead of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ,  $\text{K}_2\text{CO}_3$  and  $\text{BaCl}_2$  are taken to grow  $\text{BaCO}_3$  crystals. The grown  $\text{BaCO}_3$  crystals are shown in Figure 3.

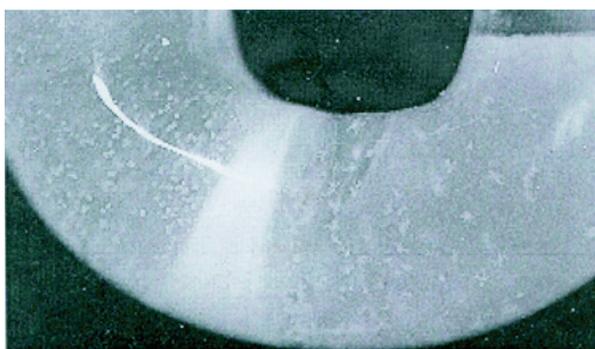


Figure 3. The gel grown  $\text{BaCO}_3$  crystals by double diffusion (U tube) method

### 3 Results and Discussion

The grown single crystal of calcium carbonate using gel technique is shown in Figure 4. The physical dimension of  $\text{CaCO}_3$  crystal is found to be around  $3 \times 2 \times 0.2$  mm. This size is sufficient for different characterizations. The grown crystals are mostly diamond shaped that may be due to changes in gel density. Further, the different shapes of crystals are also obtained. The magnified  $\text{BaCO}_3$  crystals are shown in Figure 5. The size of the crystals is about  $1 \times 1 \times 1$  mm and the radius of the sphere is about 0.5 mm. The crystal grown in  $\text{K}_2\text{CO}_3$  as one of the reactant is also having good size. This size is fairly large to be used for any studies like IR, UV, Raman scattering, *etc.* This size is sufficiently large for X-ray studies recording any type of photograph and suitable for counter techniques. The triangular  $\text{SrCO}_3$  crystals are very weak and they have deformed to tiny crystals when they recollect from the gel. Therefore, defining the dimension of the crystals becomes impossible.

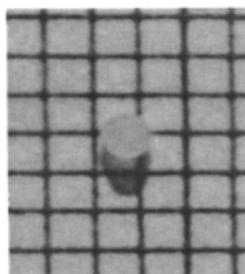
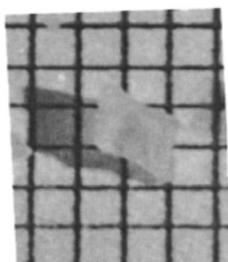
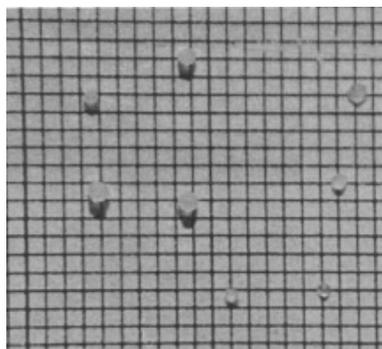
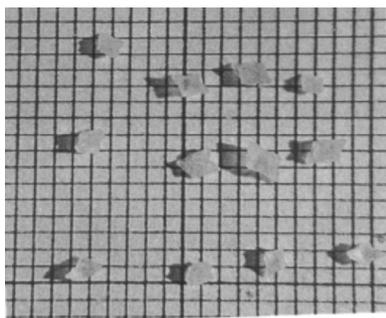


Figure 4. The magnified  $\text{CaCO}_3$  crystals

Figure 5. The magnified  $\text{BaCO}_3$  crystals

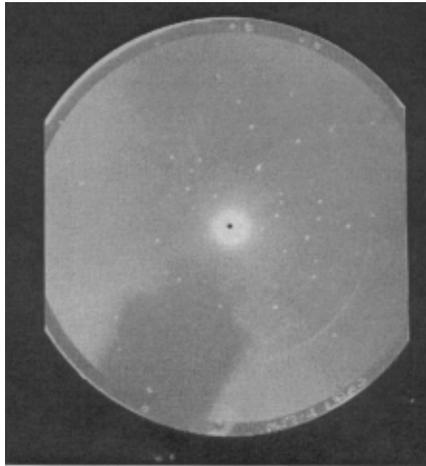


Figure 6. The X-ray Laue photograph of CaCO<sub>3</sub> crystal

#### Characterization Using X-rays

In order to determine the quality of gel grown crystals, the X-ray Laue technique is used [11] and the CaCO<sub>3</sub> crystal is chosen to serve the purpose. The X-ray is generated using 30 KV and 100 mA from copper target. Nickel filtered CuK $\alpha$  radiation is used for recording the Laue photograph. The crystal to film distance is set as 4.5 cm and exposure time is allowed about 3 hours. The recorded Laue photograph is shown in Figure 6. The Laue spots are seen to be highly perfect, without any diffuse scattering and a trace of resemblance of powder diffraction lines. Hence, the grown crystals are highly perfect single crystals, which may be suitable for further studies on structure property of the crystals.

#### 4 Conclusion

Varying the density of gel can control nucleation and the growth at each stage that may be observed in a transparent medium. Usually the crystals grown by slow evaporation method will be of inferior quality. Such crystals cannot be used for some fine physical characterization and only perfect single crystals will serve the purposes. It has been realized that the gel method is one of the best methods of growing quality single crystals that can be useful for various applications in medicine. In the present work, CaCO<sub>3</sub>, BaCO<sub>3</sub> and SrCO<sub>3</sub> crystals have been grown successfully. The comparison of size of the gel grown crystals are CaCO<sub>3</sub> > BaCO<sub>3</sub> > SrCO<sub>3</sub>. This indicates that the growth of calcite crystals is fast compared to other two, which are playing a major role in the formation of Gallstones and other problems. In the present investigation, among the numer-

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ous trace elements, that enhance the growth rate of deposits the calculi, barium and strontium have been taken and barium is showing faster growth than the strontium.

### **Acknowledgements**

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