

GROWTH OF MONO AND MIXED RARE EARTH HYDROGEN SELENITE CRYSTALS

4.1 Introduction

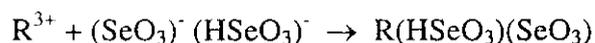
Rare earth selenites were discovered by J. J Berzelius in 1818¹. He prepared these materials by the combination of selenium and cerium, thus becoming the pioneer in this isolated field. Later the Swedish scientists, P. T. Cleve² and L. F Nilson³, as well as S. Jolin⁴ in France prepared a number of selenites, including the hydrogen selenites. The anhydrous selenites were prepared by Espil⁵. It is surprising to note that, after this initial active research period nearly a century passed before the studies were continued in Brasil by Giesbrecht etc. et al.^{6,7} and Giesbrecht and Gioloto⁸. Recently, A. Castro, Pedro et al⁹ have done some work on rare earth hydrogen selenites. They grew hydrogen selenite^{10,11} crystals of micrometer size and studied the structure of these compounds¹². In this work the author¹³ employs the technique of gel growth for the first time to prepare rare earth hydrogen selenites and its mixed crystals. This chapter gives the various techniques involved in the growth of the six crystals, where three are mono rare earth hydrogen selenite crystals and the



other three are the mixed rare earth hydrogen selenite crystals containing same elements in hydrosilica gel medium.

4.2 Chemical reaction associated with growth

In the rare earth family the lanthanides behave as typical hard acids which very easily join as oxygen donor ligands¹⁴. The complexes formed by the lanthanides are labile in solution because of the absence of extensive interaction with the 4f electrons¹⁵. Solubility difference may be due to the lanthanide contraction, i.e. the decrease in ionic radius. This results in a decrease in basicity along the series, which are reflected in a decrease in solubility of the hydroxides, oxides, carbonates, oxalates and selenites. The decrease in basicity means the increase in acidity of lanthanide which provides an opportunity for employing co-ordinating ligands with them. All these habits of the lanthanides have a characteristic role on the growth of lanthanide hydrogen selenite crystals. The trivalent lanthanide combines with selenites (HSeO_3^- , SeO_3^-) to form salts. The chemical reaction can be represented by



Where R stands for rare earth element (lanthanide) which admixture with the selenous acid (H_2SeO_3) to produce their salts. The mixed crystals can be obtained by admixing another rare earth component in a stoichiometric amount with the reactants. Mixing of Pr^{3+} , Nd^{3+} and Sm^{3+} ions, produces complexes $[\text{RR}_1(\text{HSeO}_3)(\text{SeO}_3) \cdot 2\text{H}_2\text{O}]$. The controlled diffusion of rare earths is possible by employing gel diffusion technique for the crystallisation of the compounds.

4.3 Hydrosilica gel as growth medium

The gel is found to be one of the best medium to grow number of organic and inorganic crystals¹⁶. It was prepared from commercially obtained water glass (sodium meta silicate). It is observed that the commercial grade sodium meta silicate shows better results than the analar grade one. The assay may help to start nucleation in the gel. However the presence of impurities in the gel may result in the growth of crystals having improper morphology.



4.3.1 Preparation of hydrosilica gel

A known mass of finely powdered sodium meta silicate (SMS) is dissolved in a known volume of doubly distilled water. The solution is kept idle for 2 hrs in dark room or in covered bottle for sedimenting the insoluble particles or impurities. The pure solution collected from the top of the solution is centrifuged and filtered by using double filter paper to get impurity free SMS solution. The density of this filtrate is adjusted to the desired value. The solution thus obtained is treated as 'stock solution'. The density of this clear solution is measured accurately, as it is critical for the gellation and quality of the gel¹⁶. By plotting a graph of specific gravity versus the percentage of water in the stock solution (fig. 4.1), the quantity if the water required for mixing to fix the density of the gel for any desired value can be found out. The stock solution of required volume is taken and mixed with the doubly distilled water. The volume of water to be added is found out from the graph and the solution of desired density is prepared.

In order to get quality gel it is necessary to mix an acid of required concentration to the sodium metasilicate solution, which is basic in nature. The aim of the experiment is to grow hydrogen selenite crystals of rare earth elements. The reaction technique is used to grow the crystals in the medium. Inner reactant is prepared by adding sodium metasilicate solution to selenous acid (H_2SeO_3) solution and adjusting the pH to the required value.

0.5M selenous acid solution is taken in a beaker or flask and the sodium metasilicate solution of fixed density is added drop by drop while agitating to ensure homogeneity. The pH is measured by using a digital pH meter immediately after the addition. The process has to be continued to get a required pH.



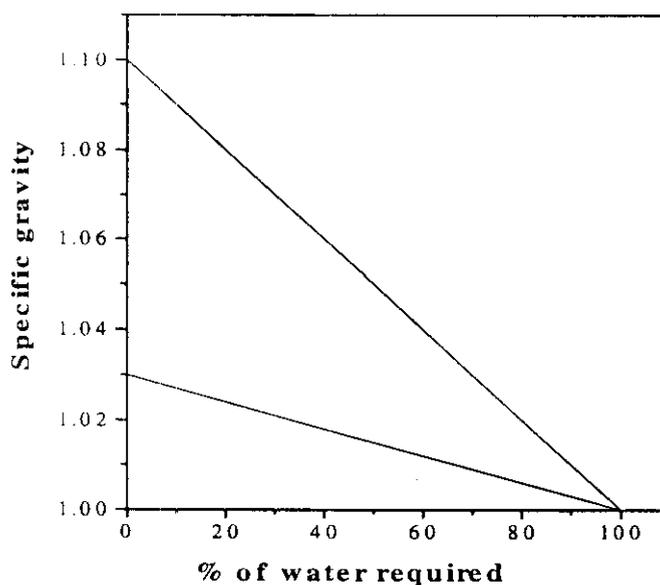


Fig. 4.1. Specific gravity of SMS solution Vs the partial volume of water

The value of pH has an important role in the gellation period. Depending on the value of pH the gellation period varies from a few minutes to some hours (fig. 4.2). When the pH is just above the neutral pH, which means that the gel is slightly basic, quick setting of the gel is observed. Pouring of quick set solution into the crystalliser will result in trapping air bubbles in the setting gel. Hence utmost care is to be taken while preparing gels of pH values between 6 and 7.5. The period of gellation is increased when the acidity of the solution increased. The dependence of pH on the growth and gel features forms a part of this study. The crystallisation vessels selected are test tubes of 20cm in length and 2.5cm diameter.

The test tubes are rinsed several times in doubly distilled water and dried. After measuring the pH of the mixture solution, it is taken into the tube and kept it for gellation. The mouth of the test-tube is covered with a stopper to avoid the inclusion of impurities during gelling. Constant temperature bath is used to maintain stable thermal condition for crystallisation.

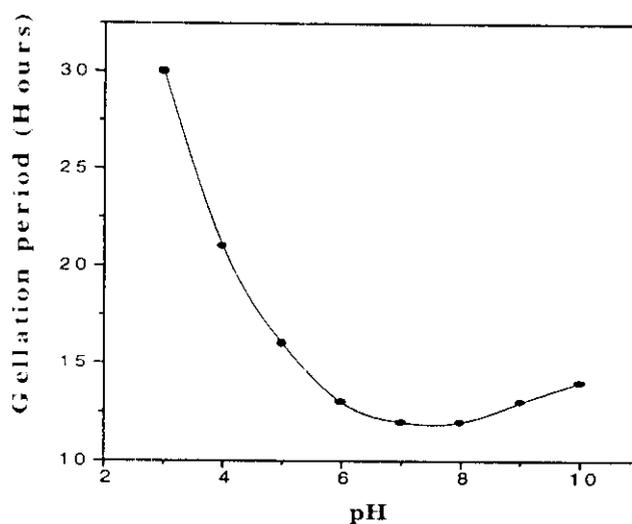


Fig. 4. 2. Gellation period Vs pH of the gel medium

4.4 Preparation of feed (supernatant) solutions

Analar grade praseodymium nitrate, neodymium nitrate and samarium nitrate (99.99% pure, supplied by IRE Co. Cochin) have been used for the preparation of the feed solution. In order to grow mixed crystals, the feed solution is prepared by mixing required proportion of the constituent rare earth nitrates.

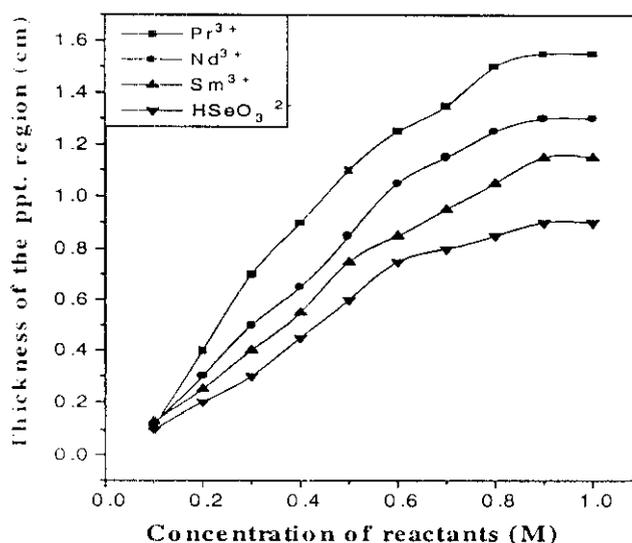


Fig. 4. 3. Thickness of the precipitation zone Vs concentration of the reactants

After pouring the outer reactants (feed solution) over the surface of the gel the mouth of the tubes (crystalliser) are covered with stoppers and kept in their parking slots of the test-tube stands for crystallisation. The growth rate of crystals depends on such factors, like diffusion rate, pH of the medium, density of the gel, concentration of the reactants, surrounding temperature etc. These are discussed in the following sections.

4.5 Observed growth kinetics of rare earth hydrogen selenite crystals

4.5.1 Praseodymium hydrogen selenite

To grow praseodymium hydrogen selenite (PHS) crystals the outer reactant praseodymium nitrate of 0.5M concentration is poured over the required aged gel. After pouring the feed solution a thin greenish white precipitate layer of small thickness is found to form on the gel solution interface. Thickness of the precipitation is increased with the concentration of the upper reactants. This is because of the greater concentration of the ions at the gel solution interface. The precipitated form is actually spurious nucleation. The actual crystallisation needs much longer time. Slow diffusion and a specific concentration are essential for perfect growth. When all the required conditions are satisfied, crystallisation starts. The concentration programming of the reactants shows remarkable changes in growth rate and quality of the crystals. It is found that the thickness of the precipitation zone near the gel solution interface is considerably reduced when the concentration of the praseodymium nitrate solution is reduced. Almost similar results have been observed by the reduction of selenous acid concentration in the gel (fig. 4.3). This may be due to the fast diffusivity of the ions at first and then its propensity to reduce the negative potentials¹⁶.

The precipitation zone is found to be predominant at the time of pouring of feed solution. As the time advances the thickness of the precipitation front reduces and after about 25-30 hrs of continuous diffusion greenish tiny crystals starts appearing at the lower part of it.



4.5.1 (i) Effect of the pH value

The pH value of the medium has a characteristic role to play in the growth process and growth features of hydrogen selenite crystals. Thickness of the precipitation region, nucleation density, etc. are influenced by the pH value. When the pH value is lowered the density of nuclei is reduced. These experiments are conducted at constant temperature, density and concentration of the reactants in all the crystallizers. The results depicted in fig. 4.4 shows the variation of population density with the change in pH. It is found that well-defined crystals having good optical qualities are obtained for a pH of 7. The observed results shows that all the three types of crystals (PHS, NHS and SHS) behave in similar manner.

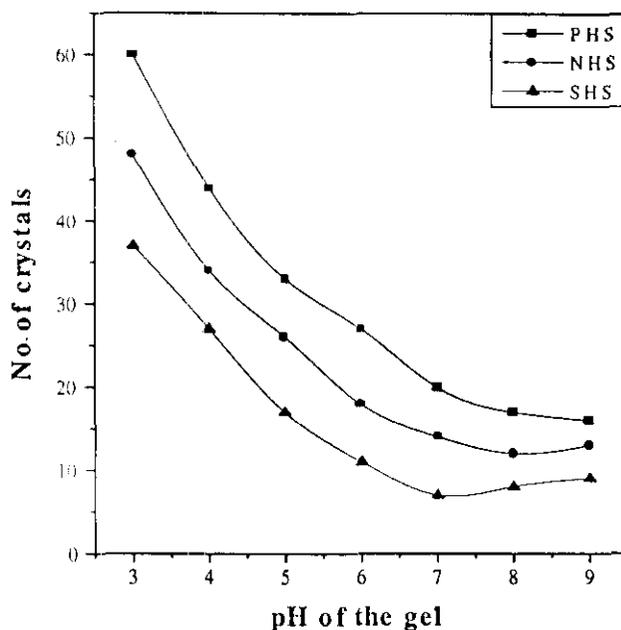


Fig. 4.4. The variation of number of crystals with the pH of the set gel of specific gravity of 1.03

4.5.1 (ii) Influence of gel density and ageing

The gel density also plays a role on the crystal size, nucleation density and quality of the crystal. The gel having a density range of 1.01-1.1 gm/cc has been utilised to study the growth of all the crystals described in this work. This has been done by

keeping constant all other parameters such as temperature, pH concentration of the reactants, etc.. The crystallisation was observed in the crystalliser below 1.06 g/cc density. It is found that the quality of the grown crystals is highly influenced by the density of the medium. In the case of the rare earth hydrogen selenite crystals, good quality crystals are obtained for densities between 1.02 –1.03g/cc. On the other hand, when the density is too high nucleation is found to be very poor (fig. 4.5). When gel becomes harder, the rate of diffusion and rate of reaction get reduced. In the current case, a few twinned crystals resulted at higher density gel. This may be due to the exertion of constraints on the growing surface of the crystals by the gel medium which results in the abnormal rate of growth of these crystals.

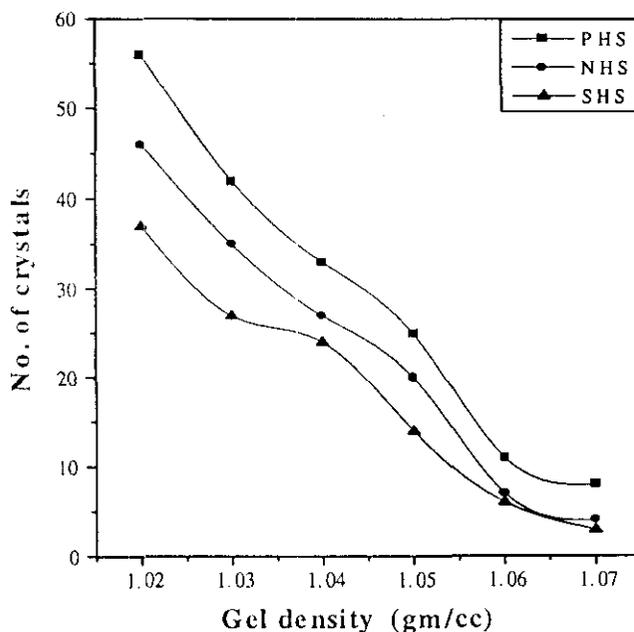


Fig. 4.5. Variation of nucleation density with the specific gravity of the gel

Ageing of the gel plays an important role on the physical property of the gel; it hardens the medium. This is due to the dehydration due to the free stay of the gel. In the case of the growth of the rare earth hydrogen selenite crystals gels of age 20 days or more do not give any crystallites up to 2.5cm below the gel solution interface, as the top surface of the gel gets dried and as a result the anions contained

in it wither off. When the diffused ions reach a particular level it attains a minimum concentration appropriate for the nucleation. It appears to be due to the non-uniform hardening of the gel column. The top surface of the gel being more hardened than that below, the transport of the anions is retarded. Fig. 4.6 shows the variation of nucleation density (number of crystals) with the age of the gel.

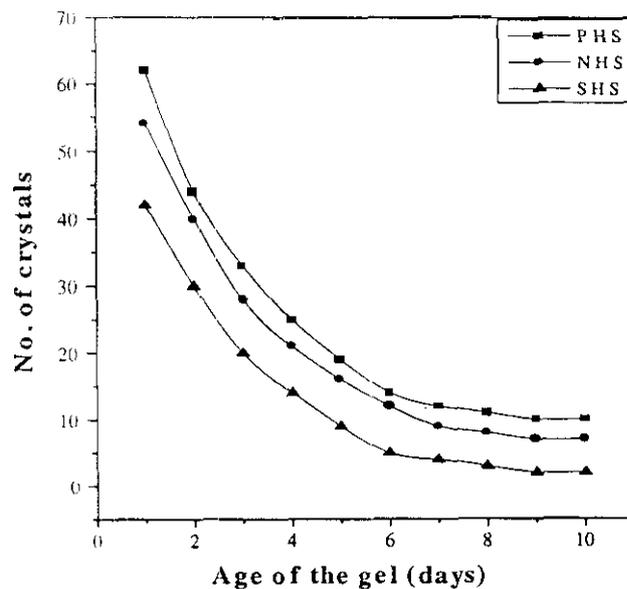


Fig. 4.6. Nucleation density Vs age of the gel

4.5.1 (iii) Influence of the concentration of reactants

The concentrations of the reactants play an important role on the growth of the crystals. In the case of a system where gel is of a fixed density 1.03 gm/cc, pH of 7 the nature of the growth of crystal will depend on the concentration of the reactants. The study has been carried out by varying the concentration of inner reactants (H_2SeO_3) or by changing the concentration of the supernatant solution. It is observed that the outer reactants play a major role on the growth rate, number of crystals and morphology of the crystals.



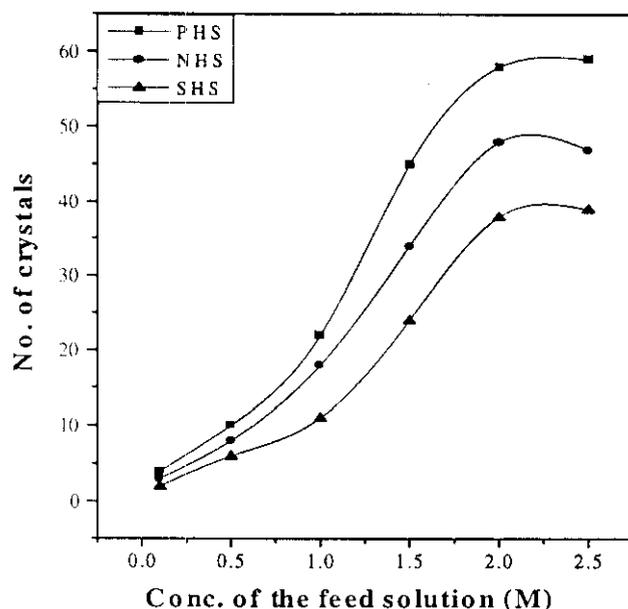


Fig. 4.7. Nucleation density Vs concentration of the feed solution

Detailed study has been done by varying the concentration of the selenous acid (0.1 to 1M) added in the gel while the concentration of praseodymium nitrate kept as a constant (0.5M). The concentration of the acid solution controls the pH of the gel, so it is observed that the results obtained by varying the concentration of the acids are similar to that of results obtained by pH variation. In another set of experiments concentration of the feed solution has been varied from 0.25M to 1M while the concentration of selenous acid in the gel is kept a constant. The growth features, morphology and number of the crystals were found to be highly influenced by the concentration change. The influence of concentration of the feed solution on the number of crystals obtained is depicted in the graph (fig. 4.7). Good quality crystals are obtained only at a range of concentrations of 0.4M – 0.6M. Below this range, the crystals formed are very small and above this range, spurious nucleation, twinning of the crystals etc. have been observed. The change in transparency is also observed due to the variation in feed solution concentration.

The mono (single) rare earth hydrogen selenite crystals, viz. praseodymium hydrogen selenite, neodymium hydrogen selenite and samarium hydrogen selenite have shown

almost similar type of growth kinetics. A typical case of mono rare earth hydrogen selenite is shown in fig 4.7. The results are the same in the case of neodymium hydrogen selenite and samarium hydrogen selenite. The slow diffusion of the anions into the gel and their subsequent reaction with the selenite ion will result in the formation of crystals of the expected morphology. The photograph (fig. 4.8) shows the crystals thus obtained in the crystalliser.

4.5.2 Growth of mixed hydrogen selenite crystals

4.5.2 (i) Praseodymium neodymium hydrogen selenite

In the case of praseodymium neodymium hydrogen selenite (PNHS) crystals, the method utilised is the same as in the growth of mono (single) rare earth hydrogen selenite crystals. The gel containing selenite ions was taken in a crystalliser and after proper setting, the required concentrations of praseodymium neodymium nitrate solutions are poured gently over the properly aged gel. The slow diffusion of the anions into the gel and their subsequent reaction with the selenite ion will result in the formation of crystals as expected (fig. 4.9). Nucleation density, morphology, advancement of the precipitation region are all influenced by the different parameters as discussed in the case of praseodymium hydrogen selenite. The results of these experiments are discussed in the following sections. After the completion of the growth process the crystals are harvested from the vessels and tested for the presence of various rare earth ions by different versatile techniques.

4.5.2 (ii) The effects of pH

One of the important factors influencing the growth features of the grown crystals is hydrogen ion concentration or pH. A wide range of pH values are selected for the current study. The influence of pH on the growth of praseodymium neodymium hydrogen selenite crystals has been studied by varying the pH of the medium from 4 to 9 by changing the acid level of the gel medium. All the other parameters are kept constant for the experiment. The variation on the nucleation density with pH is depicted on fig.4.10.



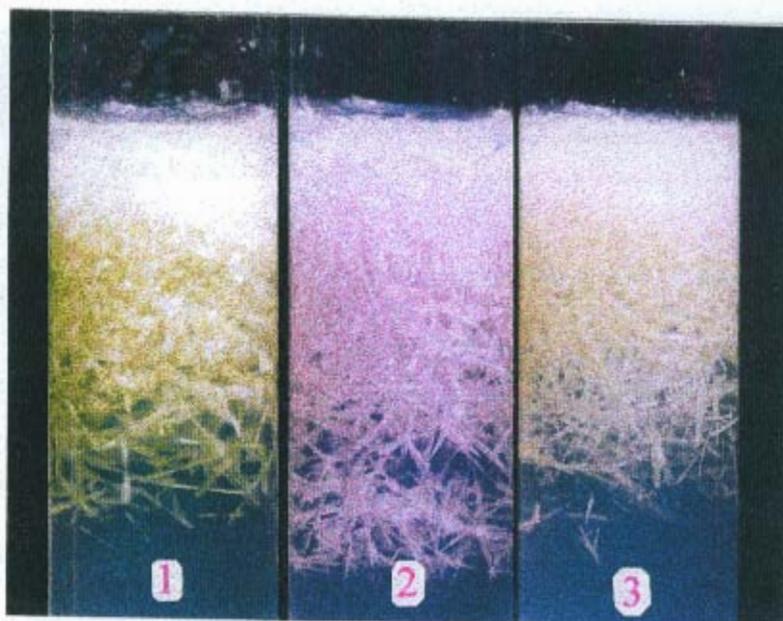


Fig. 4.8. The crystalliser containing the mono (single) rare earth hydrogen selenite crystals

1. PHS 2. NHS 3. SHS

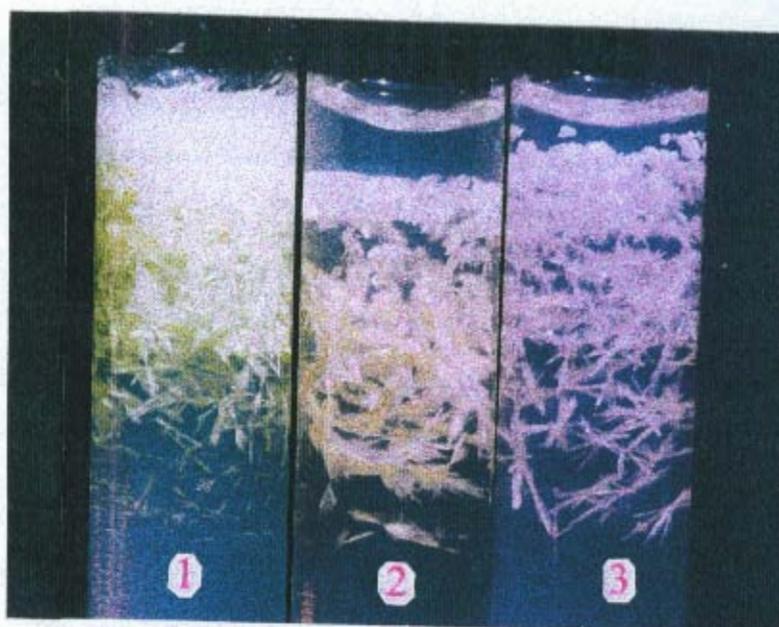


Fig. 4.9. The crystalliser containing the mixed rare earth hydrogen selenite crystals

1. PNHS 2. PSHS 3. NSHS

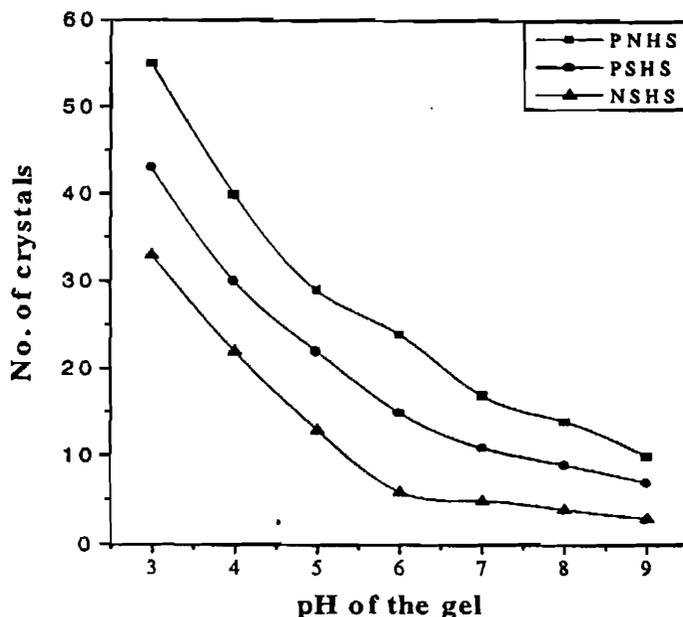


Fig 4.10. The variation of nucleation density Vs pH of the gel

Crystals are found to grow at all pH values selected for the growth. But their morphology, perfection, number etc. vary with the pH variations. When the gel pH was below 6.5, crystals are found to grow at the gel solution interface region. In the growth of rare earth hydrogen selenites, the selenous acid is the impregnated acid, which acidifies the gel and acts as one of the reactant. When the concentration of the selenous acid increases pH value is also increased. The region of the crystal growth can be varied considerably by changing the pH of the system. By increasing the pH the gel gets hardened and sets very fast and it reduces the rate of diffusion of ions. The size and density of population decrease due to this effect. The optimum pH value for the growth of these crystals is 7 at which well defined good quality crystals of average size 8mm x 3mm x 2mm have been obtained.

4.5.2 (iii) Influence of age and gel density

Variation in density and ageing of the medium is studied during the growth of the mixed crystals. As the density of the gel is increased, twinning of the crystal is found to increase and dendritic growth is observed. This may be due to the constraints on the growing face of the crystal due to the hardening of the gel. This affects



adversely on the quality of the crystal. The experimental study has given clear evidence for this phenomenon. Fig 4.11 shows the change in the density of nucleation with the density of the gel.

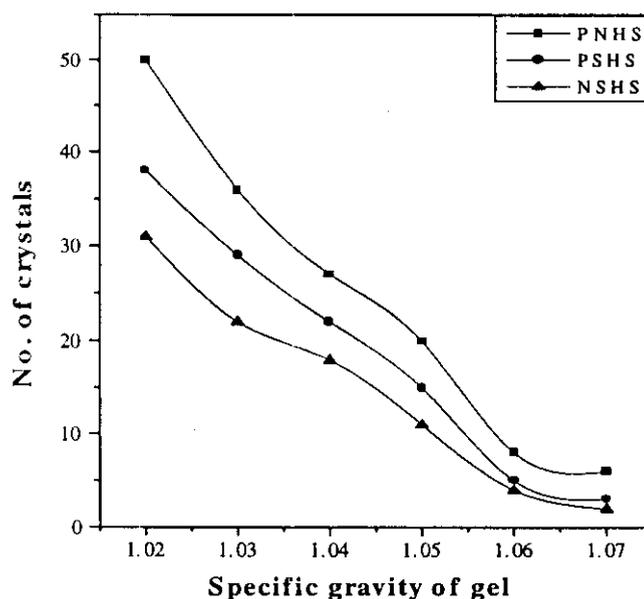


Fig. 4.11. Nucleation density Vs specific gravity of the gel

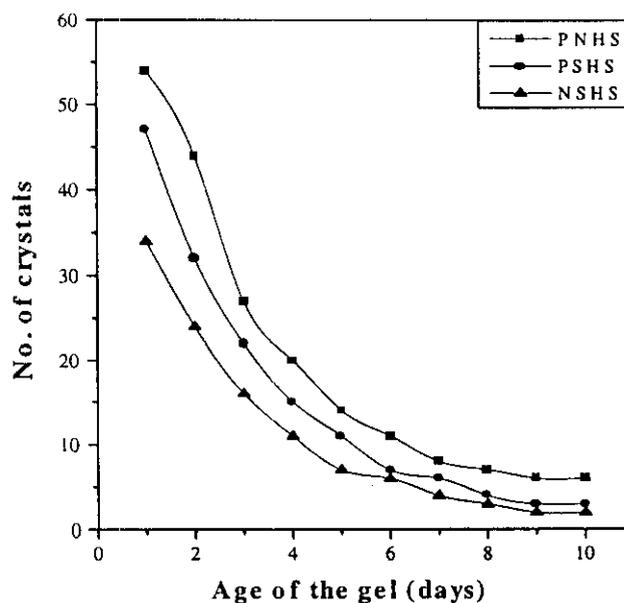


Fig. 4.12. Nucleation density Vs age of the gel

Due to ageing, dehydration of the gel occurs; this leads to the hardening of the medium. The column of gels of age 25 days or more do not produce any crystallites up to 3cm below the gel solution interface. The top of the surface becomes dried and as a result the anions are inactive and this region becomes barren. The diffusants have to travel down more to achieve the minimum concentration condition for establishing growth. There is a probability of non-uniform hardening of the gel column. The diffusion of anions may be retarded due to the uneven hardening of top surface of the gel column. Fig. 4.12 depicts the influence of age of the gel on nucleation density.

4.5.2 (iv) Effect of concentration of feed solution

It is observed that the nucleation density increases with the increase of the concentration of the feed solution containing the rare earth ions (fig.4.13). The size, quality and morphology of the crystals are influenced by the variation in the concentration of the cations.

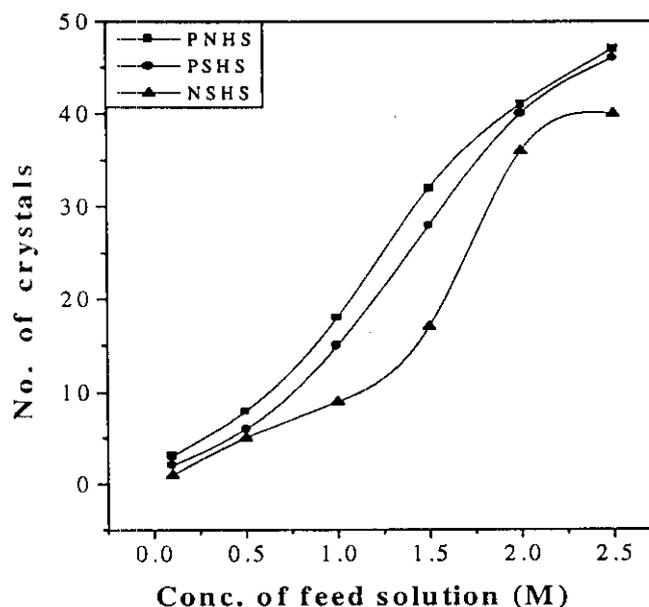


Fig. 4.13. Nucleation density Vs concentration of the feed solution

4.5.3 General features observed on the growth of mixed rare earth hydrogen selenite crystals

It is observed that there are so many similarities between the growth of praseodymium samarium hydrogen selenite (PSHS) and neodymium samarium hydrogen selenite (NSHS) with that of praseodymium neodymium hydrogen selenite (PNHS) crystals. Detailed study has been undertaken for these crystals. The kinetics of the growth are furnished in the corresponding graphs given for all the three hydrogen selenite crystals.

4.6 Conclusion

The summary of the findings in the growth of these six types of crystals, viz. praseodymium hydrogen selenite (PHS), neodymium hydrogen selenite (NHS), samarium hydrogen selenite (SHS) and its mixed in different ratios; praseodymium neodymium hydrogen selenite (PNHS), praseodymium samarium hydrogen selenite (PSHS) and neodymium samarium hydrogen selenite (NSHS) can be summarised as follows:

1. Crystal morphology and transparency depends on the concentration of the feed solution
2. The growth rates and nucleation densities are highly influenced by the pH and density of the hydrosilica gel medium.
3. The concentration of the anions also has a significant role on the morphology of the crystal.

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