

Growth of praseodymium samarium hydrogen selenite mixed crystals and their characterisation

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Abstract : Following chemical reaction method, mixed crystals of praseodymium samarium hydrogen selenite were grown in silica gel by single diffusion method. The difference in growth features by varying different growth parameters was studied in detail. Optimum growth conditions yielded good quality crystals of praseodymium samarium hydrogen selenite (PSHS). These crystals were characterised by X-ray, UV-Visible and infrared spectroscopic methods. The energy dispersive analysis by X-rays was utilised to find the percentage of praseodymium and samarium ions in the grown crystals. The unit cell parameters of the crystals were obtained from single crystal and powder X-ray diffraction techniques. The molecular formula of the crystals was clarified with TG in complement with infrared study. The micro-indentation studies were carried out to study the hardness of well faceted PSHS crystals.

Keywords : Rare earth crystals; crystal growth; spectroscopic studies; thermogravimetric studies; microhardness

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1. Introduction

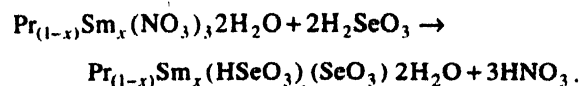
Rare earth crystals have attracted considerable attention on account of their invaluable and technologically exploited physical properties [1]. A variety of materials containing rare earths are recognised for their magnetic, electronic and optical properties [2, 3]. Hydrogen selenite crystals have evinced much interest because of their ionic, optical and thermal properties [4, 5]. Using gel method a number of investigators have grown crystals of rare earth oxalates and its tartrates [6-8]. Studies on praseodymium samarium hydrogen selenite (PSHS) crystals are scarce. Previous reports utilised hydrothermal technique to synthesise the material [3, 9]; whereas in the present work, we utilised the well-established hydrosilica gel diffusion technique to grow these crystals.

Hydrosilica gel diffusion technique is found suitable for the growth of praseodymium samarium hydrogen selenite crystals [10]. This technique is used to grow the crystals having low aqueous solubility and thermal decomposition. The PSHS crystal shows both of these properties and is a suitable candidate for

this technique. The present investigation has been carried out to study the effect of various gel parameters such as density of sodium meta silicate (SMS) solution, pH of the gel, concentration of the reactants and the age of the gel on the growth process. PSHS crystals $[\text{Pr}_{(1-x)}\text{Sm}_x(\text{HSeO}_3)(\text{SeO}_3)2\text{H}_2\text{O}]$ grown in gels, are characterised by X-ray diffraction, optical absorption, thermogravimetric analysis (TG and DTA) and Vicker's microhardness studies.

2. Experimental

Praseodymium samarium hydrogen selenite (PSHS) crystals were grown by the controlled diffusion of praseodymium samarium nitrate solution (upper reactant) into the pre-set gel impregnated with selenous acid (inner reactant). The proportions of the praseodymium, as well as samarium ion concentrations were varied for obtaining the stoichiometrically different crystals. The chemical reaction can be depicted as below



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The main parameters affecting the growth features of the crystals are briefly discussed here.

2.1 Effect of different growth parameters on PSHS crystals :

(i) Effect of pH

The pH value of the SMS gel solution plays a characteristic role in the growth process and growth features of hydrogen selenite crystals. Thickness of the precipitate region and nucleation density were influenced by the pH value. When the pH value was lowered, the density of nuclei was reduced. These experiments were conducted at room temperature, with gel density of 1030 kg/m^3 , upper reactants concentration of 0.5 M and concentration of inner reactants as 1 M . It is found that well-defined PSHS crystals having good optical qualities are obtained for a pH of 7.

(ii) Influence of gel density and age

The gel density has its own role on the crystal size, nucleation density and quality of the crystal. The gel having a density range of $1010\text{--}1100 \text{ kg/m}^3$ was used in the present study, keeping all other parameters constant such as pH [7], concentration of the upper reactants 0.5 M and inner reactants 1 M . Crystallisation was observed in the crystalliser below a density of 1060 kg/m^3 . It was found that the quality of the grown crystals was highly influenced by the density of the medium. Good quality PSHS crystals were obtained for a density range of $1020\text{--}1030 \text{ kg/m}^3$. On the other hand, when the density was too high, nucleation was very poor due to the reduced rate of diffusion and reaction.

Since age of the gel hardens the gel medium, it plays an important role on the physical property of the gel. This is due to the dehydration of the free stay of the gel. Gels of age 20 days or more, did not give any crystallites up to 0.025 m below the gel solution interface. 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 harder than that below, the transport of the anions is retarded. A growth period of 28 days, yielded smooth surfaced crystals.

(iii) Concentration of the reactants

The concentrations of the reactants played an important role on the growth of the crystals. Gel had a fixed density of 1030 kg/m^3 , pH of 7 and growth period was 28 days, then the nature of the growth of crystal was found to 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.

Detailed study was carried out by varying the concentration of the selenous acid (0.1 to 1 M) added in the gel by keeping the

concentrations of praseodymium nitrate, samarium nitrate solutions constant (0.5 M). The concentration of the acid solution controls the pH of the gel. The results obtained by varying the concentration of the acid are similar to those obtained by pH variation. In another set of experiments, concentration of the feed solution was varied from 0.25 M to 1 M while the concentration of selenous acid in the gel was 1 M . The growth features, morphology and number of the crystals were found to be highly influenced by the concentration change. Good quality crystals were obtained only in a range of concentrations of $0.4 \text{ M}\text{--}0.6 \text{ M}$. Below this range, the crystals formed were very small and above this range, spurious nucleation was observed.

In the present study, the best quality (PSHS) crystals of size $0.01 \text{ m} \times 0.005 \text{ m} \times 0.003 \text{ m}$ are obtained for gel density of 1030 kg/m^3 , pH = 7, concentration of H_2SeO_3 1 M and praseodymium nitrate and samarium nitrate solutions 0.5 M for a growth period of 28 days. The crystals have layered structure and show two different morphologies as shown in Figure 1.

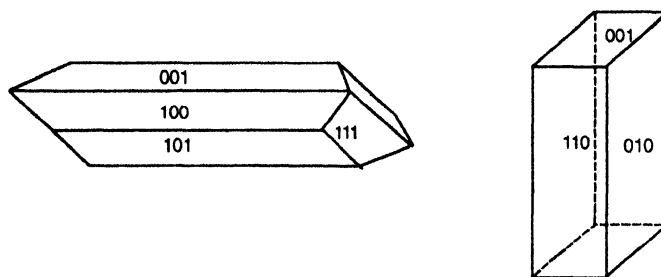


Figure 1. The morphology of the PSHS crystals

3. Characterisation studies

3.1 X-ray diffraction studies :

X-ray diffraction pattern of the powdered $\text{Pr}_{1-x}\text{Sm}_x(\text{HSeO}_3)(\text{SeO}_3)2\text{H}_2\text{O}$ ($x = 0.5$) reveals the crystallinity of the sample by the appearance of well-defined Bragg peaks. The single crystal data of the unit cell parameters of the PSHS crystals are

Space group = $P2_1/c$, $a = 11.2422 \text{ \AA}$, $b = 9.6127 \text{ \AA}$, $c = 10.2501 \text{ \AA}$, $\beta = 114.849^\circ$ and volume $V = 1005.2 \text{ \AA}^3$. Table 1 gives the peak intensities noted from the powder pattern (Figure 2).

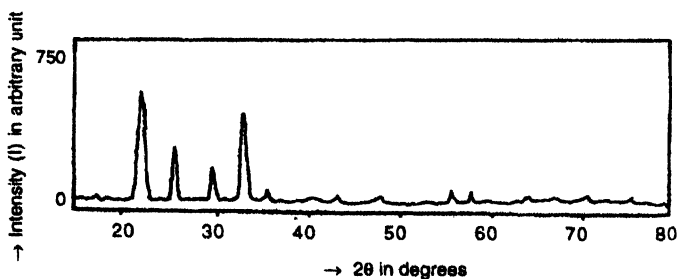


Figure 2. The X-ray powder pattern of PSHS crystals.

Table 1. XRD data of praseodymium samarium hydrogen selenite crystals.

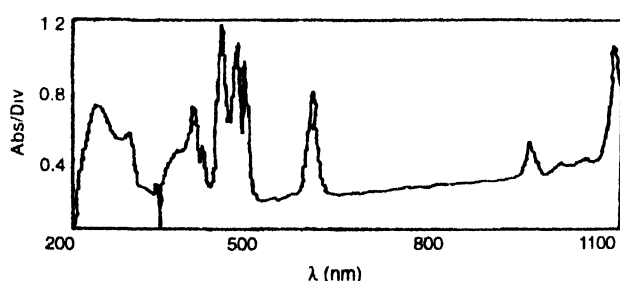
2 θ (°)	d(nm)	Intensity (I)	I/I ₀
21.662	4.103	965	100.00
25.476	3.496	96	9.94
29.635	3.015	40	4.145
32.722	2.737	698	72.3316
35.399	2.536	46	4.7668
55.959	1.643	39	4.0414
57.77	1.596	42	4.3523

3.2 UV-visible NIR spectrum

The UV- visible absorption spectrum is recorded in a SHIMADZU 160. A spectrophotometer using nujol-mull method. The electronic spectrum of PSHS crystal is shown in Figure 3. The absorption peaks correspond to various excitations of praseodymium and samarium ions from their ground states, are given in Table 2.

Table 2. Assignment of UV-Visible NIR absorption spectrum of praseodymium samarium hydrogen selenite.

Ion	Wavelength (nm)	Energy (cm ⁻¹)	Assignments
Pr ³⁺	472	21186	¹ P ₁
	596	16778	¹ D ₂
	1043	9587	³ G ₄
Sm ³⁺	402	24875	⁴ F _{3/2}
	445	22471	⁴ G _{7/2}
	948	10548	⁶ F _{11/2}
	1086	9208	⁶ F _{9/2}

**Figure 3.** UV-Visible NIR absorption spectrum of praseodymium samarium hydrogen selenite.

3.3 IR spectrum :

A SHIMADZU IR-470 spectrophotometer was employed to obtain IR spectrum using KBr pellet method. The Infrared absorption spectrum of the PSHS crystal shows a broad band at 3500-3100cm⁻¹ due to the vibration of the water molecule. The SeO₃²⁻ vibrations lie in between 840cm⁻¹ and 440cm⁻¹. A very significant band at 1220 cm⁻¹ is ascribed to hydrogen selenite (HSeO₃⁻). The bands at 2406 cm⁻¹ and 3447 cm⁻¹ show the

presence of OH [11]. In the stretching region of the OH vibrations, trio bands are observed in the IR spectra of the crystal. One good intense broad band observed at 2406 cm⁻¹ and other two bands are obtained with weak intensity [4, 12].

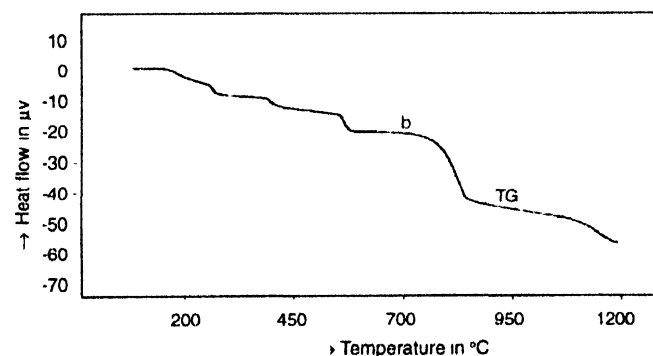
Table 3. IR-Spectral data and band assignments of PSHS Crystals.

IR (ν) cm ⁻¹	Assignments
437 - s	ν ₂ (SeO ₃ ²⁻)
493 - s	ν (Se-O)
670 - s	δ (Se-OH)
700 - s	ν ₁ (HSeO ₃ ⁻)
755 - s	ν ₁ (Se-O)
820 - m	ν ₁ (SeO ₃ ²⁻)
843 - m	ν ₁ (HSeO ₃ ⁻)
1227 - s	δ (O-Se-OH)
1640 - s	δ (O-Se-OH)
2406 - s	ν(OH)
3447 - w	ν(OH)

s-strong m - medium w -weak

3.4 TG-DTA analysis :

A SETRAM TGD/TA92 in Ar + O₂ atmosphere was used to study thermal decomposition of the crystal. This was performed in six steps between 130°C to 1180°C corresponding to successive losses of H₂O and SeO₂ (Figure 4). The first and

**Figure 4.** TGA curve of PSHS crystals.

second processes are from 130°C to 200°C and 230°C to 360°C which are attributed to the loss of one and four water molecules respectively leading to an anhydrous praseodymium selenite Pr₁Sm_{1-x}Se₄O₁₁ (x = 0.5). The third step of the degradation was from 375 °C to 475°C corresponding to the degradation of the phase with elimination of SeO₂ leading to the formation of PrSmSe₇O₂₀ [11]. The thermodynamical analysis of the molecular species confirmed the proposed chemical formula. The DTA curve shows five endothermic peaks in accordance with each mass loss observed in the thermogravimetric analysis

(Figure 5). The curve corresponding to the decomposition of $\text{PrSmSe}_4\text{O}_{11}$ shows an exothermic peak. This may be due to the

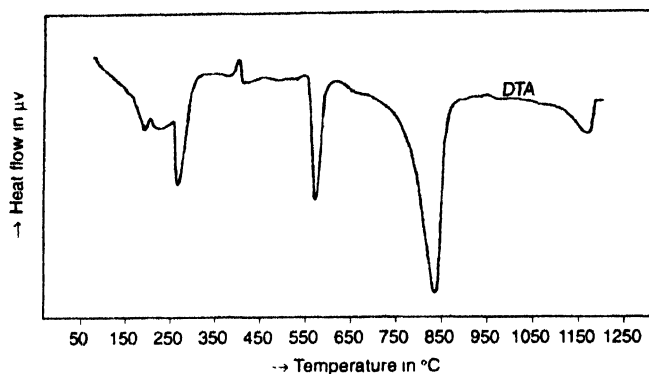


Figure 5. The DTA plot of PSHS crystals

elimination of SeO_2 and simultaneous crystallographic transformation [11]. On the basis of these results, the complete decomposition of the PSHS is formulated and all the calculated and observed values for the different steps of degradations are given in Table 4.

Table 4. Thermal degradation data of PSHS crystals.

DTA temp (°C)	Range of temp. T G (°C)	Observed % of weight loss	Calculated % of weight loss
170	125-200	2.5	2.06
265	200-300	8.1	8.40
*375	300-420	7.2	7.40
555	420-600	7.5	7.69
840	600-900	32.2	33
1160	900-1200	20.8	20

3.5 EDAX of PSHS:

The energy dispersive analysis by X-rays is an important analytic technique used to determine the chemical composition of the elements present in the material. The praseodymium samarium hydrogen selenite crystals are grown by the diffusion of 0.5M of $\text{Pr}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ in different stoichiometric combinations. The EDAX of the crystals is taken for the grown PSHS crystals. Figures 6 (A-C) show the EDAX pattern obtained for the crystals of different stoichiometries. The peak value of the binding energy, 5.03 keV, corresponds to the L_{α} line of Pr, the peaks at 5.63 keV, 6.2 keV and 6.58 keV being the L_{α} , $L_{\beta 1}$

Table 5. Summary of EDAX analysis of PSHS crystals.

Expt. No.	Elements present in the mixed crystals	The ratio of the upper reactants (by volume)	The observed % of rare earths
1	Pr, Sm	25 : 75	25.302, 74.698
2	Pr, Sm	50 : 50	50.401, 49.599
3	Pr, Sm	75 : 25	75.212, 24.788

and $L_{\beta 2}$ peaks of Sm. The observed experimental data are summarised in the Table 5.

It is noteworthy that the percentage of Pr and Sm in the crystals is in accordance with the proportion of the corresponding rare earths taken in the supernatant solution. The presence of Pr and Sm in the PSHS crystal is established by the presence of L_{α} and L_{β} peaks of Pr and L_{α} , $L_{\beta 1}$ and $L_{\beta 2}$ peaks of Sm, which match well with the EDAX international chart and previous results [13]. It is also noted that the increase in concentration of the Pr ions changes the heights and area of the L_{α} and L_{β} peaks of Pr. The same effect was observed in the case of Sm also.

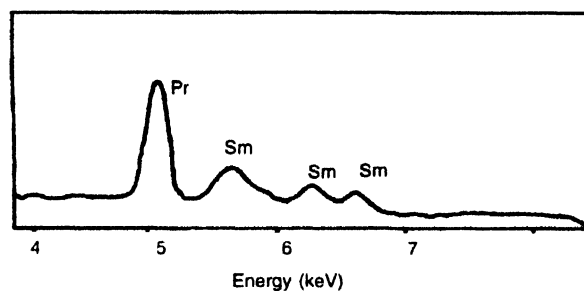


Figure 6A. The EDAX pattern of PSHS (75 : 25) crystal.

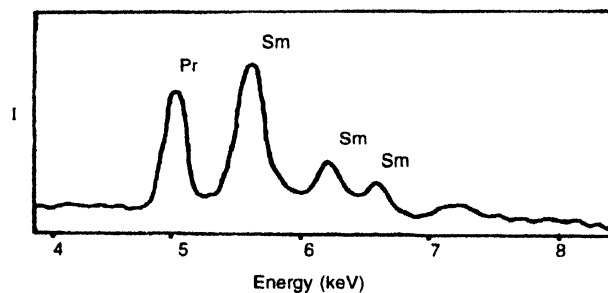


Figure 6B. The EDAX pattern of PSHS (50 : 50) crystal.

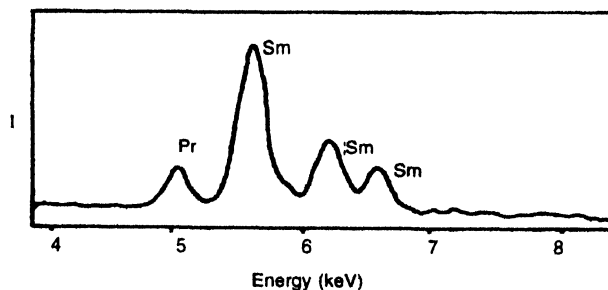


Figure 6C. The EDAX pattern of PSHS (25 : 75) crystal.

4. Micro-indentation studies

The microhardness measurements of crystals are of great importance. In this study the hardness of the PSHS crystals was measured by using a 'Leitz Miniload L' fitted with a diamond pyramidal indenter attached to an incident light microscope. The Vickers diamond indenter was applied perpendicular to the

(100) plane of the crystals. Loads in the range 0.005 kg to 0.05 kg were used in the study. The time of indentation was 20 seconds for all trials and samples. The distances between any two indentations were kept at least four times of the diagonal of the nearest indentation. After several trials of indentation of each crystal, the average values of the diagonal length of indentation marks were obtained. The Vickers microhardness number H_v for each load was calculated using the relation

$$H_v = 1.8544 P/d^2 \text{ (kg/mm}^2\text{)},$$

where P is the applied load in kg and d is the diagonal length of the indentation in mm.

The crystals that have been studied in this work, show relatively low hardness. For a low load of 0.005 kg, the PSHS ($P : S = 50 : 50$ or $x = 0.5$), crystal showed high hardness value. Increase in the load decreases the hardness number and then it attains a relatively stable value (Figure 7).

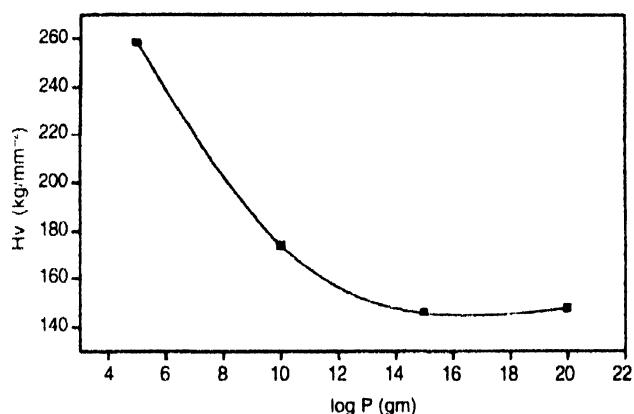


Figure 7. Variation of hardness vs load of PSHS crystal

Studies were also conducted on crystals having different stoichiometric combinations of praseodymium and samarium ions and interesting results were observed. Hardness values

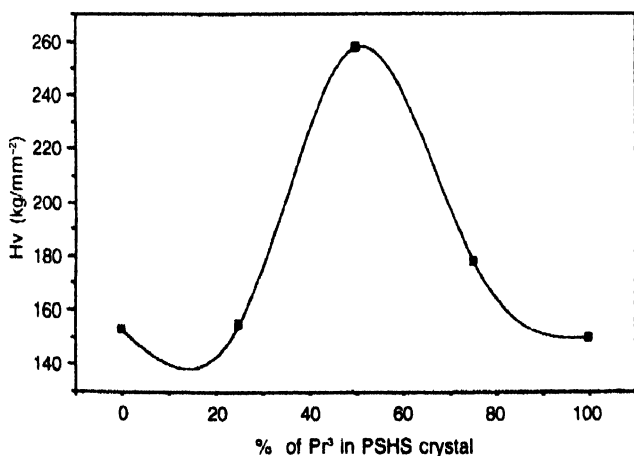


Figure 8. Stoichiometric variation of hardness vs load in PSHS crystal.

reached maximum for 50 : 50 composition of the praseodymium and samarium ions (Figure 8). It may be explained as follows ; when the component is in a lower concentration the minority atoms might be going into the structure replacing the other component and as an interstitial. When Pr and Sm ions are in equal proportion, the atoms may get a chance to be arranged in an order since it will have a minimum energy configuration. In short, at the equal proportion of ions, the structure of the material attains a more ordered form.

5. Conclusion

Good quality PSHS crystals were grown and characterised by different techniques. EDAX gives the details of the stoichiometric combinations; the other spectroscopic and thermogravimetric methods confirmed that the crystal is PSHS. The Micro indentation studies describe the variation in hardness for various stoichiometric combinations of rare earth ions.

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