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# Growth of praseodymium tartrate crystals in silica gel

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The growth of praseodymium tartrate crystals in the system $Pr(NO_3)_3$–$Na_2SiO_3$–$C_4H_6O_6$, using a single-tube–single-gel technique is described. The growth conditions are delineated and a spherulitic morphology is reported. The spikes attached to the spherulites are single crystals of praseodymium tartrate. The mechanisms of crystallization for various types of spherulites are described. The information presented contributes to the understanding of spherulitic growth in general, and that of praseodymium tartrate in particular.

## 1. Introduction

Several workers in recent years have studied the growth of single crystals in gels. However, there have been few attempts [1–4] to explain the growth of materials exhibiting polycrystallinity and assuming a spherulitic morphology, although spherulitic crystallization has been recognized for many years by mineralogists, and is defined as the growth of radiating crystal fibres or concentric bandings. The mechanism underlying the formation of spherulites is still one of the most formidable and intriguing problems in crystal growth and requires in-depth study. The crystal growth of praseodymium tartrate offers an opportunity to assist in the explanation of the growth mechanism of spherulitic formation in gels.

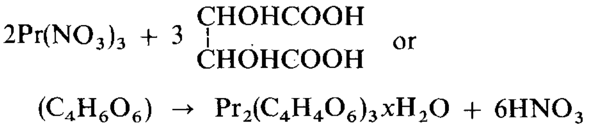
Recent studies have indicated that most rare-earth (Nd, Dy, Di and Gd) tartrates have a tendency to grow in the form of spherulitic crystals containing water of crystallization [5–8]. Studies on the thermal behaviour of these materials confirm that these materials are unstable even at moderate temperatures (50 °C) [9–13]. In this paper the growth and crystallization mechanisms of praseodymium tartrate crystals are described. The effects of varying parameters such as gel pH, age and density, concentration of upper and lower reactants, and the resultant morphologies are also described and discussed.

## 2. Results and discussion

### 2.1. Growth procedure

The growth of praseodymium tartrate was achieved by allowing controlled diffusion of praseodymium ions through silica gel impregnated with tartaric acid in a crystallizer consisting of a single glass tube 2.5 cm in diameter and 20 cm in length.

The gel was prepared from a pure solution of sodium metasilicate ($Na_2SiO_3$). The solution was then impregnated with tartaric acid (lower reactant) of a concentration in accordance with the requirements of a particular pH value. The solution was then allowed to set. The praseodymium nitrate solution (upper reactant) of the required concentration was then poured slowly along the sides of the tube containing the pre-set gel of the desired age, to avoid breaking the gel. Slow diffusion of the upper reactant occurred through the gel, resulting in crystal growth. The reaction expected to take place in the gel medium is as follows:



$$2Pr(NO_3)_3 + 3\ \begin{matrix} CHOHCOOH \\ | \\ CHOHCOOH \end{matrix}\ \text{or}\ (C_4H_6O_6) \rightarrow Pr_2(C_4H_4O_6)_3xH_2O + 6HNO_3$$

Through physico-chemical characterization techniques (EDAX, chemical, infrared, and thermogravimetric) it could be inferred that the material grown was praseodymium tartrate of the stoichiometry $Pr_2(C_4H_4O_6)_35H_2O$ [14].

### 2.2. Mechanism of crystallization

Table I gives a summary of the experiments and the results on size, morphology and nucleation density of these crystals. The results show that under all conditions, the crystals attain spherulitic morphology.

The three zones where distinct mechanisms of crystallization become operative are shown in Fig. 1. The first zone (A) is the immediate vicinity of the gel–reactant interface, where spontaneous formation of the crust occurs as a result of an instant reaction between the upper and lower reactants. The crust is a mass of poor quality crystallites, the gel having little role to play in the diffusion of ions.

The second operative mechanism is effective in the precipitate zone (BC), where crystals tend to grow out of the precipitates. The precipitate formation, at the gel reactant interface, starts immediately on pouring of the upper reactant solution. After attaining some thickness, the precipitate begins to advance into the gel. Both upper as well as lower fronts of the precipitate begin to advance into the gel, but the rate of advancement of the lower front is relatively faster than that of the upper front. Consequently a precipitate

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TABLE I Details of experiments for the growth of praseodymium tartrate crystals

| Experiment | Constant parameters | Changing parameters | Results |
|---|---|---|---|
| 1. Variation of gel ageing | Top reactant (praseodymium nitrate): 0.5 M<br>Bottom reactant (tartaric acid): 0.5 M<br>Gel pH: 4.5<br>Dimensions of crystallizer: 2.5 cm diam; 20 cm length | Gel ageing:<br>48 h<br>72 h<br>92 h<br>120 h | Morphology:<br>(i) normal spherulites and coalesced spherulites in the above region for all ages;<br>(ii) fibrous spherulites in middle region for 48 & 72 h of gel ageing.<br>Spherulitic growth is accompanied by long needles all along the surface, giving the appearance of fibrous growth even to the unaided eye.<br>Max. size of normal spherulite: ~ 3 mm diam<br>Max. size of fibrous spherulite: ~ 4.5 mm diam<br>Nucleation density: max. at 48 h of gel ageing; min. at 120 h of gel ageing |
| 2. Variation of pH | Top reactant (praseodymium nitrate): 0.5 M<br>Bottom reactant (tartaric acid): 0.5 M<br>Gel age: 72 h<br>Dimension of crystallizer: 2.5 cm diam; 20 cm length | Gel pH:<br>4<br>4.3<br>4.5<br>4.75<br>5.0 | Morphology: normal spherulites and coalesced spherulites in all tubes. Fibrous spherulites for pH 4.75 & 5<br>Max. size of normal spherulite: ~ 5 mm in diam (at pH = 4.3)<br>Max. size of fibrous spherulite ~ 4.5 mm diam (at pH = 4.75)<br>Nucleation density: Max. at 5 pH; min. at 4 pH |
| 3. Variation of upper reactant concentration | Lower reactant concentration (Tartaric acid): 0.5 M<br>Gel pH: 4<br>Gel age: 72 h<br>Dimensions of crystallizer: 2.5 cm diam; 20 cm length | Upper reactant concentration (praseodymium nitrate)<br>0.25 M<br>0.50 M<br>0.75 M<br>1.00 M | Morphology: normal and coalesced spherulites in all the cases<br>Max. size of normal spherulite: ~ 3.5 mm diam<br>Nucleation density: min. at 0.25 M conc. of upper reactant; max. at 1 M conc. of upper reactant[a] |
| 4. Variation of lower reactant concentration | Upper reactant concentration (praseodymium nitrate): 0.5 M<br>Gel pH: 4<br>Gel age: 72 h<br>Dimensions of crystallizer: 2.5 cm diam; 20 cm length | Lower reactant concentration (tartaric acid)<br>0.25 M<br>0.5 M<br>0.75 M<br>1.00 M | Morphology: normal and coalesced spherulites in all tubes.<br>Max. size of normal spherulite: ~ 4.25 mm (at 0.75 M of lower reactant concentration)<br>Nucleation density: max. at 1 M; min. at 0.50 M[b] |
| 5. Variation of gel concentration | Upper reactant concentration (praseodymium nitrate): 0.5 M<br>Lower reactant concentration (tartaric acid): 0.5 M<br>Gel pH: 4<br>Gel age = 72 h<br>Dimensions of crystallizer: 2.5 cm diam; 20 cm length | Gel concentration.<br>0.25 M<br>0.50 M<br>0.75 M<br>1.00 M | Morphology: normal and coalesced spherulites.<br>Max. size of normal spherulite: ~ 0.25 mm diam (at 0.25 M of gel concentration)<br>Nucleation density: max. at 0.25 M of gel concentration; min. at 1 M of gel concentration.[c] |

[a] Spherulites in the form of discs were also obtained which could probably result due to cracking of gel (at 1 M).

[b] 0.25 M concentration of tartaric acid was not found to be suitable for the setting of the gel for pH = 4, even after keeping for five days.

[c] At 1 M gel concentration an agglomerate (5 mm in diam) of spherulitic shape appears in a halo.

TABLE II Rate of advancement of precipitate in the gel column[a]

| Tube no. | Concentration of praseodymium nitrate | Period of advancement of precipitate (h) | Reading of precipitate boundaries from gel reactant interface | | Observed length of precipitate of gel column (cm) | Rate of advancement | |
|---|---|---|---|---|---|---|---|
| | | | Upper boundary (cm) | Lower boundary (cm) | | Upper boundary ($\times 10^{-3}$ cm h$^{-1}$) | Lower boundary ($\times 10^{-3}$ cm h$^{-1}$) |
| 1 | 0.25 M | 451 | 0.7 | 2.1 | 1.4 | 1.552 | 4.656 |
| 2 | 0.50 M | 766 | 1.7 | 6.00 | 4.3 | 2.21 | 7.832 |
| 3 | 0.75 M | 766 | 2.9 | 8.3 | 5.4 | 3.78 | 10.83 |
| 4 | 1.00 M | 766 | 3.6 | 10.5 | 6.9 | 4.69 | 13.707 |

[a] Constant parameters: 1. Concentration of lower reactant (tartaric acid) = 0.5 M; 2. pH of gel: 4; 3. density of gel = 1.06 g cc$^{-1}$; 4. gel age: 72 h.

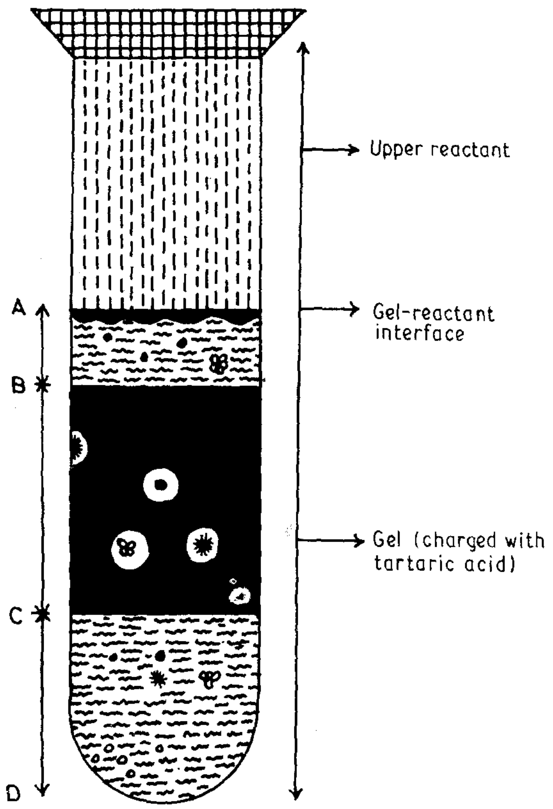


*Figure 1* Schematic diagram showing different mechanisms of crystallization of praseodymium tartrate crystals. ●, Normal; *, fibrous; and ○, transparent spherulites.

column is formed. The advancement of the precipitate continues until the maximum size is reached, which takes about 40 days. At this stage, further advancement of the precipitate stops. Usually the precipitate column is observed to be stationed in the middle of the gel column.

Table II gives the rate of advancement of the upper and lower fronts of the precipitate column for different concentrations of the upper reactant. The length of the precipitate column increases with the increase in upper reactant concentration. Fig. 2 illustrates a precipitate after it ceased to advance into the gel column. The precipitate phenomenon finds an explanation on the basis of adsorption properties and its dependence on the pH of the gel [15]. This type of phenomenon has been observed by Abdulkhadar and Ittyachen [16] for barium and lead tartrate crystals, and by Kotru *et al.* [5–8] for rare-earth tartrates ($R$ = Gd, La, Nd, Dy, and Di) and the same explanation is valid in this case too. Fig. 3 shows spherulitic praseodymium tartrate crystals, grown under different conditions in the precipitate zone. The pH value of 4.5–5 is conducive for the growth of fibrous spherulites (Fig. 3a).

The second operative mechanism of crystallization of the praseodymium tartrate is in the precipitate zone. Each nucleation centre is associated with a halo (a spherical region) which is depleted of colloidal particles. The colloidal particles surrounding the crystal nucleation centre tend to migrate radially towards it from all directions. In this way a spherical region of far greater volume than that of the growing spherulite is depleted of colloidal particles, rendering the surrounding space clear from any precipitate and thus

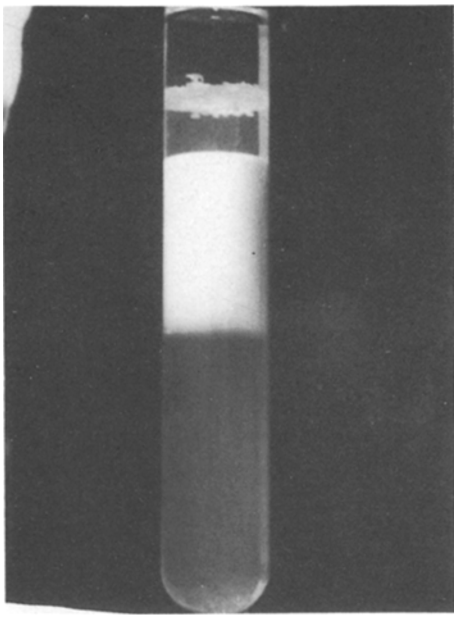


*Figure 2* A photograph showing a typical precipitate of praseodymium tartrate crystals.

resulting in the formation of a halo. The process of crystallization continues till the colloidal particles within the precipitate are consumed in building the crystal.

The third zone (CD) where praseodymium tartrate crystallizes is the clear zone at the bottom of the gel column. Here the crystals grow without any preformation of precipitate. Apart from normal and fibrous spherulites, very small (of the order of 0.15-mm radius) and nearly transparent spherulites are observed almost at the bottom of the tube. The near transparency of these spherulites may be because of factors such as lower concentration gradients and relatively stable pH value for longer duration, resulting in slower growth rates of spherulites. The different types of spherulites (normal, coalesced and fibrous) growing within the halo are depicted in Fig. 4. The spherulites may be broadly classified as normal and fibrous (spiky).

## 2.3. Morphology

There have been several reports on the spherulitic morphology of crystals. Morse *et al.* [17, 18] have described the growth of various spherulitic morphologies of inorganic compounds in gelatin and jellies. An extensive discussion on the equilibrium nature of spherulitic crystallization has been reported by Keith & Padden [1]. Nassau [19] has reported a wide variation of spherulitic morphologies for gel-grown crystals of $Cu(IO_3)_2 \cdot 2/3H_2O$, $Cu(IO_3)_2 \cdot 2H_2O$, $Cu(OH)IO_3$, $\alpha$-$Cu(IO_3)_2$, $\beta$-$Cu(IO_3)_2$ and $\gamma$-$Cu(IO_3)_2$. Bolotov & Murayev [3] have discussed the structure and crystallization mechanism of selenium spherulites. According to their description, a spherulite develops from a single crystal nucleus drawn out in a direction perpendicular to the *c*-axis lying in the plane of the crystal, the curving of the lattice being a result of surface tension forces acting on different faces. Sulphur has also been found to crystallize as spherulites [20–22]. Various spherulitic morphologies of $Cu_3(PO_4)_2 \cdot 3H_2O$, $Ca_5(PO_4)_3OH$, $CaF_2$, $CaWO_4$, $CaCO_3$, $BaCO_3$, $SrCO_3$, $Nd_2(CO_3)_3 8H_2O$ crystals have been reported by McCauley & Roy [2]. According to their observations, the nucleus of a spherulite is a tiny prismatic crystal, and owing to poison, there is subsequent radial growth of acicular crystals. This is

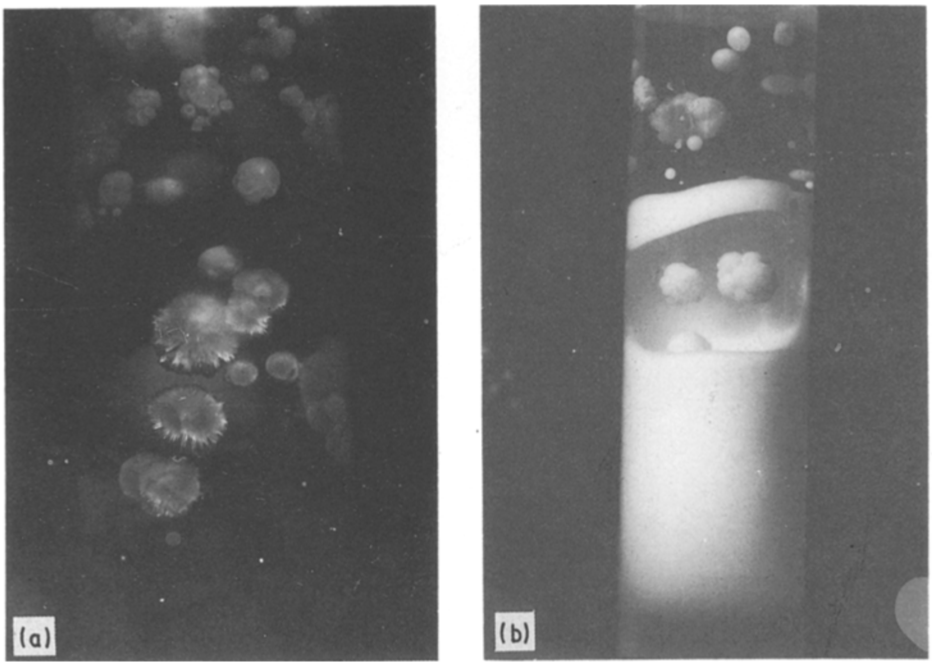
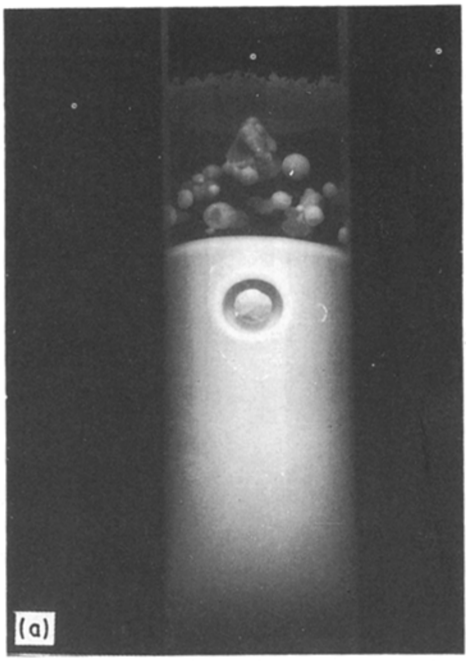
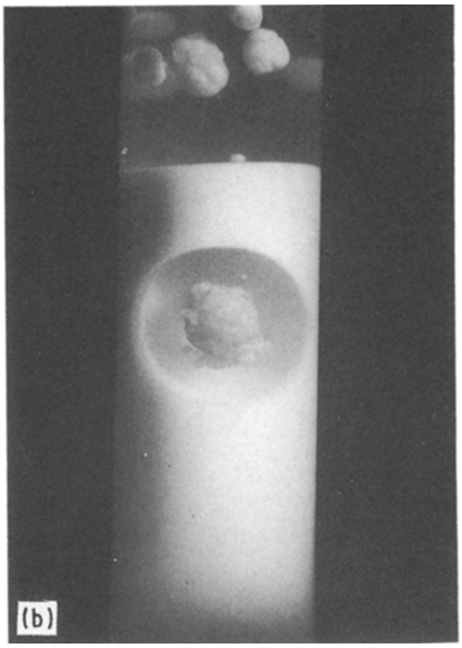


*Figure 3* Growth of spherulites of praseodymium tartrate under different conditions. (a) Gel age = 72 h; pH = 4.5; density = 1.06 g cc$^{-1}$; upper reactant concentration = 0.5 M; Lower reactant concentration = 0.5 M. b) Gel age = 72 h; pH = 4; density = 1.06 g cc$^{-1}$; upper reactant concentration = 0.75 M; lower reactant concentration = 0.5 M.





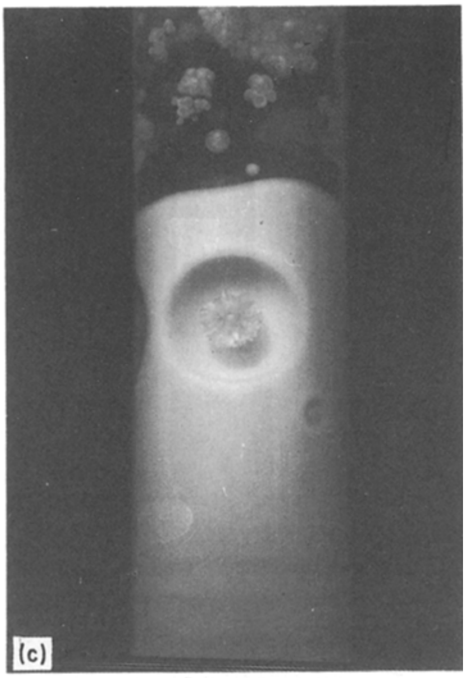


*Figure 4* Photographs showing (a) normal, (b) coalesced and (c) fibrous spherulite growing within a halo.

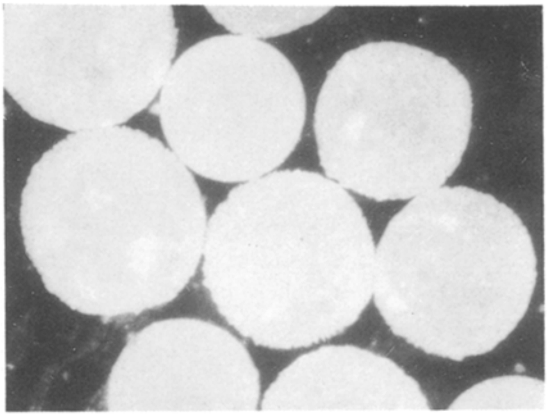


*Figure 6* A photomicrograph showing spherulites (growing in the clear zone of the crystallizer) of praseodymium tartrate. The spherulites are relatively transparent. (× 15)

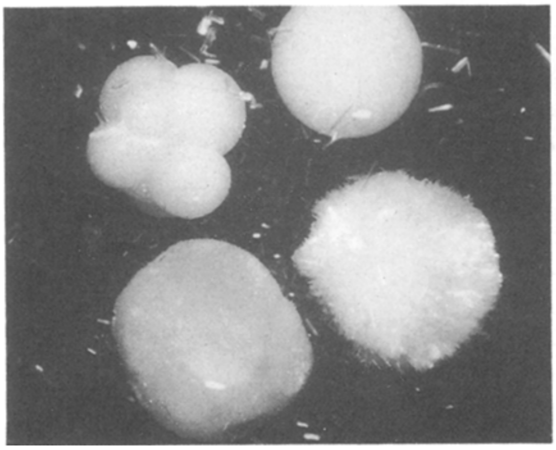


*Figure 5* A photomicrograph showing varied morphologies of spherulites of praseodymium tartrate. (× 10)

followed by rounding of acicular crystals, leading finally to a spherulitic formation.

More recently Kotru & Raina [4] have reported that in the case of $R_2(C_4H_4O_6)_3xH_2O$ ($R$ = Nd, Dy, Di), the nucleus of a spherulite is not a single crystal but a polycrystalline mass, from where there is a divergence of crystal fibres.

Two distinct types of spherulites were observed to grow in the case of praseodymium tartrate crystals, one with a normal rounded surface and the other having a fibrous surface. Fig. 5 shows coalesced, normal and fibrous spherulites grown within the precipitate zone. The other set of spherulites, relatively more transparent, grown at the bottom of the crystallizer, is illustrated in Fig. 6. The spherulites appear almost perfectly rounded. Fig. 7 shows optical micrographs giving an enlarged view of fibrous spherulites.

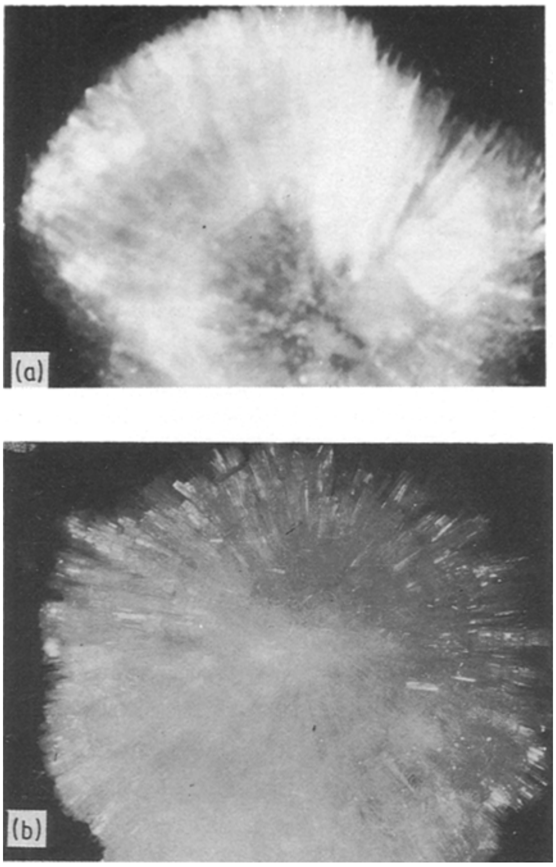


*Figure 7* Photomicrographs showing fibrous spherulites. ( × 20)

*Figure 8* Collection of fibres detached from a fibrous spherulite showing single crystallinity of the fibres. ( × 25)

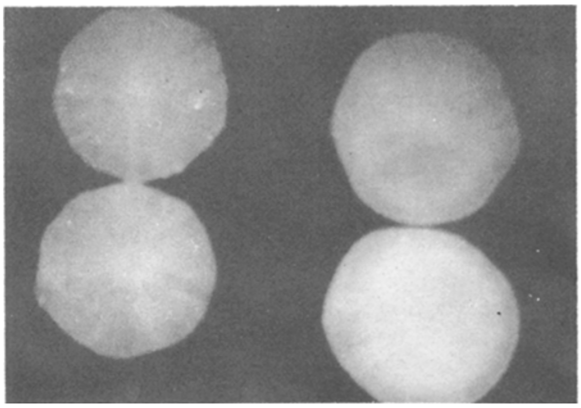


*Figure 9* A photograph showing sectioned halves of spherulites (having grown out of precipitate). ( × 10)

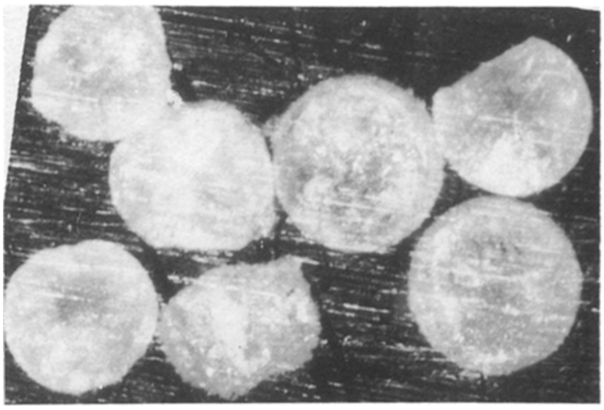


*Figure 10* A photomicrograph showing sectioned halves of spherulites (having grown in the clear zone at the bottom of the crystallizer). ( × 15)

The fibres appear to get diverged from a central region of the spherulite. Some fibres detached from the spherulites are displayed in Fig. 8, where they are seen as single-crystal needles.

To learn about its internal mechanism, a normal spherulite was cleaved into two sections. Fig. 9 shows a typical micrograph depicting four halves of two spherulites. Although the resolution is not high, it appears that the fibres originate from the central region of the spherulite. Fig. 10 shows the sectioned halves of the transparent spherulites (grown at the bottom of the crystallizer). Due to the transparent nature of these spherulites the divergence of the fibres is not clearly revealed.

## 3. Conclusions

From these experiments on the growth of praseodymium tartrate crystals in the system $Pr(NO_3)_3$–$Na_2SiO_3$–$C_4H_6O_6$, the following conclusions may be drawn.

1. Growth of praseodymium tartrate crystals is accomplished by allowing diffusion of praseodymium nitrate through silica gel impregnated with tartaric acid in a single-gel–single-tube system. The crystals exhibit spherulitic morphology even under varied conditions of growth.
2. Three distinct mechanisms play a part in the crystallization of praseodymium tartrate: one as a result of instantaneous reaction at the gel–reactant interface; the second involving growth from colloidal precipitate; and the third as a result of the interaction of reactants in the clear zone without any intermediate step of precipitate formation.
3. The property of adsorption of gel plays an important role during the crystallization of praseodymium tartrate crystals.
4. The internal texture of the spherulites suggests that the crystal fibres emanate somewhere from the centre of the spherulite.

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