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Crystal growth and morphology of rare earth phosphates

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Abstract : Rare earth phosphates (RP_5O_{14} and KRP_4O_{12}, where R = La, Ce, Pr, Nd) were obtained from phosphoric acid solutions at 400, 500 and 650°C The effect of growth parameters on the growth morphology has been studied with a special reference to its surface morphology.

Keywords : Rare earth pentaphosphates, alkali rare earth tetraphosphate, aqueous solution growth, spontaneous nucleation, surface morphology, miniature laser

PACS Nos. : 61.50 Jr, 81.10 Dn

1. Introduction

Rare earth phosphates form an important group of technological materials owing to their applications in optoelectronics. In 1973, laser beams were obtained from NdP_5O_{14} crystals [1,2] containing 3.86×10^{21} ions of Nd/cm^3. Thus the possibility of developing miniature lasers in the crystals containing high concentration of Nd ions was proved. There are several hundreds of reports in literature on various aspects of rare earth phosphates. In the recent years there is a tendency to obtain high power CW lasers from bulk crystals of NdP_5O_{14} or glass rods of NdP_5O_{14}. There are various methods of growing rare earth phosphates : from phosphoric acid solutions [3], aqueous solutions [4], solid phase synthesis [5], synthesis by thermal condensation [6], flux method [7], melt technique [8] and hydrothermal technique [9,10,11]. However, crystal growth from phosphoric acid solution is most popular. The growth of optically perfect monocrystals for miniature lasers is feasible and it varies little from the general problems of growing high quality crystals for other purposes. In case of the growth of rare earth phosphates the basic requirements are as follows : i) the existence of rare earth ions as inter-isolated complex, ii) the lowest possible amounts of hydroxyl and other

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impurities which quench the optical emission in the crystals. Although there are several hundreds of reports on the growth of rare earth phosphates, there are only a few reports in the literature dealing with the study of the morphology [12,13]. Such studies are extremely important on these compounds having device potential. Therefore, an attempt has been made by the present authors to study the general and surface morphology of these compounds. The morphology of these crystals significantly varies with several growth parameters. A systematic study of these parameters will help to understand the growth technology of these rare earth phosphates and also to introduce a desired morphology during the growth process. In this report, the authors discuss the crystal growth and morphology of some selected rare earth phosphates like RP_5O_{14} and KRP_4O_{12} (R = La, Ce, Nd and Pr).

2. Crystal growth

RP_5O_{14} and KRP_4O_{12} crystals have been obtained from aqueous phosphoric acid solutions at varying temperatures. The procedure adopted in the growth of these crystals corresponds to the earlier reports [3]. The formation of a mixture of phosphoric acids of various degree of condensation takes place depending upon the temperature in the system P_2O_5–H_2O. The method of the growth of ultraphosphates can be described as follows : a given rare earth oxide is taken in a vitreous carbon crucible and dissolved in 85% H_3PO_4 at 200°C to 300°C until complete homogenization of the solution takes place and then slowly heated up to a predetermined temperature. After the experiment the resultant product is washed in warm water. Crystallization is carried out through spontaneous necleation. Here supersaturation, which is the driving force for the crystallization process, is obtained through the evaporation of the solvent. In case of the growth of mixed metaphosphates a mixture of M_2CO_3 (M = alkali metal or NH_4^+) and R_2O_3 is taken in a vitreous carbon crucible and 85% H_3PO_4 is added into this mixture. The crucible is heated up to a predetermined temperature in a reactor for 8 days. In the process of heating this mixture becomes homogeneous and gives rise to metaphosphate crystals. In the present work, rare earth phosphate crystals were obtained in the following molar ratio : R_2O_3 : P_2O_5 = (1:5 – 12) for RP_5O_{14} ; K_2O : R_2O_3 : P_2O_5 : H_2O = (2–5) : 1 : (12–25) : (5–15) for KRP_4O_{12} at different temperatures.

3. Results and discussion

X–ray powder diffraction studies showed the resultant products to be homogeneous in composition. The cell parameters were calculated for the representative samples and are found to be similar to the reported values [2].

The crystals obtained in all the experiments were subjected to a systematic morphological analysis. The crystals usually exhibit plate like, tabular, needle or rod like habits with vitreous lustre. The size of the crystals vary from 1 mm to 8 mm. The duration of growth was kept constant (8 days) for all the experiments. Using phase contrast microscope (Leitz – Laborlux, Germany), the crystal morphology of the representative crystals from each experiment was studied. Also the interfacial angles were measured. Table 1 gives the nutrient composition, growth temperature, and the morphology of the crystals of rare earth phosphates. A number of factors such as degree of supersaturation, pH of the solution,

Table 1. Morphology of rare earth phosphate crystals under different growth conditions.

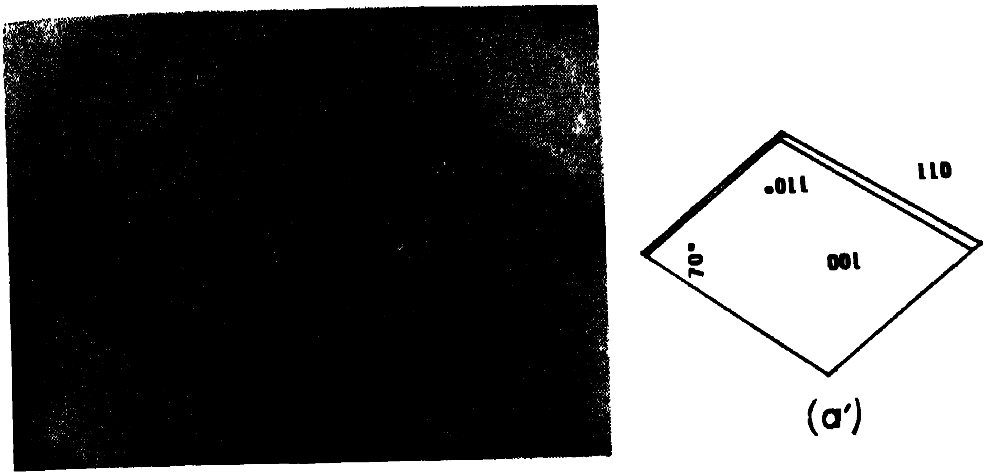
Compound	Starting Composition	Molar ratio	Growth temp (°C)	Size (mm)	Morphology of rare earth phosphate crystals
LaP_5O_{14}	$La_2O_3 : P_2O_5 : H_2O$	1.5 · 18 · 6	500	8.0	Broad thin rhombohedral transparent plates
LaP_5O_{14}	$La_2O_3 : P_2O_5 : H_2O$	1.5 . 15 · 7	500	4.0	Broad transparent rhombohedral plates, twinned
LaP_5O_{14}	$La_2O_3 : P_2O_5 : H_2O$	1.5 · 12–14 . 6	500	3.5	Thick transparent rhombohedral plates, twinned
LaP_5O_{14}	$La_2O_3 : P_2O_5\ H_2O$	1 5 : 16–18 · 6	400	2.9	Small medium thickness twinned transparent plates
LaP_5O_{14}	$La_2O_3 . P_2O_5 \cdot H_2O$	1.5 . 15 · 6	650	1.8	Small rhombohedral plates of uniform size
LaP_5O_{14}	$La_2O_3 \cdot P_2O_5 . H_2O$	1.5 · 17 7	650	2.2	Small twinned thick plates
CeP_5O_{14}	$Ce_2O_3 : P_2O_5 : H_2O$	1 5 · 17 · 7	500	4 0	Transparent equidimensional crystal
NdP_5O_{14}	$Nd_2O_3 : P_2O_5 . H_2O$	1 16 · 5	500	8.0	Needles, tabular, prisamatic
PrP_5O_{14}	$Pr_2O_3 . P_2O_5 \cdot H_2O$	1 14 . 6	500	7.0	Broad rhombohedral plates
SmP_5O_{14}	$Sm_2O_3 \cdot P_2O_5 \cdot H_2O$	1 · 16 . 8	500	6.0	Prisamatic, tabular
ErP_5O_{14}	$Er_2O_3 \cdot P_2O_5 : H_2O$	1 · 15 7	400	5 0	Prisamatic, tabular
$KLaP_4O_{12}$	$La_2O_3 \cdot P_2O_5 \cdot K_2O . H_2O$	1 . 12 . 3.5	500	2–3	Small tabular prisamatic needle, transparent crystals
$KLaP_4O_{12}$	$La_2O_3 \cdot P_2O_5 . K_2O : H_2O$	1 · 12 · 4:5	400	0.6	Small crystals, often irregular
$KLaP_4O_{12}$	$La_2O_3 : P_2O_5 \cdot K_2O : H_2O$	1:14 4 · 6	500	2.0	Semitransparent needles
$KLaP_4O_{12}$	$La_2O_3 : P_2O_5 : K_2O . H_2O$	1:15 · 3 · 6	650	3.0	crystals of medium size with different morphology

impurities, growth temperatures, type of cation, etc., play an important role in determining the morphology of rare earth phosphates. The LaP_5O_{14} and $KLaP_4O_{12}$ crystals are highly transparent and colourless. The most common faces observed in pentaphosphates are pinacoidal (001), (100), prism (010), (110) and occasionally pyramidal faces like (102), (201), etc. The most common crystal habits are the rhombohedral plates followed by tabular or disc like and needle or columnar. In laser applications the most useful crystal habit is the needle or columnar habit. The pH of the solution, growth temperature and impurities even in small traces (0.01%) influence the crystallization process and in turn control the crystal habit [14,15]. The characteristic photographs of the rare earth phosphates along with their schematic diagrams are shown in Figure 1 (a–g).

LaP_5O_{14} crystals obtained with relatively higher concentration of P_2O_5 and at 500°C exhibit broad (>10 mm) plate like habits. The crystals are very thin (< 0.5 mm), highly transparent and exhibit a well developed morphology. With the reduction in the concentration of P_2O_5 and at 500°C the crystals become smaller (4 mm), thick (1 mm), transparent and the prism faces become more prominent than the basal pinacoidal. Similarly, with the reduction in growth temperature (400°C) and relatively high P_2O_5 concentration, the crystals become smaller, medium thick (1 mm) and with a slightly different morphology. Twinning becomes very common and the crystals grow longer. The LaP_5O_{14} crystals obtained at higher temperature (650°C) are small, equi-dimensional and thick (>2 mm). However, the crystals retain perfect tabular and rhombohedral habits.

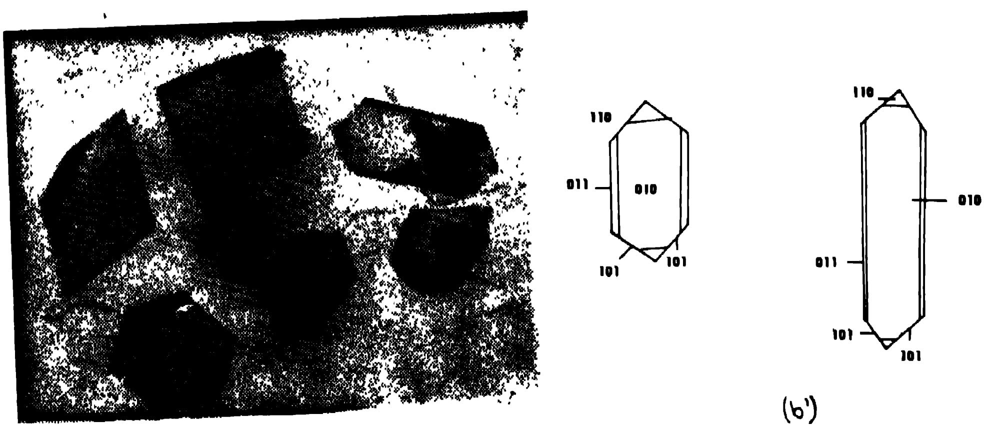
This variation in the morphology with the growth temperature and concentration of P_2O_5 and K_2O becomes more evident in the growth of $KLaP_4O_{12}$ crystals. The crystals obtained at 500°C with a moderate amount of K_2O and P_2O_5 show very well developed morphology. The crystals are transparent, vitreous in lustre, tabular (4 mm) and thick (2 mm). With an increase in the concentration of P_2O_5 and K_2O the crystals grow like needles or columns (>5 mm) and quality of the crystals is fairly good. On the contrary, with an increase in the temperature, the quality of the crystals becomes poor, but equi-dimensional and occasionally tabular habits are obtained.

An understanding of the morphological variation with respect to the growth parameters is essential to study the effect of the degree of supersaturation, concentration of P_2O_5 and K_2O in the system, and the growth temperature. The Figures 2–4 show the variation in the growth rates of rare earth phosphates with the concentration of P_2O_5, K_2O and also with the temperature. The variation in the crystal morphology with the rare earth cations is clearly seen in Figure 1 (a–g). In the present work, an attempt has been made to study the defects in the grown crystals through the study of the surface morphology. The pentaphosphates show very interesting surface morphology which varies accordingly with the growth temperature, supersaturation and impurity atoms in the starting mixture. These variations in the morphology also depend on the magnitude and anisotropy of the growth rates along different directions. The surface morphology of rare earth phosphates is given in Table 2. As evident from Table 2, most of the growth features observed are on the faces (100). Since the crystals obtained belong to lower symmetry, the effect of growth temperature, supersaturation and the impurity concentration is very well depicted in their surface morphology Figure 5 (a–c). The most commonly observed surface growth features are growth spirals, growth layers, growth steps and also dendritic patterns. The dendrites are very common in crystals obtained with higher rate of growth. The presence of microcracks in most of these rare earth phosphates obtained under these conditions,support the formation of dendrites due to the flow of solution from high pressure to low pressure region. Further these microcracks are observed, particularly in crystals which were grown with higher thermal oscillations. If a crystal grows by two dimensional nucleation growth mechanism there is a high probability that it takes



(a)

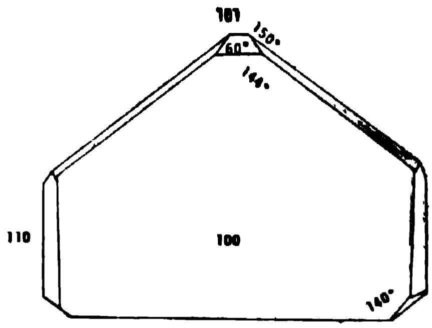
Figure 1 (a). Representative photographs of rare earth phosphates along with their schematic diagram : LaP_5O_{14} (100x).



(b)

Figure 1 (b). Representative photographs of rare earth phosphates along with their schematic diagram : CeP_5O_{14} (25x).

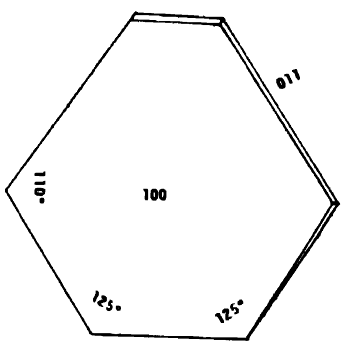
(c)



(c')

Figure 1 (c). Representative photographs of rare earth phosphates along with their schematic diagram : LaP_5O_{14} (40x)

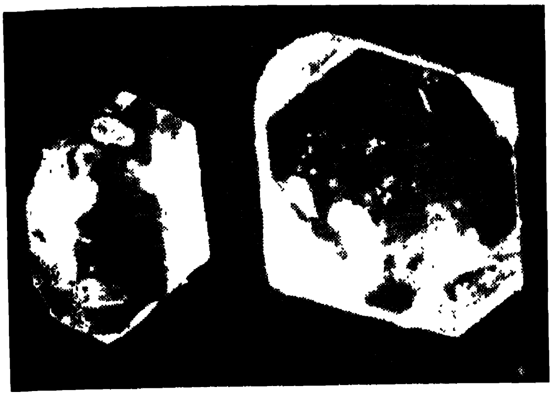
(d)

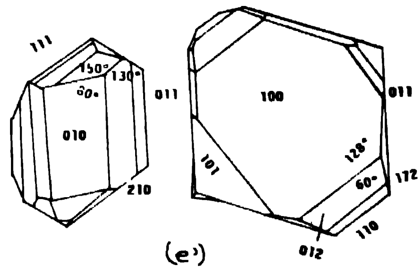


(d')

Figure 1 (d). Representative photographs of rare earth phosphates along with their schematic diagram : LaP_5O_{14} (25x)

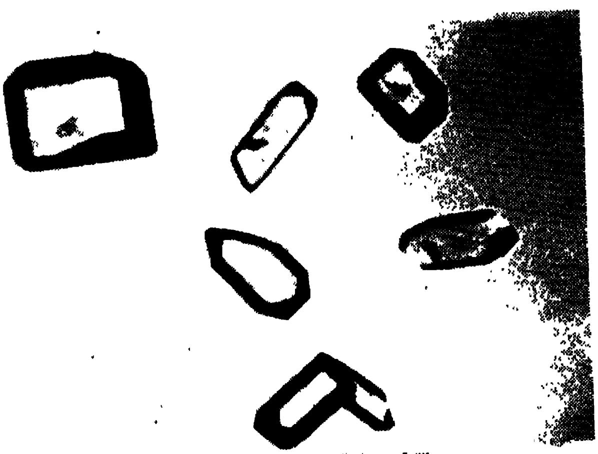
Plate III



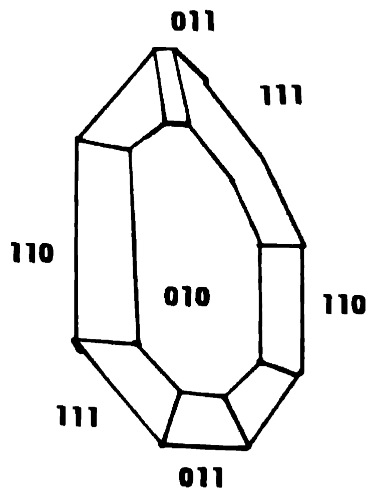


(e')

Figure 1 (e). - Representative photographs of rare earth phosphates along with their schematic diagram : PrP_5O_{14} (40x).



(f)



(f')

Figure 1 (f). - Representative photographs of rare earth phosphates along with their schematic diagram : $KLaP_4O_{12}$ (25x).

(g)

Figure 1 (g). Representative photographs of rare earth phosphates along with their schematic diagram : $KNdP_4O_{12}$ (40x).

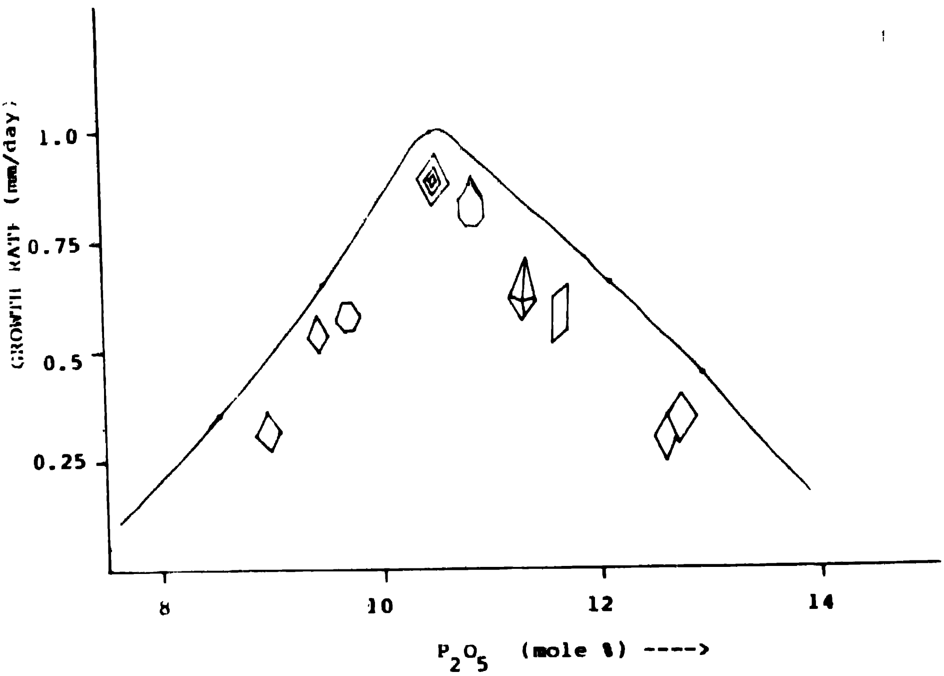


Figure 2. Effect of P_2O_5 concentration on the growth rate of rare earth phosphates.

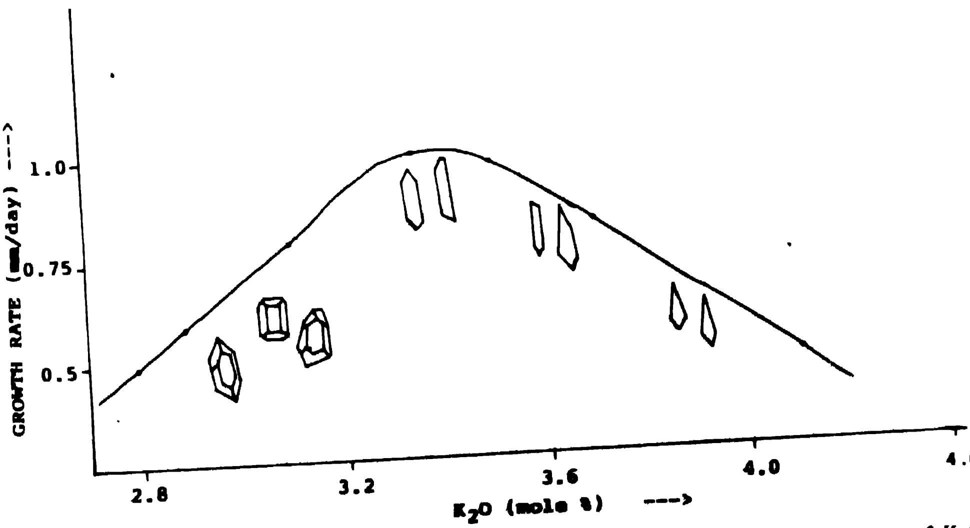


Figure 3. Variation in the growth rate of rare earth phosphates as a function of K_2O concentration in the system.

hopper morphology (Figure 5b). The octagonal spirals are noticed on (100) face of $KLaP_4O_{12}$. With an increase in the supersaturation, temperature and viscosity, the polygonal growth layer shows a tendency to become rounded one. The concentration of impurity also tend to turn polygonal layer into rounded ones. The middle void surface corresponds to the

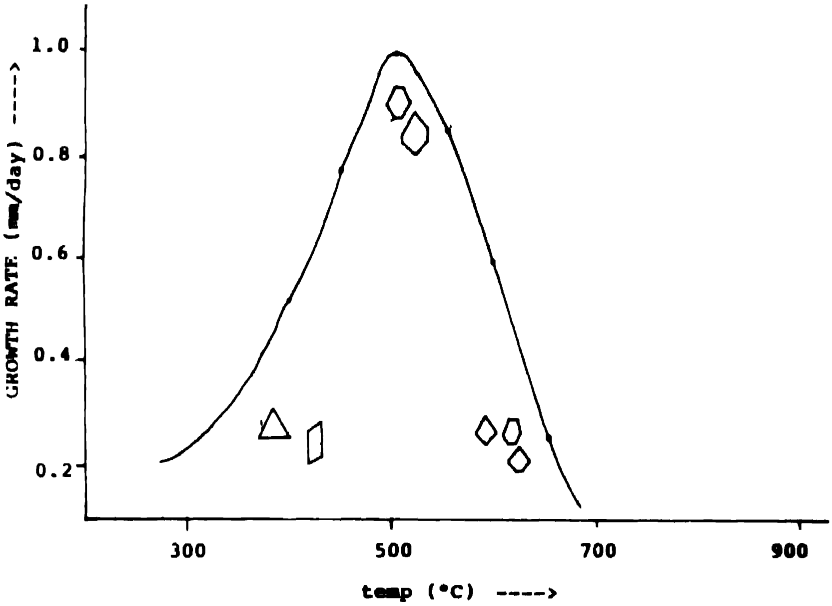


Figure 4. Variation in the growth rate of rare earth phosphates as a function of temperature.

dissolution pit (Figure 5c). It is well-known that rare earth phosphates show a negative temperature coefficient of solubility. During cooling the crystals undergo dissolution and

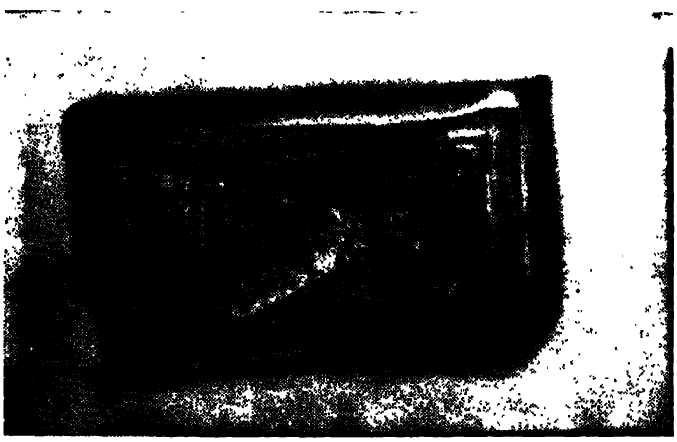
Table 2. Surface morphology of LaP_5O_{14} and $KLaP_4O_{12}$ Crystals.

Compound	Growth temp (°C)	Common faces	Growth rate	Face	Growth feature
LaP_5O_{14}	500	(100), (011)	$v(011) > v(100)$	(100)	dendritic pattern
LaP_5O_{14}	·650	(100), (011)	$v(011) > v(100)$	(100)	growth layers (hopper crystal)
$KLaP_4O_{12}$	500	(100), (011)	$v(101) > v(011) >$ $v(101) > v(100)$	(100)	growth spiral rings
$KLaP_4O_{12}$	650	(011), (101), (001), (100)	$v(011) > v(101) >$ $v(001) > v(100)$	(100)	macrosteps

hence dissolution features are observed in most of the rare earth phosphates. Consequently, the rare earth phosphates do not insist further etching to study the surface morphology. The schematic diagram (Figure 5c′) represent the probable spiral patterns which were dissolved during the cooling of the crystal. A careful observation of Figure 5c reveals the presence of such spirals (as shown in the schematic diagram Figure 5c′). The study of surface

(a)

Figure 5 (a). Surface morphology of the characteristic photographs of LaP_5O_{14} and $KLaP_4O_{12}$ crystals : dendritic pattern on the (100) face of LaP_5O_{14} crystals (100x).



(b′)

Figure 5 (b). Surface morphology of the characteristic photographs of LaP_5O_{14} and $KLaP_4O_{12}$ crystals : hopper crystals of LaP_5O_{14} showing growth layers on the (100) face (100x).

Plate V

(C)

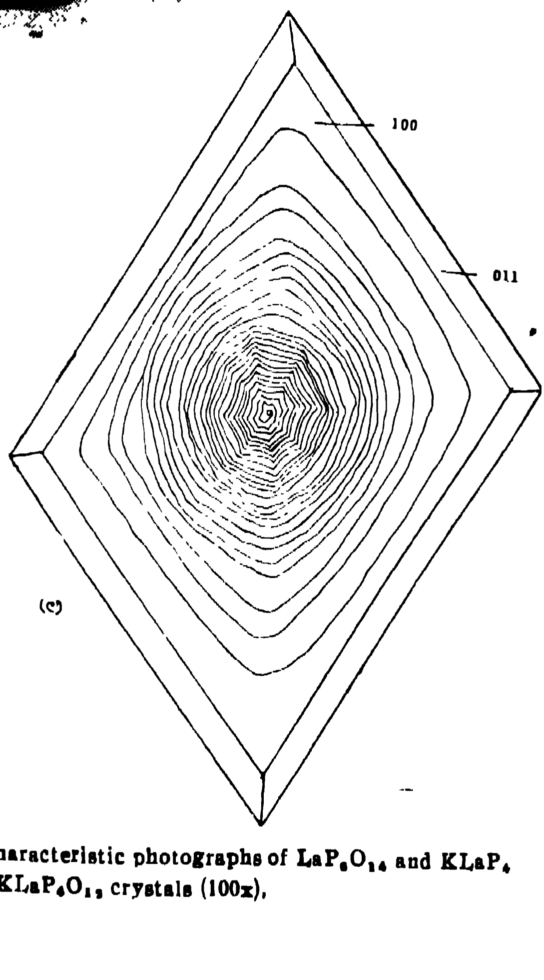


Figure 5 (c). Surface morphology of the characteristic photographs of LaP_6O_{14} and $KLaP_4$ crystals : spiral rings on the (100) face of $KLaP_4O_{12}$ crystals (100x).

morphology clearly indicates the requirement of a slow heating rate, moderate supersaturation and a slow rate of growth to obtain high quality single crystals of rare earth phosphates. The thermal oscillations should be minimum in order to avoid the dendritic growth. Furthermore, the nutrient, *e.g.* rare earth oxide should be of the highest purity.

4. Conclusions

i) Rare earth phosphates – miniature laser materials have been obtained in the form of single crystals from phosphoric acid solutions at various temperatures.

ii) The crystals obtained at 500°C show well developed crystal morphology and the quality is good, whereas the crystals obtained at 650°C are small and equi-dimensional.

iii) The needle like crystals of KRP_4O_{12} can be obtained with moderate P_2O_5 and K_2O concentration and at 500°C, whereas the rhombohedral or plate like crystals of RP_5O_{14} can be obtained with moderate P_2O_5 concentration and at 500 and 650°C.

iv) The surface morphology shows growth spirals, dendrites and macrosteps.

v) The study of crystal habit and surface morphology clearly indicates that the growth of good quality rare earth phosphates insists a slow heating rate, moderate supersaturation and slow rate of growth.

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