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Growth, morphology and structure of $CsRP_4O_{12}$ crystals

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We have grown $CsRP_4O_{12}$ (R^{3+} is a rare-earth ion) crystals from 85% phosphoric acid solutions. Morphological, optical and X-ray studies have been carried out on all the crystals. $CsRP_4O_{12}$ crystallizes in four different structural modifications. The variation in growth temperature causes variation in their morphology and crystal structure.

1. Introduction

Six types of rare-earth phosphates have been reported so far: orthophosphates [$R^{3+}PO_4$, $M^1_3R^{3+}(PO_4)_3$ and $M^1_3R^{3+}(PO_4)_2$], pyrophosphates [$R_4^{3+}(P_2O_7)_3$], tripolyphosphates [$R^{3+}H_2P_3O_{10}$], metaphosphates [$R^{3+}(PO_3)_3$], ultraphosphates [$R^{3+}P_5O_{14}$] and tetraphosphates [$M^1R^{3+}(PO_3)_4$], where M is Li, Na, K, Rb, Cs or NH_4; R^{3+} is a rare-earth ion. Orthophosphates, metaphosphates and ultraphosphates containing the rare-earth ions have been prepared by many workers, for example, Beucher [1], Hong [2], Bonder and Tananaev [3] and Kizilyalli [4], but only a few rare-earth tetraphosphates are known, although many of them serve as important source materials in optoelectronics. We have made an attempt, therefore, to grow Cs tetraphosphates containing all the rare-earth ions by slow heating of aqueous solutions containing Cs_2CO_3 and various rare-earth oxides in 85% phosphoric acid. The present paper reports the growth of $CsRP_4O_{12}$ crystals with special reference to their morphological, optical and X-ray characterization.

2. Crystal growth

We have studied phase formation in the system $Cs_2O–R_2O_3–P_2O_5–H_2O$ within the temperature range 350 to 670° C and at a constant partial pressure of water (~ 1 atm) in order to grow CsR tetraphosphate monocrystals. A mixture of 85% phosphoric acid and Cs_2CO_3 was placed in a vitreous carbon glass crucible and it was held at room temperature till evolution of CO_2 was complete. Later, corresponding R_2O_3 was added to this mixture and the crucible was kept inside the furnace. The rare-earth oxide dissolves completely in 85 % orthophosphoric acid at nearly 250° C to form a homogeneous solution. It is well known that CsR tetraphosphates show a negative temperature coefficient of solubility in phosphoric acid. Therefore, this homogeneous solution was held at 250 to 300° C for 1 to 2 days until the desired equilibrium between vapour and solution had been established. Then the temperature of the reactor (furnace) was slowly increased to a predetermined temperature at a rate of 3.5 to 4° C per hour and held for 7 to 8 days. A more detailed account of the growth is given by Litvin *et al.* [5]. The $CsRP_4O_{12}$ crystals were obtained using different concentrations of $Cs_2O = 27$ to 45 wt %; $P_2O_5 = 52$ to 70 wt %.

The crystals resulted from homogeneous nucleation and they range in size from 1 to 3 mm. We found that the variation in the ratio of the nutrient components did not influence the size of the crystals. The results of our experiments are shown in a composition diagram showing fields of crystallization for $CsRP_4O_{12}$ crystals in the system $Cs_2O–R_2O_3–P_2O_5–H_2O$ (Fig. 1). The changes in composition of Cs_2O and P_2O_5 determine boundaries of crystallization for various phases. Good quality crystals can be obtained by selecting suitable concentrations for Cs_2O and P_2O_5 within the boundaries indicated. The crossed region in the composition diagram represents fields of simultaneous crystallization of neighbouring phases. The study of optical, morphological and X-ray characterization revealed four different modifications of $CsRP_4O_{12}$ crystals.

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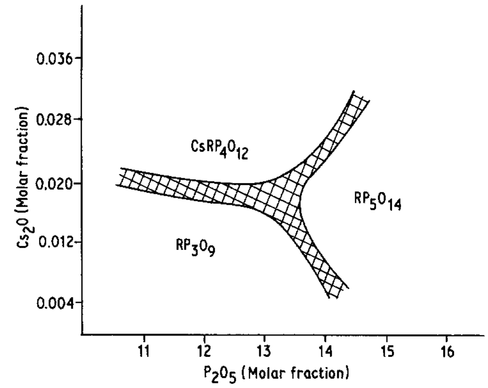

Figure 1 Diagram showing starting compositions of solutions.

3. Crystal morphology

The morphology of $CsRP_4O_{12}$ crystals is given in Table I. On the basis of the morphology of these crystals, we conclude that the tetrahedral faces (Fig. 2a) characteristic of crystals grown at lower temperature (~ 350 to 500° C) with rare-earth ions of higher ionic radii are replaced by tabular, prismatic and clinohedral faces (Fig. 2b and c) in crystals containing rare-earth ions of lower ionic radii. The crystals showing prismatic and clinohedral forms are extended longitudinally parallel to the *c*-axis. The crystals grown at higher temperatures (> 520° C) are characterized by prism and pyramidal forms (crystals with rare-earth ions form La to Er, Fig. 2d and e) and clinohedral forms (crystals with rare-earth ions from Tm to Lu). With a further increase in growth temperature (> 680° C), the crystals become smaller and more equi-dimensional (Fig. 2f) due to the higher ionic mobility, low viscosity and higher concentration of the solute ions. Plate-like crystals are not observed in the tetraphosphates, contrary to what is observed in the ultraphosphates.

The crystals belonging to the second structure type (crystals containing rare-earth ions from La to Nd) resemble an ideal crystal of monazite (Fig. 2d). These crystals were obtained at 580° C and they show a diamondiferous lustre. The faces are very well developed with highly polished surfaces. We have obtained these crystals using higher concentrations of R_2O_3 and at higher temperatures of growth ranging from 580 to 670° C; the quality of the crystals was exceptional. This does not agree with the results of Miyazawa *et al.* [6], who observed that higher temperatures of growth and higher concentrations of R_2O_3 caused too rapid crystallization, resulting in poor quality and small size of $KNdP_4O_{12}$ crystals. We observed that the variation in concentration of the nutrient components within the crystallization field of Fig. 1 has no influence on the size and optical quality of the crystals.

4. X-ray study

An X-ray diffractometer URS-50 IM with CuKα radiation was used in the study of $CsRP_4O_{12}$ crystals. Fig. 3 shows the dependence of the four different modifications, upon the ionic radii of the rare-earth ions and the growth temperatures. The

TABLE I Morphological characterization of $CsRP_4O_{12}$ crystals

Rare-earth ions	Growth temperature (° C)	Structure type	Morphology	Common faces in the crystals
La–Eu	350	I	Trigonal tetrahedral	(1 1 1), (0 1 1), (1 0 1)
Sm–Er	350	II	Tabular, prismatic, clinohedral and tetrahedral	(1 0 0), (1 1 1), (1 1 0), (0 1 0), (0 0 1), (1 0 1), (0 1 1), $(1\,\bar{3}\,1)$
La–Nd	580	II	Tabular	(1 0 0), (1 1 0), (0 1 0), (1 0 1), (1 1 1), $(\bar{1}\,1\,1)$
Sm–Er	580	II	Prismatic, tabular and clinohedral	(1 1 0), (0 1 0), (0 0 1), $(1\,\bar{3}\,1)$, (1 1 1)
Tm–Lu	580	II	Clinohedral and tabular	(1 1 0), (0 1 1), $(\bar{1}\,1\,0)$, (0 1 0), $(1\,\bar{3}\,1)$, (1 1 1)
La–Nd	720	II	Small equi-dimensional	$(1\,\bar{1}\,1)$,, $(\bar{1}\,1\,1)$, (0 1 0), (0 1 1)
Tm–Lu	350	III	Clinohedral and tabular	(1 1 0), (0 1 1), (0 1 0), $(\bar{1}\,1\,0)$, $(1\,\bar{3}\,1)$, (1 1 1)
La–Nd	580	IV	Tabular, prismatic (poor development of the faces)	–

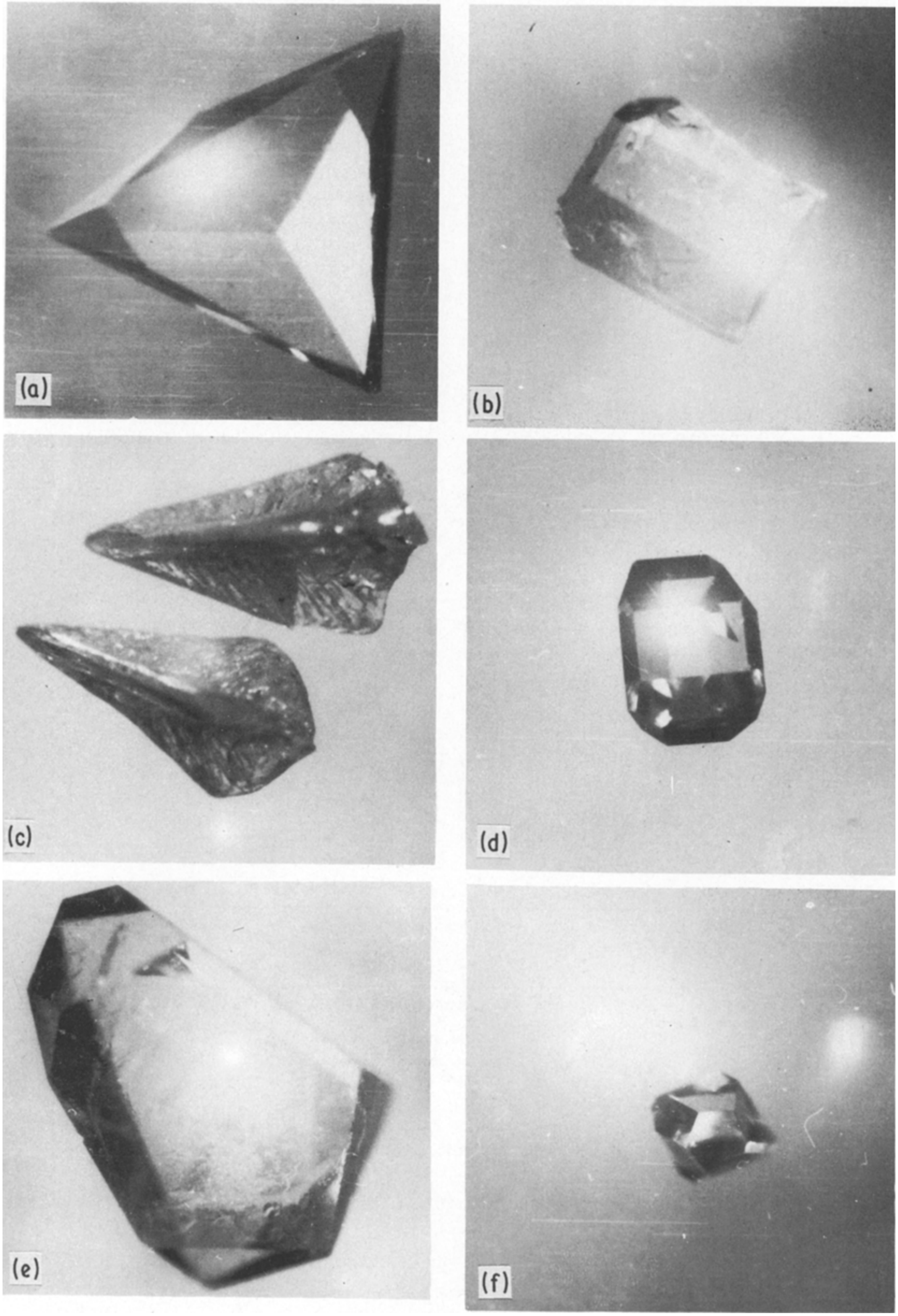

Figure 2 Representative photographs of $CsRP_4O_{12}$ cyrstals: (a) $CsNd(PO_3)_4$ crystals from first structure type obtained at 350° C; (b) $CsTb(PO_3)_4$ crystals from second type obtained at 350° C; (c) $CsLu(PO_3)_4$ crystals from third structure type obtained at 350° C; (d) α-$CsNd(PO_3)_4$ crystals from second structure type obtained at 580° C; (e) $CsSm(PO_3)_4$ crystals from second structure type obtained at 580° C; and (f) β-$CsNd(PO_3)_4$ crystals from fourth structure type obtained at 720° C.

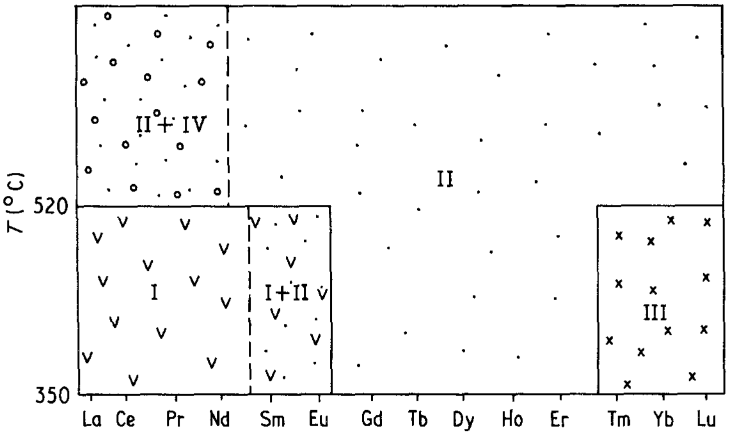

Figure 3 Different structural types of $CsRP_4O_{12}$, illustrating the relationship between the ionic radii of the rare-earth ions and the growth temperature: (I) Cubic, optically isotropic crystals; (II) Monoclinic, optically negative crystals; (III and IV) Monoclinic, optically positive crystals.

cell parameters for representative crystals from each group and their optical constants are given in Table II. The compounds with the rare-earth ions La to Eu form the first structure type, and the compounds with Sm and Eu ions occur in two modifications. Palkina *et al.* [7] reported the cubic modification of $CsRP_4O_{12}$, where R = Nd and Pr. We have determined the absolute cell parameters for all the compounds of this structure type. The values of the cell parameters were plotted against the ionic radii of the rare-earth ions (Fig. 4) which shows a linear dependence between the two. However, $CsCeP_4O_{12}$ proved to be an exception. The values of ionic radii for the rare-earth ions are taken from Ahrens [8].

For the second and third structure types of $CsRP_4O_{12}$ crystals, we determined the cell parameters of $CsGd(PO_3)_4$ and $CsLu(PO_3)_4$, respectively. The cell parameters of the latter have not been reported in the literature, therefore, a detailed structural analysis of this modification is being carried out by us.

For the fourth structure type, the cell parameters of β-$CsNd(PO_3)_4$ are given in Table II. With a further increase in growth temperature, this structure type continues to crystallize. Thus, the X-ray study revealed that $CsRP_4O_{12}$ crystallizes in four different modifications. Those containing rare-earth ions La to Nd form three different modifications and those containing the remainder

TABLE II Cell parameters and optical constants for $CsRP_4O_{12}$ crystals

Structure type	Crystal composition	Cell parameters		Optical constants	
		Structure	Space group	Refractive indices	$2V$(°)
I	$CsNd(PO_3)_4$	*Cubic* $a = 15.232$ nm	$I4_132$*	1.533	–
II	$CsGd(PO_3)_4$	*Monoclinic* $a = 10.449$ (3) nm $b = 13.057$ (4) nm $c = 8.930$ (3) nm $\gamma = 56.13°$	$P2_1/b$	$N_g = 1.632$ $N_m = 1.627$ $N_p = 1.621$	−50
III	$CsLu(PO_3)_4$	*Monoclinic* $a = 9.955$ (3) nm $b = 13.961$ (3) nm $c = 20.023$ (5) nm $\gamma = 52.39°$	$B2/b$	$N_g = 1.573$ $N_m = 1.562$ $N_p = 1.556$	+85
IV	β-$CsNd(PO_3)_4$	*Monoclinic* $a = 7.145$ nm $b = 8.809$ nm $c = 9.146$ nm $\gamma = 99.65°$	$P2_1$	$N_g = 1.636$ $N_m = 1.630$ $N_p = 1.617$	+68

*See Palkina *et al.* [3].

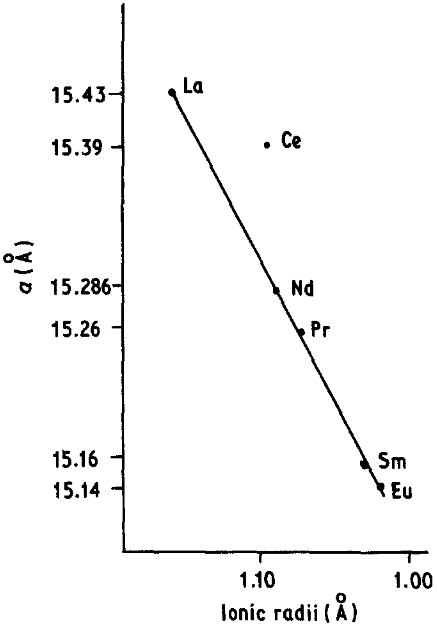

Figure 4 Linear dependence of the cell parameters and ionic radii of the rare-earth ions (for first structure type of the crystals).

of the rare-earth ions crystallize in two different modifications (Fig. 3).

5. Conclusions

(a) Morphological, X-ray and optical studies reveal four different structural groups among the $CsRP_4O_{12}$ crystals.

(b) The variation in growth temperature and ionic radii of the rare-earth ions changes the morphology and crystal structure.

(c) Three structural modifications of $CsRP_4O_{12}$ occur with the rare-earth ions La to Nd depending upon the growth temperature, and two additional structural modifications occur with the rest of the rare-earth ions.

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