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Preparation of lanthanide orthophosphates by crystallisation from phosphoric acid solution

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Highly crystalline solids of the composition of $LnPO_4 \cdot nH_2O$ (Ln = La, Ce, Pr, Nd. Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) were prepared by crystallisation from boiling phosphoric acid solution with the initial concentration 2 M/1 of H_3PO_4 and 0.02 M/1 of Ln. The number of molecules of water (n) was close to 1. The crystallisation process was completed within two hours. Scanning electron micrographs showed that the diameter of the $LnPO_4 \cdot H_2O$ crystalline particles was increasing within the group of elements from below 1 μm ($LaPO_4 \cdot H_2O$) to above 5 μm ($TmPO_4 \cdot H_2O$). Such large crystals of lanthanide phosphates cannot be obtained by usually applied precipitation methods. The light lanthanides (La → Sm) formed clusters of shapeless particles with the tendency to form 'rod-like' crystals. The heavy lanthanides (Ho → Lu, and $YPO_4 \cdot H_2O$) consisted of spherical globules. The $TbPO_4 \cdot H_2O$ and $DyPO_4 \cdot H_2O$, formed a mixture of the spherical and rod-like crystals. © *2003 Kluwer Academic Publishers*

1. Introduction

Lanthanide phosphates are usually obtained by precipitation from aqueous solutions of their salts using, for example, sodium or ammonium phosphates. When they are precipitated from phosphoric acid solution, Na_2CO_3 or NH_4OH are used as precipitants [1–9]. The precipitate obtained tends to be gelatinous, very often unfiltrable and is contaminated with foreign ions derived from the precipitant. Recently, under hydrothermal conditions, Haase *et al.* prepared Eu-doped nanocrystals of $LaPO_4$ [10], while Ito *et al.* precipitated lanthanide phosphates by simultaneous decomposition of Ln-EDTA chelates in the presence of PO_4^{3-} ions [11].

Lanthanide phosphates are known as scarcely soluble salts. Their solubility products are on the level of 10^{-25}–10^{-27} [12]. The solubility of lanthanides in phosphoric acid has been sporadically investigated in the 1960s [1–7]. The published data are rather limited to La and Ce phosphates and indicate that their solubility, within the investigated temperature range 20°C–80°C, decreases with the temperature increase. It also increases with an increase of H_3PO_4 concentration.

The aim of the present work was to develop a simple method of lanthanide phosphate preparation. Instead of usually applied precipitation method, a crystallisation process from phosphoric acid was applied. The method combines two physical phenomena characteristic to rare earth phosphates. They are (1) the effect of temperature and (2) the effect of H_3PO_4 concentration on lanthanide solubility.

2. Materials and methods

2.1. Materials

The lanthanide phosphate crystallisation was carried out from the solution with the initial concentration 2 M/1 of H_3PO_4 and 0.02 M/1 of Ln(III), where Ln(III) = La, Ce, Pr, Nd. Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. The reagents used were:

- La_2O_3, Pr_6O_{11}, Sm_2O_3, Dy_2O_3, specure (Johnson Matthey Chemicals Ltd, London),
- Eu_2O_3 (99.9%) (Int. Enzymes Ltd., England),
- Gd_2O_3 (puriss.), Er_2O_3 (99.9%), Yb_2O_3 (99.9%), $Nd(NO_3)_3 \cdot 6H_2O$ (puriss.) (Fluka AG, Buchs SG),
- Lu_2O_3 (99.9%) (SERVA Feinbiochemica, Heidelberg),
- Ho_2O_3 (99.9%), Tm_2O_3 (99.9%), Tb_4O_6 (99.9%), $Ce(NO_3)_3 \cdot 6H_2O$ (99%), (Aldrich), and phosphoric acid (15 M/1 H_3PO_4), p.a. POCh S.A, (Poland).

100 to 200 ml of the solution prepared for the crystallisation resulted in an amount of a solid sufficient for physico-chemical analyses.

2.2. Crystallisation procedure

The experimental procedure has been based on the assumption that a solution of lanthanide in a concentrated phosphoric acid prepared at ambient temperature, next, diluted to some extent of H_3PO_4 concentration, and heated to the boiling point becomes oversaturated with respect to lanthanide phosphate sufficiently for the crystallisation to occur.

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An amount of the appropriate lanthanide oxide sufficient for the 100 ml of 0.02 M/l Ln solution, was treated with the 13.5 ml of concentrated phosphoric acid (15 M H_3PO_4/l). Some decrease in viscosity of phosphoric acid solution facilitated the dissolution of the Ln-oxide. To achieve it, 3–4 ml of distilled water was added do the slurry obtained. The mixture was left to stay overnight or for a longer period of time within which the Ln-oxide was dissolving. The clear solution obtained was diluted with water to the volume of 100 ml, transferred to a flask covered with reflux condenser, heated and kept boiling for two hours. There was no need to apply a stirrer, for the boiling solution was stirring by itself, while the reflux condenser protected the solution from evaporation. The solid obtained was filtered off, washed with distilled water and dried at 60°C.

To characterise the crystallised solids powder X-ray diffraction (XRD), scanning electron microscopy (SEM), IR- absorption spectroscopy, and thermal decomposition methods were applied. The XRD and IR results constitute a separate paper [13], while selected SEM micrographs are presented below.

3. Results and discussion

To find out the most effective crystallisation parameters, some preliminary experiments evaluating the effect of temperature and phosphoric acid concentration on the $LnPO_4$ apparent solubility were carried out. As an example the concentration of Eu in 2 M/l H_3PO_4 solution after 6 hours of crystallisation at different temperatures is presented in Fig. 1, while Eu concentration depending on the phosphoric acid concentration after 2 hours of crystallisation at boiling point is presented in Fig. 2. The apparent solubility drastically increases while the acid concentration is higher than 2 M/l H_3PO_4 (Fig. 2). However, an increase of temperature brings the solubility drastically down (Fig. 1). A combination of these two phenomena enables effective crystallisation of lanthanide phosphates from boiling solution of phosphoric acid with the concentration not higher than 2 M/l H_3PO_4.

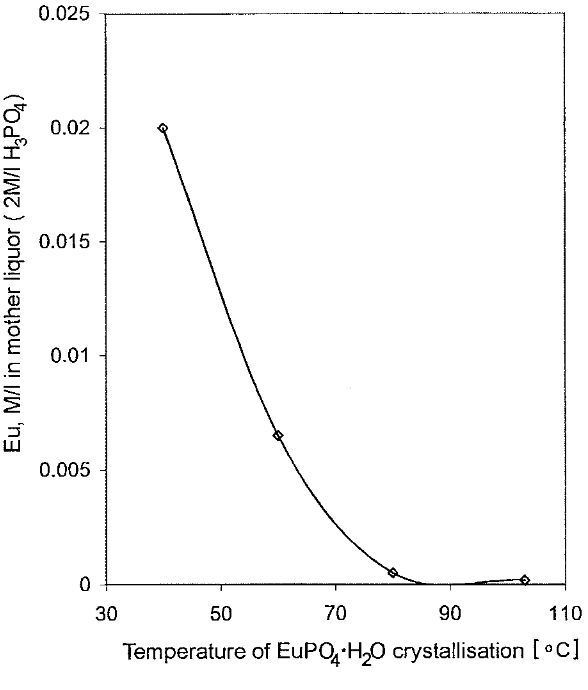

Figure 1 Eu concentration in 2 M/l H_3PO_4 solution after 6 hours of $EuPO_4 \cdot H_2O$ crystallisation at different temperatures.

TABLE I Lanthanide concentration in 2 M/l H_3PO_4 after two hours of $LnPO_4 \cdot H_2O$ crystallisation

Lanthanide	M/l	Efficiency of crystallisation (%)
La	2.0×10^{-5}	99.9
Pr	1.4×10^{-4}	99.3
Nd	1.3×10^{-4}	99.4
Sm	1.8×10^{-4}	99.1
Eu	1.8×10^{-4}	99.1
Gd	5.2×10^{-4}	97.4
Dy	1.0×10^{-3}	95.0
Ho	1.4×10^{-3}	93.0
Er	2.0×10^{-3}	90.0
Yb	2.3×10^{-3}	88.5
Lu	3.0×10^{-3}	85.0

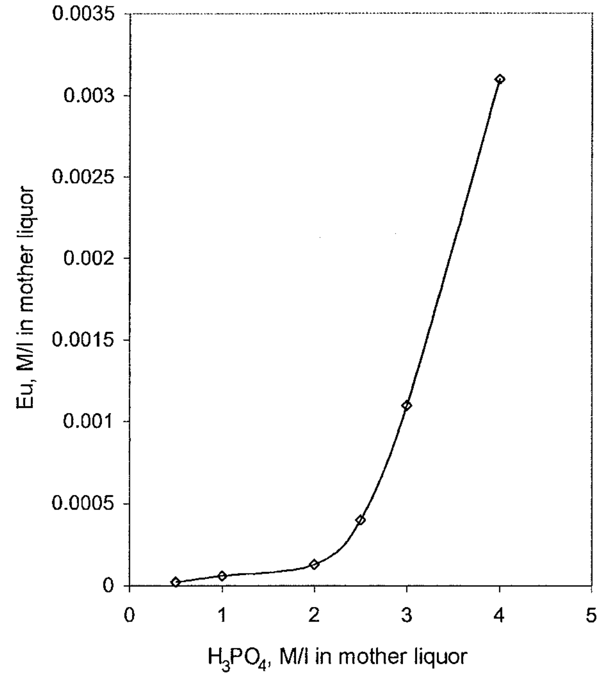

Figure 2 Eu concentration after 2 hours of $EuPO_4 \cdot H_2O$ crystallisation in boiling phosphoric acid of different H_3PO_4 concentration.

The concentration of the lanthanide in the mother liquor, after two hours of crystallisation, presented in Table I, is on the level of 10^{-5}–10^{-3} M/l and is related to the solubility of lanthanide in phosphoric acid. The efficiency of the separation of the lanthanide phosphate by crystallisation from the boiling phosphoric acid solution containing 2 M/l H_3PO_4 and 0.02 M/l Ln is higher than 99% for the first half of the group (La – Eu) and is decreasing for the second half of the group.

The well crystallised solid of the composition of $LnPO_4 \cdot nH_2O$, where n was close to 1, was obtained. The solid crystallised either in the hexagonal modification (La – Tb) or the tetragonal (Ho – Lu + Y), except the dysprosium phosphate which was orthorombic [13].

Scanning electron micrographs of the $LnPO_4 \cdot H_2O$ obtained by crystallisation from 2 M/l H_3PO_4 are presented in Fig. 3A–F. The morphology of the phosphate crystals differs between the subgroups of light and heavy lanthanides. The lanthanides with the hexagonal modification tend to form 'rod-like' crystals (Fig. 3B), however, the light lanthanides (La – Sm) form clusters of shapeless or of 'sphere-like' particles (Fig. 3A). The morphology of the tetragonal modification of the heavy lanthanides beginning with $HoPO_4 \cdot H_2O$ appears as spheres similar to $YPO_4 \cdot H_2O$ (Fig. 3E and F). The

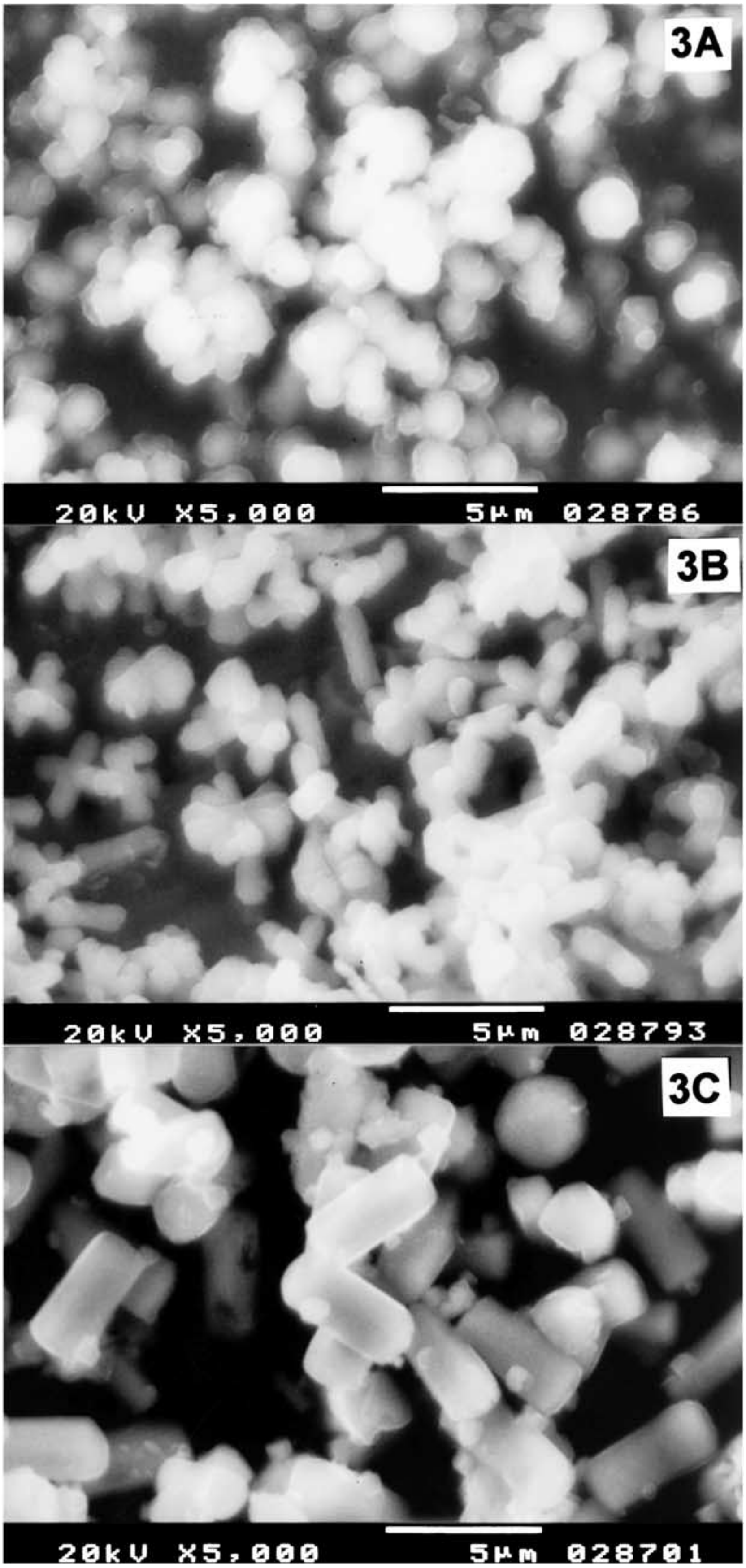

Figure 3 SEM micrographs of phosphates crystallised from 2 M/1 H_3PO_4 boiling solution. 3A = $NdPO_4 \cdot H_2O$ 3B = $GdPO_4 \cdot H_2O$ 3C = $DyPO_4 \cdot H_2O$ 3D = $TbPO_4 \cdot H_2O$ 3E = $TmPO_4 \cdot H_2O$ 3F = $YPO_4 \cdot H_2O$. (*Continued.*)

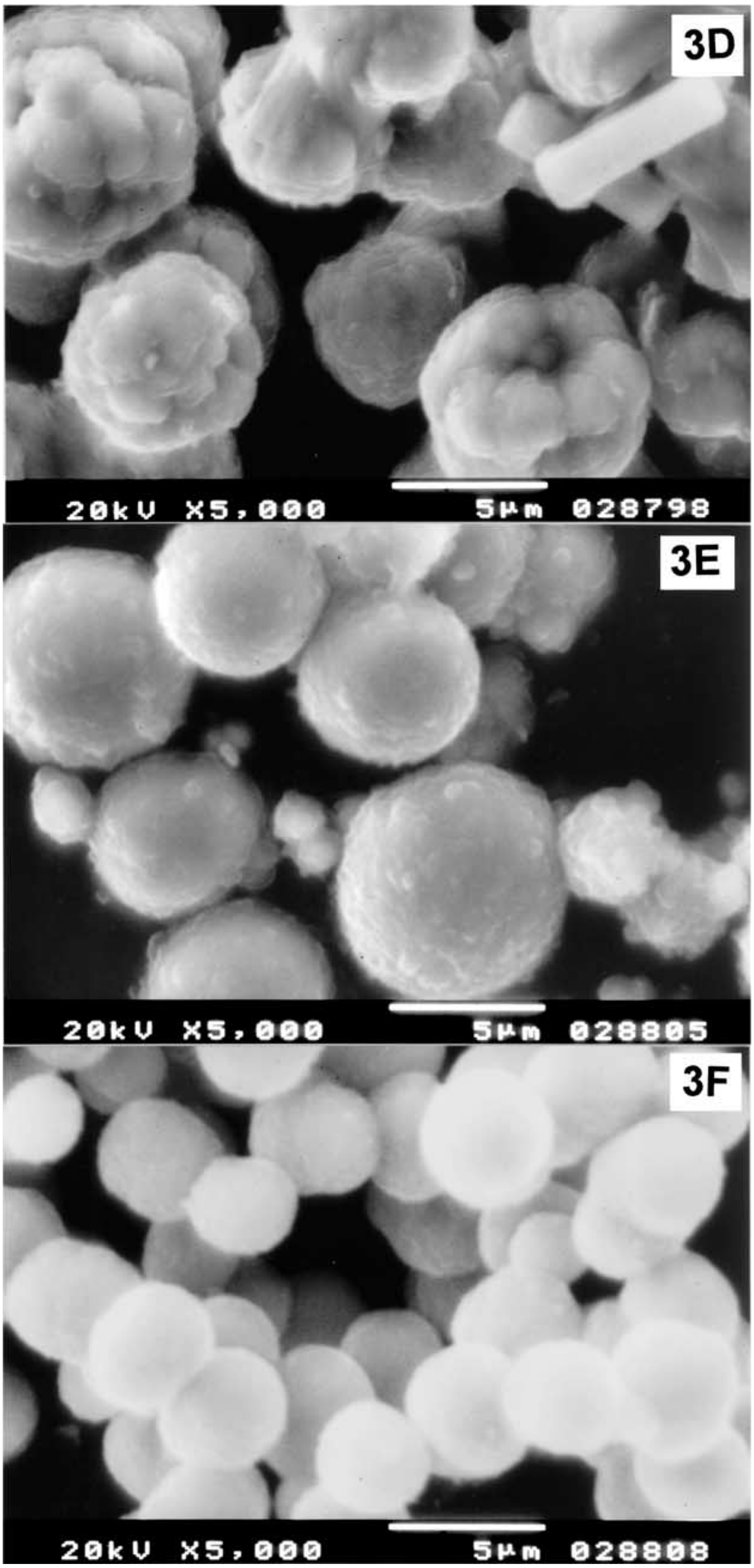

Figure 3 (*Continued*).

$TbPO_4 \cdot H_2O$ or $DyPO_4 \cdot H_2O$ form a mixture of the spherical and rod-like crystals (Fig. 3C and D).

The size of the $LnPO_4 \cdot H_2O$ crystal was increasing from La to Lu. That might be explained in terms of their solubility, demonstrated in Table I. The concentration of Ln in the mother liquor was increasing, whereas the initial concentration of the lanthanide in all solutions prepared for crystallisation was on the same level (0.02 M/1). As a result the oversaturation with respect to $LnPO_4$ was decreasing and the spontaneous crystallisation process might have been less and less rapid along the group, which should be in favour of the higher crystallinity of the heavy lanthanides. The remarkable result has been obtained for the $YPO_4 \cdot H_2O$. The crystals are organised in spherical globules of the uniform size. The diameter of $YPO_4 \cdot H_2O$ was close to 5 μm, while the diameter of the $TmPO_4 \cdot H_2O$ spheres was even larger than 5 μm. Such large crystals cannot be obtained by usually applied precipitation methods.

4. Conclusion

A preparation method of lanthanide phosphates by crystallisation from phosphoric acid has been developed.

The principle of the method is to dissolve at ambient temperature as much Ln-oxide as possible in a concentrated phosphoric acid solution (15 M/1 H_3PO_4), next, dilute the clear solution obtained to some desirable level of concentration (advisable below 2 M/1 H_3PO_4) and heat the solution to the boiling point. Usually crystallisation of $LnPO_4 \cdot nH_2O$ is completed within two hours, ($n \approx 1$).

The method can be utilised to prepare highly crystalline lanthanide phosphate materials, especially for the heavy elements of that group and yttrium.

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