Effect of Ca on gadolinium phosphate crystallisation from phosphoric acid solution

R. KIJKOWSKA
Institute of Inorganic Chemistry and Technology, Cracow University of Technology,
31-155 Kraków, Warszawska 24, Poland
E-mail: kij@chemia.pk.edu.pl

Gadolinium phosphate, obtained through crystallisation from phosphoric acid solution containing Ca-ions, has been characterised by X-ray diffraction, IR-spectra and scanning electron microscopy methods. The presence of Ca-ions in solution resulted in Ca for Gd substitution coupled with simultaneous HPO_4^{2-} incorporation in crystalline hexagonal $GdPO_4 \cdot H_2O$. The HPO_4^{2-} compensated for the difference in the electric charge between divalent calcium and trivalent gadolinium in the crystallised solid. The amount of Ca in the solid obtained did not exceed 2.5 wt%. Calcium incorporation in gadolinium phosphate caused significant enlargement along the *c*-axis and less significant contraction along the *a*-axis of the $GdPO_4 \cdot H_2O$ unit cell. © *2004 Kluwer Academic Publishers*

1. Introduction

Lanthanide phosphates ($LnPO_4$) doped with other elements of that group have been considered as potential phosphate based-phosphor materials for several applications, such as phosphor lamps of high luminescence or television monitors [1–3]. Some applications require materials of high purity. The purity is affected not only by the grade of initial (raw) materials, but also by the chemical method of preparation. There are several methods of lanthanide phosphate preparation, mostly involving precipitation from aqueous solutions or solid-state reactions [4–14]. Quite frequently precipitation methods yield solids contaminated by ions derived from a precipitant or by products of co-precipitation. Crystallisation methods usually enable solids of higher purity to be obtained. A preparation method for lanthanide phosphates by crystallisation from boiling phosphoric acid solution, yielding crystalline solids of $LnPO_4 \cdot nH_2O$, (Ln: La → Lu and Y) has been reported [15]. The phosphates obtained by that method, depended on the ionic radius and crystallised in the following forms: hexagonal, isostructural with the mineral rabdophane (La → Tb) and tetragonal (Ho → Lu and Y), isostructural with the xenotime (zircon – type structure), while dysprosium phosphate appeared to be in the orthorhombic form [16]. This was in agreement with the literature data [17–22].

The aim of the present work was to investigate effect of the presence of Ca-ions in phosphoric acid solution on the crystallisation of gadolinium phosphate. The hypothesis was that Ca^{2+} and Gd^{3+} ions, having comparable radii, could substitute for each other in the phosphate.

2. Experimental
2.1. Materials and methods

Reagent grade chemicals, Gd_2O_3 (puriss.) (Fluka AG, Buchs SG), $Ca(NO_3)_2 \cdot 4H_2O$ and phosphoric acid (15 M H_3PO_4), p.a. POCh S.A, (Poland), were used without further purification.

Crystallisation was carried out in boiling solution by the method described earlier [15]. The principle of the method is to dissolve at ambient temperature as much lanthanide oxide as possible in concentrated phosphoric acid (for example, 15 M). Next, the clear solution obtained is diluted to some desirable level of the acid concentration (below 2 M) and the solution is heated to boiling point. The increased temperature makes the solution oversaturated with respect to lanthanide phosphate and crystallisation results.

A series of solutions with 2 M H_3PO_4, 0.02 M Gd and different Ca concentrations: 0, 0.05, 1.125, 0.25, 0.5, and 1.0 M were prepared. The reagents were dissolved in two different solutions. The first solution contained Gd_2O_3 treated with concentrated (15 M) phosphoric acid. The slurry obtained was left overnight or for a longer period of time to dissolve the Gd_2O_3. In the second solution an amount of calcium nitrate, equivalent to the required Ca concentration was dissolved in a small amount of water and the solution obtained was introduced into the first solution. If the solutions are mixed in reverse order a gelatinous gadolinium phosphate may spontaneously precipitate at room temperature before the solution is heated. The mixed solution was carefully diluted with water to give 2 M H_3PO_4 and 0.02 M Gd concentration in the final solution. The clear solution obtained was transferred to a flask, covered with a reflux condenser, heated to the boiling point, (~100°C)

and, after the crystallisation started, kept boiling for two hours. The crystalline solid was filtered off, washed with distilled water and dried in an oven at 60°C.

To characterise the crystallised solids chemical analysis, powder X-ray diffraction (XRD), IR-absorption spectroscopy, thermal decomposition and scanning electron microscopy (SEM) methods were used. Philips X'pert XRD equipment with a graphite monochromator (PW 1752/00) Cu K_α, (λ = 0.15418 nm) radiation, a Ni filter and 2Θ from 10 to 60 degrees at 30 kV, 30 mA was used. The unit cell parameters were determined using the Unit Cell program (Tim Holland and Simon Redfern). A Fourier Transform IR Spectrometer (FTIR-FTS 175, Bio-Rad) was used to record IR spectra (1 wt% of sample in KBr pressed pellet), over the wavenumber range 400–4000 cm^{-1}. Thermal decomposition was investigated using a TGA-DTA (simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)) fully automated system (Universal V2.3C TA Instruments).

ICP (Inductively Coupled Plasma) method was used for Ca analysis, while for Gd and P spectrophotometric methods were applied. For the phosphate analysis ammonium molybdate (1 wt%) in sulphuric acid (5 wt% of H_2SO_4) and 0.5 wt% of amidol (2,4-diaaminophenol hydrochloride) in $NaHSO_3$ (10 wt% in water solution) were used. The extinction was measured at a wavelength of 660 nm. For Gd analysis, 0.1 wt% of arsenazo-III [2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic acid] dissolved in water was introduced into buffered solution (acetate buffer, pH = 3) and the extinction was measured at 625 nm.

3. Results and discussion

All the solids, obtained through crystallisation from phosphoric acid solution without/or containing Ca, were hexagonal (Fig. 1) isostructural with the mineral rhabdophane, already described in the literature [17–22]. No other phases were observed.

There is an uncertainty about the number of H_2O molecules in lanthanide phosphates and their role in the crystal structure. The H_2O is reported to be of zeolitic nature and is related to the specific structure of $LnPO_4 \cdot nH_2O$ [11, 17, 23]. According to Mooney [17] who was the first to describe the hexagonal crystal structure of synthetic lanthanide phosphates, the open channels along the c-axis can accommodate up to 1.5 molecules of water per unit cell. Therefore, with
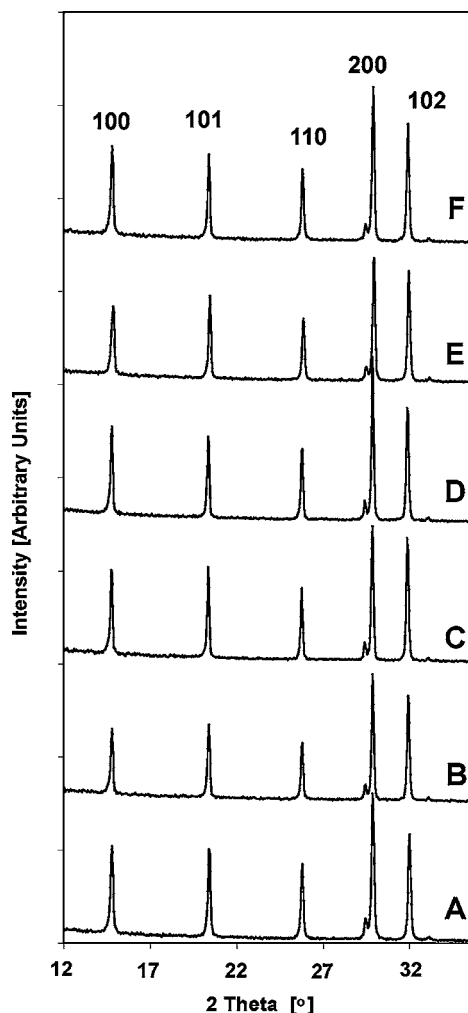

Figure 1 X-ray diffraction patterns of hexagonal $GdPO_4 \cdot H_2O$ (A) and Ca-substituted gadolinium phosphates crystallised from phosphoric acid solution, containing Ca: (B) – 0.05 M, (C) – 0.125 M, (D) – 0.25 M, (E) – 0.5 M, and (F) – 1.0 M.

three molecules of $LnPO_4$ in the unit cell of the hexagonal structure, there should be no more than 0.5 M of H_2O per Ln atom. However, different authors have reported different amounts of water in the hexagonal $LnPO_4 \cdot nH_2O$ ranging in (n) from 0.3 to 3 [11, 17, 19, 22, 24–28]. If the water is of zeolitic nature it can be speculated that such a wide range of water uptake may result from different experimental conditions of the precipitation.

In the present work the amount of water determined by TGA was at a constant level of 6.5–7 wt% in Ca-free or Ca-containing gadolinium phosphates. From the

TABLE I Chemical composition of the solids crystallised from aqueous solution containing 2 M of H_3PO_4, 0.02 M Gd and 0–1 M Ca

Solution Ca (M)	Crystallised solid (wt%)								
	Analysed element				Calculated		Component		
	Gd	Ca	P	H_2O	Gd_2O_3	CaO	P_2O_5	$Gd_2O_3 + CaO + P_2O_5 + H_2O$	Volume of the unit cell (nm^3)
0	58.4 ± 1.5	0	11.5 ± 0.3	6.5 ± 0.1	67.3 ± 1.7	0	26.2 ± 0.7	100 ± 1.8	26.12 ± 0.01
0.050	54.7 ± 1.4	1.4 ± 0.1	12.3 ± 0.3	6.9 ± 0.1	62.9 ± 1.6	2.0 ± 0.1	28.2 ± 0.7	100 ± 1.8	26.17 ± 0.05
0.125	53.6 ± 1.3	1.6 ± 0.1	12.8 ± 0.5	6.9 ± 0.1	61.7 ± 1.5	2.2 ± 0.1	29.2 ± 0.7	100 ± 1.7	26.19 ± 0.05
0.250	52.1 ± 1.3	1.9 ± 0.1	13.1 ± 0.5	7.3 ± 0.1	60.0 ± 1.5	2.7 ± 0.1	30.0 ± 0.8	100 ± 1.7	26.20 ± 0.07
0.500	51.5 ± 1.3	2.1 ± 0.2	13.4 ± 0.5	7.0 ± 0.1	59.4 ± 1.5	2.9 ± 0.2	30.7 ± 0.8	100 ± 1.7	26.19 ± 0.07
1.00	51.3 ± 1.3	2.5 ± 0.2	13.2 ± 0.5	7.1 ± 0.1	59.1 ± 1.5	3.5 ± 0.2	30.3 ± 0.8	100 ± 1.7	26.15 ± 0.08

chemical composition (Table I) the total amount of water (without distinction between hygroscopic and zeolitic forms) can be approximated to give $GdPO_4 \cdot H_2O$. A similar amount of water was recorded for other lanthanide phosphates of rabdophane structure [29] obtained by the method of crystallisation from boiling phosphoric acid solution [15].

When Ca-ions were present in solution, Ca was co-precipitated in the solid. The amount of Ca in the solid did not exceed 2.5 wt% even when Ca concentration in the solution was as high as 1 M (50/1 mole ratio of Ca/Gd). It has to be pointed out that calcium uptake by gadolinium phosphate was already high (1.4 wt% Ca) when Ca concentration in the acid was 20 times lower (0.05 M Ca in the solution).

The presence of Ca in gadolinium phosphate can be explained on the grounds of ionic radius comparability. According to Shannon effective crystal (CR) ionic radius of the eight-coordinated trivalent Gd cation is 0.1193 nm, while divalent Ca is about 0.126 nm [30]. That makes possible the substitution of Gd by Ca, while crystallisation of phosphate is proceeding. The effect of the Ca presence on the lattice parameters of the hexagonal gadolinium phosphate is shown in Fig. 2. Ca causes significant enlargement along the c-axis and less sig-
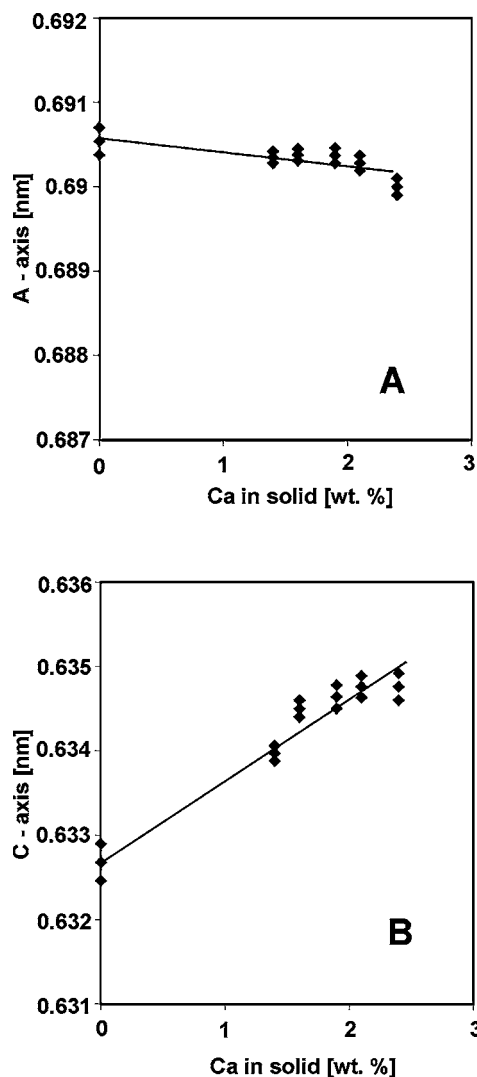
Figure 2 Spacing along (A): a-axis and (B): c-axis of hexagonal gadolinium phosphate plotted against wt% of Ca in the solid.
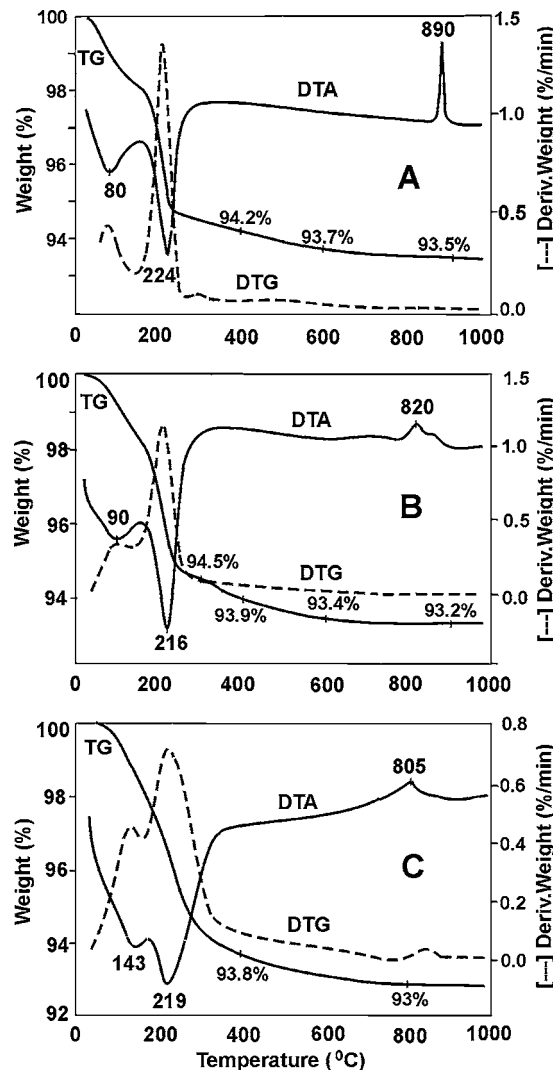
Figure 3 Thermal decomposition of $GdPO_4 \cdot H_2O$ (A) and Ca-substituted gadolinium phosphates crystallised from phosphoric acid solution, containing Ca: (B) – 0.05 M, and (C) – 0.5 M (Heating rate: 20 deg·min^{-1}. Purge gas: air, 100 cm^3 min^{-1}).

nificant contraction along the a-axis of the unit cell. However, the changes in the lattice parameters do not affect significantly the volume of the unit cell (Table I). The Ca-ion, which has a larger radius than the Gd ion, did not expand the unit cell in all directions. This may suggest that the substitution takes place at some preferential sites in the unit cell.

TGA-DTA analyses revealed that thermal decomposition of the investigated phosphates is similar to that of the pure $GdPO_4 \cdot H_2O$ of rabdophane structure (Fig. 3). According to literature the rabdophane structure dehydrates at $\sim$200°C and transforms into the monoclinic, monazite type structure at 900°C [11, 22, 24, 25, 27, 28, 31]. The temperature of the polymorphic transformation depends on the ionic radius of the lanthanide and on the heating rate if thermal treatment is carried out under dynamic conditions. For example, using a heating rate 20 deg·min^{-1} the temperature of rabdophane to monazite transformation, reported by the author previously increased from 717–735°C (Ce, La) to 910°C (Tb).

The exothermic peak associated with polymorphic transformation of the hexagonal to monoclinic form of the Ca-substituted gadolinium phosphate is less marked
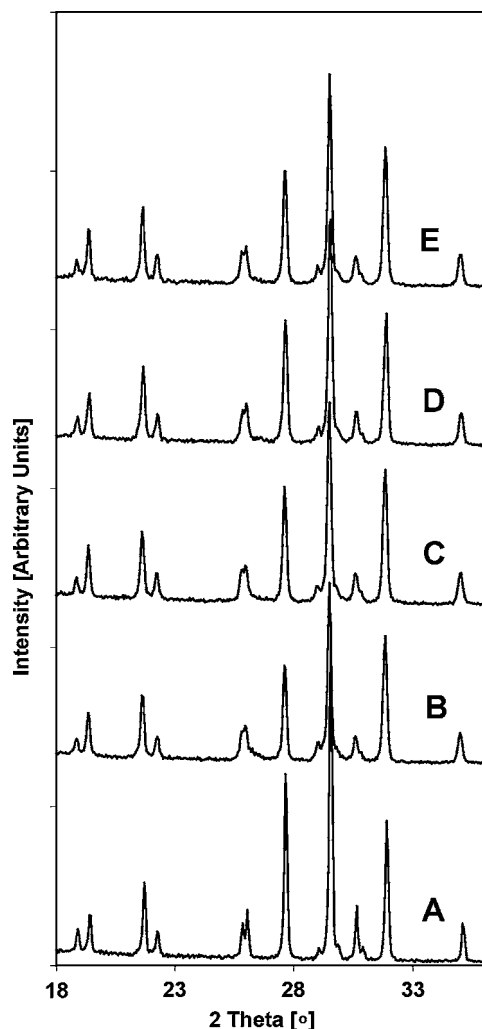
Figure 4 X-ray diffraction patterns of monoclinic GdPO$_4$ (A) and Ca-substituted gadolinium phosphates crystallised from phosphoric acid solution containing Ca: (B) – 0.05 M, (C) – 0.25 M, (D) – 0.5 M, (E) – 1.0 M and heated to 900°C.

Figure 5 IR spectra of as prepared hexagonal (A) GdPO$_4$·H$_2$O without Ca, and (B) containing 2.5 wt% of Ca and after heating at 900°C. (C) and (D), respectively.

and at lower temperature (Fig. 3B and C) than for the pure gadolinium phosphate (Fig. 3A). The effect of polymorphic transformation is illustrated by X-ray diffraction patterns characteristic of the monoclinic form (Fig. 4). The XRD data are consistent with those reported in the literature [12, 14, 20, 32].

IR spectra of lanthanide phosphates, including GdPO$_4$·H$_2$O (Fig. 5A and C) without Ca have been discussed previously in detail [16]. In IR spectra of Ca-substituted gadolinium phosphates (Fig. 5B and D), some additional bands have been recorded. They are the band from HPO$_4^{2-}$ at wavenumber 880 cm^{-1} in as prepared Ca-containing samples (Fig. 5B) and the band from P$_2$O$_7^{4-}$ at wavenumber 735 cm^{-1} in Ca-containing gadolinium phosphate after heat to 900°C (Fig. 5D).

The HPO$_4^{2-}$ band is characteristic of hydrogen phosphates. HPO$_4^{2-}$ incorporation is also well known in Ca-deficient phosphates such as hydroxyapatite and fluoroapatite, especially, when the precipitate is formed at lower pH [33, 34]. The appearance of the HPO$_4^{2-}$ band in IR spectra of Ca-containing gadolinium phosphate before heating, and the P$_2$O$_7^{4-}$ band after heating, indicates that the difference in the electric charge between divalent calcium and trivalent gadolinium in

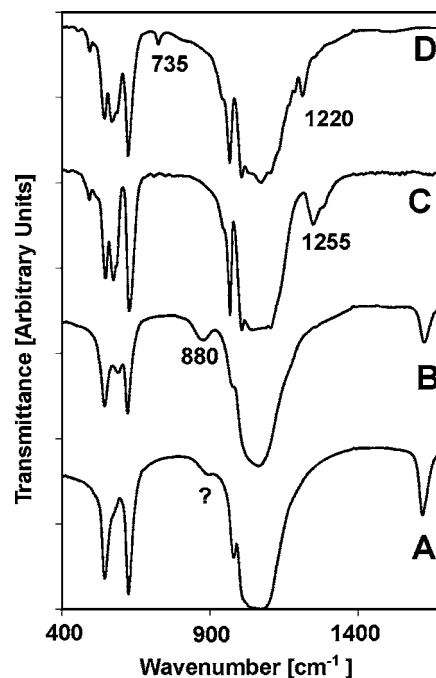the crystallised solid is compensated for by simultaneous substitution of divalent HPO$_4^{2-}$ for trivalent PO$_4^{3-}$, which should increase the amount of P in the crystallised solid. Chemical analyses seem to support this hypothesis. The data presented in Table I indicate that Ca incorporation in gadolinium phosphate is associated with some increase in phosphate content. The absence of any additional phase, such as calcium diphosphate, in the XRD data of the samples heated to 900°C indicates that P$_2$O$_7^{4-}$ ion is probably incorporated in the monoclinic crystal structure of gadolinium phosphate.

The diphosphate band at about 1200 cm^{-1} (Fig. 5C) appears sometimes (not always) in heated Ca-free lanthanide phosphates, although there is no P$_2$O$_7^{4-}$ band at 725–735 cm^{-1} [16, 29]. The presence of the P$_2$O$_7^{4-}$ band at 1255 cm^{-1} in Fig. 5C and a very weak band at ∼880 cm^{-1} (marked as ? in Fig. 5A) indicates that Ca-free gadolinium phosphate (GdPO$_4$·H$_2$O) may also contain some very small amount of HPO$_4^{2-}$ in the crystal structure. However, the small amount of HPO$_4^{2-}$ generates, during heating, a small amount of P$_2$O$_7^{4-}$. In effect, the weak band at 725–735 cm^{-1} has not been observed.

Scanning electron micrographs of the samples, presented in Fig. 6, reveal some differences in morphology between GdPO$_4$·H$_2$O (twinned "peanut-like" particles, Fig. 6A) and Ca-substituted gadolinium phosphates (hexagonal needle-like crystals, Fig. 6B and C). To prepare the Ca-containing solution for crystallisation, calcium nitrate was introduced into phosphoric acid. That created a solution medium of increased ionic strength which affected the ionic activity. In practice, the solubility of gadolinium phosphate, in the presence of an other electrolyte (Ca-nitrate), should be higher, while the supersaturation and the rate of crystallisation should be lower. It is possible that nucleation of Ca-substituted gadolinium phosphate was less rapid
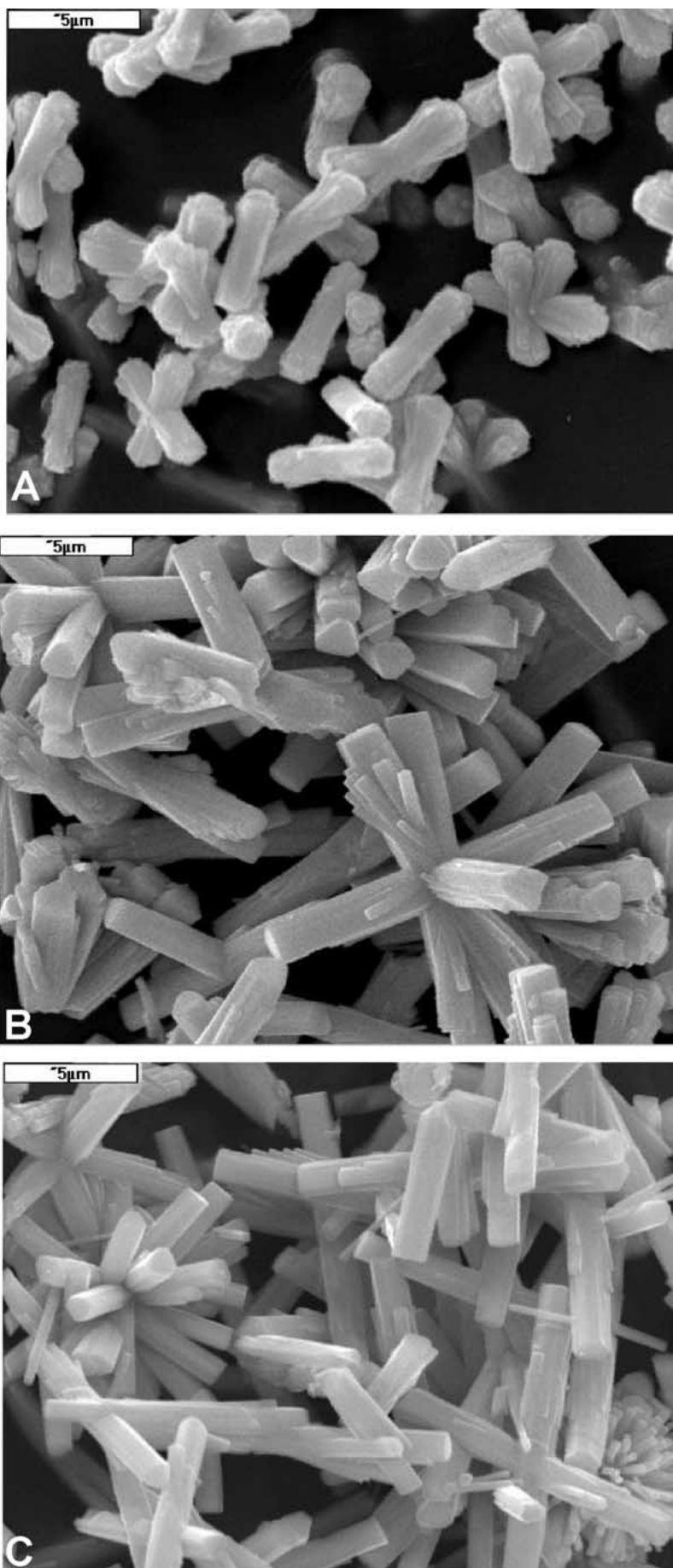
Figure 6 SEM micrographs of $GdPO_4 \cdot H_2O$ without Ca (A) and Ca-substituted gadolinium phosphates crystallised from phosphoric acid containing Ca: (B) – 0.125 M, and (C) – 0.25 M.

and that the crystal growth was slowed down resulting in larger hexagonal-section crystals, with an average length of 5 μm (Fig. 6B and C).

4. Conclusion
Crystallisation of gadolinium phosphate from phosphoric acid solution, containing Ca-ions, results in limited Ca for Gd substitution coupled with simultaneous HPO_4^{2-} incorporation in $GdPO_4 \cdot H_2O$. The substitution causes significant expansion of the unit cell in the *c*-direction of the hexagonal gadolinium phosphate and less significant contraction in *a*-axis direction.

References
1. S. L. NG, Y. L. LAM, Y. ZHOU, B. S. OOI, C. H. KAM, K. S. WONG, U. RAMBABU and S. BUDDHUDU, *J. Mater. Sci.* **37** (2000) 495.
2. M. HAASE, K. RIWOTZKI, H. MEYSSAMY and A. KORNOWSKI, *J. All. Comp.* **303/304** (2000) 191.
3. J. C. BOURCET and F. K. FONG, *J. Chem. Phys.* **60** (1974) 34.
4. N. A. VASILENKO and M. L. CHEPELEVETSKI, *Z. Neorg. Khim. (Russ)* **2** (1957) 2486.
5. V. I. SVESHNIKOVA and V. L. GINSBURG, *ibid.* **7** (1962) 1169.
6. I. V. TANANAEV and V. P. VASILIEVA, *ibid.* **8** (1963) 1070.
7. *Idem., ibid.* **9** (1964) 213.
8. A. I. ULYANOV and T. I. KAZAKOVA, *Izvestia Akad. Nauk, USSR, Khimya (Russ)* **3** (1963) 393.
9. *Idem., ibid.* **7** (1963) 1157.
10. A. N. YLYANOV, T. I. KAZAKOVA and E. J. RUMIANTZEVA, *ibid.* **11** (1962) 1910.
11. P. A. BONDAR, A. I. DOMANSKI, H. MEZENTSEVA, M. G. DEGEN and N. E. KALININA, *Zh. Neorg. Khim.* **21**(8) (1976) 2045.
12. M. KIZILYALLI and A. J. E. WELCH, *J. Appl. Cryst.* **9** (1976) 413.
13. Y. HIKICHI, K. HUKUO and J. SHIOKAWA, *Bull. Chem. Soc. Japan* **51** (1978) 3645.
14. J. G. PEPIN and E. R. VANCE, *J. Inorg. Nucl. Chem.* **43** (1981) 2807.
15. R. KIJKOWSKA, *J. Mater. Sci.* **38** (2003) 229.
16. R. KIJKOWSKA, E. CHOLEWKA and B. DUSZAK, *ibid.* **38** (2003) 223.
17. R. C. L. MONEY, *Acta Cryst.* **3** (1950) 337.
18. F. WEIGEL, V. SHERRER and H. HENSCHEL, *Radiochim. Acta* **4** (1965) 18.
19. A. HEZEL and S. D. ROSS, *J. Inorg. Nucl. Chem.* **29** (1967) 2085.
20. K. K. PALKINA, *Neorgan. Mater.* **18**(9) (1982) 1413.
21. H. ITO, Y. FUJISHIRO, T. SATO and A. OKUWAKI, *British Ceram. Trans.* **94** (1995) 146.
22. K. P. PETROV, I. W. TANANAEV, V. G. PERVIKH and S. M. PETUSHKOVA, *Zh. Neorg. Khim.* **12** (1967) 2645.
23. S.-L. TIE, Y-Y. LI and Y.-S. YANG, *J. Phys. Chem. Solids* **58** (1997) 957.
24. I. HORVATH, I. A. BONDAR and L. P. MEZENTSEVA, *Zh. Neorg. Khim. (Russ)* **31** (1986) 2250.
25. I. HORVATH, I. A. BONDAR and L. P. MEZENTSEVA, *J. Therm. Anal.* **33** (1988) 755.
26. J. F. W. BOWLES and D. J. MORGAN, *Mineral. Mag.* **48** (1984) 146.
27. R. G. JONASSON, *Thermochim. Acta* **108** (1986) 65.
28. Y. HIKICHI, T. SASAKI, K. MURAYAMA and T. NOMURA, *J. Amer. Ceram. Soc.* **72** (1989) 1073.
29. R. KIJKOWSKA, *Therm. Acta.* **404** (2003) 81.
30. R. D. SHANNON, *Acta Cryst.* **A32** (1976) 751.
31. O. TERRA, N. CLAVIER, N. DACHEUX and R. PODOR, *New J. Chem.* **6** (2003) 957.
32. Y. NI and J. M. HUGHES, *Amer. Mineral.* **80** (1995) 21.
33. R. Z. LEGEROS, "Calcium Phosphates in Oral Biology and Medicine" (Krager, New York, 1991) p. 95.
34. R. KIJKOWSKA, S. LIN and R. Z. LEGEROS, "Bioceramics," Vol. 14 (http—Trans Tech Publications, Switzerland, 2002) p. 31.