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## Barium titanium phosphates: $\text{Ba}^{2+} - 2\text{H}^+$ ion exchange in $\gamma$ -titanium phosphate and thermal behaviour of barium and calcium exchanged phases

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### Abstract

The  $\text{Ba}^{2+} - 2\text{H}^+$  ion exchange process has been studied, and exchange isotherms and titration curves have been obtained at 25.0, 40.0 and 55.0°C ( $\pm 0.1^\circ\text{C}$ ). The  $\gamma$ -Ti( $\text{Ba}_{0.5}\text{HPO}_4$ )( $\text{PO}_4$ )  $\cdot$  1.5H<sub>2</sub>O phase was formed by using BaCl<sub>2</sub> and HCl solutions. Equilibrium constants, free energy, enthalpy and entropy of the exchange reaction were determined. The barium half-exchanged phase loses water stepwise at progressively higher temperatures until it becomes anhydrous. At 900°C a mixture of two crystalline solid phases ( $\text{BaTiP}_2\text{O}_8$  and  $\alpha$ -TiP<sub>2</sub>O<sub>7</sub>) is obtained. The results are compared with those obtained by decomposition of the  $\gamma$ -Ti( $\text{Ca}_{0.37}\text{H}_{1.25}\text{PO}_4$ )( $\text{PO}_4$ )  $\cdot$  3.5H<sub>2</sub>O phase at 900°C, which produces a mixture of CaTi<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and  $\alpha$ -TiP<sub>2</sub>O<sub>7</sub> phases.

*Keywords:* Barium compound; Calcium compound; Ion exchange; Phosphate; Titanium compound

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### 1. Introduction

Layered phosphates of tetravalent metals have many potential applications in renal dialysis, water softening, chromatography, catalysis, membranes and solid electrolytes [1–6]. The exchange of alkaline-earth-metal cations in layered phosphates has received considerable attention [7–10].  $\gamma$ -Titanium phosphate ( $\gamma$ -TiP),

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$\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>) · 2H<sub>2</sub>O ( $d_{001} = 11.6 \text{ \AA}$ ) [11], belongs to this family of materials, and presents very interesting behaviour in ion exchange [12] and intercalation processes [13]. There have been some studies on the ion exchange  $M^{2+} - 2H^+$  (M is Mg, Ca, Sr) in  $\gamma$ -TiP [9,15–17], but the behaviour of this material with  $Ba^{2+}$  ions has not so far been studied.

Layered metal(IV) phosphates are solid acids but calcination produces  $MP_2O_7$ . However, if ions are present between the layers, a multitude of phases can be produced depending upon the type of metal and the amount present [18,19]. A variety of compounds can be prepared in this way, including three-dimensional compounds, solid solution phases and layered compounds of different layer disposition.

This paper describes the results obtained in the study of  $Ba^{2+} - 2H^+$  ion exchange in  $\gamma$ -TiP and the thermal decomposition of this material when it is partially substituted by barium and calcium ions.

## 2. Experimental

All chemicals used were of reagent grade.  $\gamma$ -TiP was obtained by using 16.5 M H<sub>3</sub>PO<sub>4</sub> and reflux times of 10 days, as previously described [20]. The  $\gamma$ -TiP was equilibrated (48 h) with  $2 \times 10^{-2}$  M (BaCl<sub>2</sub> + HCl) solutions at constant temperature ( $\pm 0.1^\circ\text{C}$ ) using a batch procedure (the solid was present in the solution at  $\approx 4 \text{ g l}^{-1}$  mass concentration).

The concentrations of phosphorus and titanium in the solids were determined gravimetrically. The pH measurements were made with an Orion model SA-720 pH-meter. The released phosphate groups were measured spectrophotometrically using a Perkin-Elmer model 200 instrument [21]. The barium in solution was determined by atomic absorption spectroscopy with a Varian model SpectrAA-300. Thermal analysis was performed on a Mettler model TA4000 (TG50, DSC30; rate of heating  $5^\circ\text{C min}^{-1}$ ). The diffractometer used was a Philips model PV 1050/23 ( $\lambda = 1.5418 \text{ \AA}$ ).

## 3. Results and discussion

Exchange isotherms are shown in Fig. 1. The substitution progresses as  $Ba^{2+}$  is added, and conversions of 50% are reached more easily at higher temperatures. The equilibrium pH increases slightly with the degree of conversion. The hydrolysis of the exchanger was  $\leq 1\%$ , as determined from the analysis for phosphorus in the equilibrium solutions. Treatment of the exchanged solids with hydrochloric acid solutions and subsequent analysis of phosphorus in solution indicates that there is no precipitation of barium phosphate.

In Fig. 2a, X-ray patterns of samples stabilized in air with composition  $0.00 < X < 0.50$  are shown, where  $X$  is the molar fraction of exchange defined as the fraction of hydrogens substituted in  $\gamma$ -TiP; its value is the equivalent fraction of

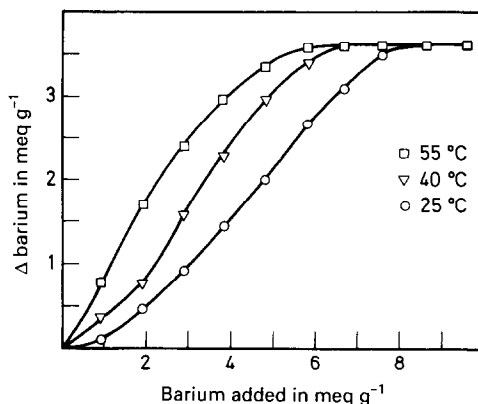


Fig. 1. Exchange isotherms of  $\text{Ba}^{2+} - 2\text{H}^{+}$

barium in the solid when all the interchangeable hydrogens of the exchanger are involved in the substitution process. X-ray patterns of samples of intermediate composition may be reproduced by combining those corresponding to the pure phases ( $X=0.0$  and  $X=0.5$ ). This indicates the formation of an individual ion-exchanged crystalline phase. The weight loss of the half ion-exchanged sample on calcination at  $900^{\circ}\text{C}$  is 10.85%. Thus, the composition  $\gamma\text{-Ti}(\text{Ba}_{0.5}\text{HPO}_4)(\text{PO}_4) \cdot 1.5\text{H}_2\text{O}$  can be assigned (theoretical weight loss 10.76%).

The exchange reaction can be expressed in its ionic form as in Eq. (1). In order to express the ion exchange process more clearly, the equilibrium reaction can be expressed in terms of the solid phases involved as in reaction (2). This has the

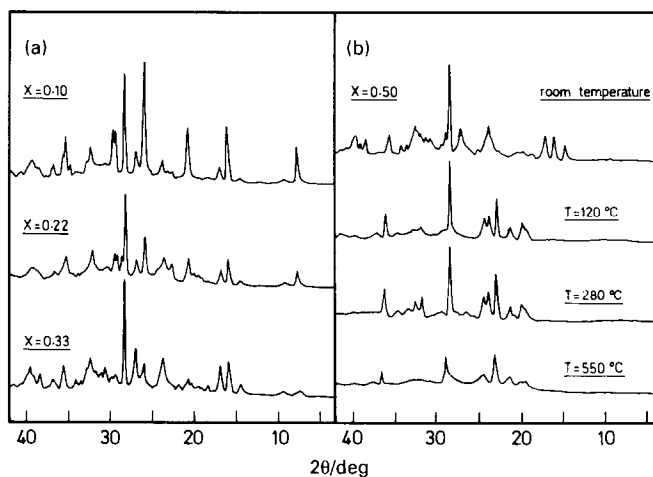
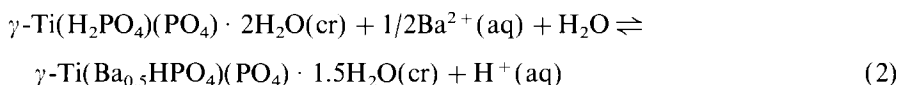
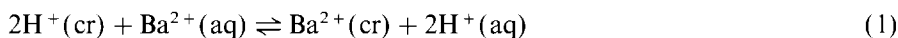


Fig. 2. X-ray diffraction patterns of (a) the  $\gamma\text{-Ti}(\text{Ba}_x\text{H}_{2-2x}\text{PO}_4)(\text{PO}_4) \cdot n\text{H}_2\text{O}$  solids obtained at  $40^{\circ}\text{C}$  stabilized in air at room temperature, and (b) the  $\gamma\text{-Ti}(\text{Ba}_{0.5}\text{HPO}_4)(\text{PO}_4) \cdot 1.5\text{H}_2\text{O}$  phase treated thermally in air.

advantage of indicating the composition of the crystalline solid phases involved and, thus, the real exchange capacity of the exchanger in the substitution step considered. From Eq. (2), we can define an equilibrium quotient in the form (3). The equilibrium quotient expressed in Eq. (3) is calculated for each experimental point. The equilibrium constant is obtained from Eq. (4) by application of the Gaines and Thomas thermodynamic treatment [22].



$$K_1' = [X(\text{Ba}_{0.5}\text{H})/X(\text{HH})][m(\text{H}^+)/m(\text{Ba}^{2+})^{1/2}][f_{\text{aq}}(\text{H}^+)/f_{\text{aq}}(\text{Ba}^{2+})^{1/2}] \quad (3)$$

$$\log_{10} K_1 = \int_0^1 (\log_{10} K_1') d[X(\text{Ba}_{0.5}\text{H})] \quad (4)$$

By plotting the equilibrium constants against  $1/T$  one obtains the value of  $\Delta H^\ominus$ .  $\Delta G^\ominus$  is obtained from the  $K$  values and  $\Delta S^\ominus$  is obtained from  $\Delta H^\ominus$  and  $\Delta G^\ominus$ . Table 1 shows the values obtained from the thermodynamic constants in the  $\text{Ba}^{2+} - 2\text{H}^+$  ion exchange in  $\gamma\text{-TiP}$ .

The thermal analysis of the 50% substitution sample stabilized in air (Fig. 3) shows the existence of two different zones of mass loss. The first occurs at temperatures below  $300^\circ\text{C}$ , its value corresponding to 1.5 mol of  $\text{H}_2\text{O}$  per mol of Ti. In this type of compound this temperature region is associated with the loss of water of crystallization [23,24]. Moreover, the DSC curve shows three minima at  $70$ ,  $120$  and  $220^\circ\text{C}$  respectively indicating three steps in the dehydration. At higher temperatures ( $300\text{--}700^\circ\text{C}$ ) the material again loses mass as a consequence of the condensation of hydrogenphosphate groups. The minimum values in the DSC curve at  $430$  and  $535^\circ\text{C}$  suggest that this dehydration takes place in two steps. A similar behaviour of  $\gamma\text{-TiP}$  was explained by La Ginestra and Massucci [24] as the formation of a phosphate–pyrophosphate phase with an interlayer distance of  $8.3 \text{ \AA}$ . Other partial substitution ion exchange phases show analogous behaviour [25].

X-ray diffraction patterns of samples obtained at room temperature and by thermal treatment of the  $\gamma\text{-Ti}(\text{Ba}_{0.5}\text{HPO}_4)(\text{PO}_4) \cdot 1.5\text{H}_2\text{O}$  phase (Fig. 2(b)) indicate that the solids obtained have poor crystallinity. The relative intensity of the

Table 1  
Thermodynamic values for the  $\text{Ba}^{2+} - 2\text{H}^+$  ion exchange in  $\gamma\text{-TiP}$

| Stage  | $-\log_{10} K$     |                    |                    | $\Delta H_m^\ominus/(\text{kJ mol}^{-1})$ | $\Delta G_m^\ominus/(\text{kJ mol}^{-1})$ | $\Delta S_m^\ominus/(\text{J K}^{-1} \text{ mol}^{-1})$ |
|--|--------------------|--------------------|--------------------|---|---|---|
|  | $25^\circ\text{C}$ | $40^\circ\text{C}$ | $55^\circ\text{C}$ |   |   |   |
| $\text{HH} \rightleftharpoons \text{Ba}_{0.5}\text{H}$ | 0.37               | 0.17               | -0.11              | 30.01                                     | 2.10                                      | 94  |

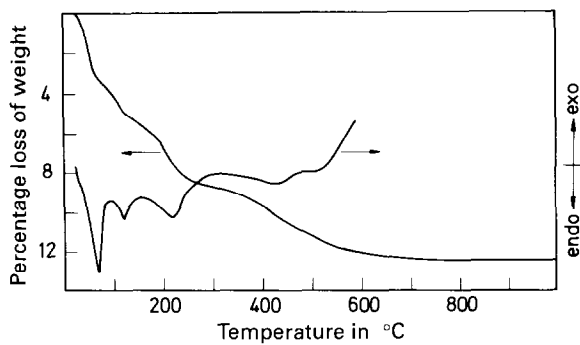


Fig. 3. TG and DSC curves of the  $\gamma$ -Ti(Ba<sub>0.5</sub>HPO<sub>4</sub>)(PO<sub>4</sub>) · 1.5H<sub>2</sub>O phase.

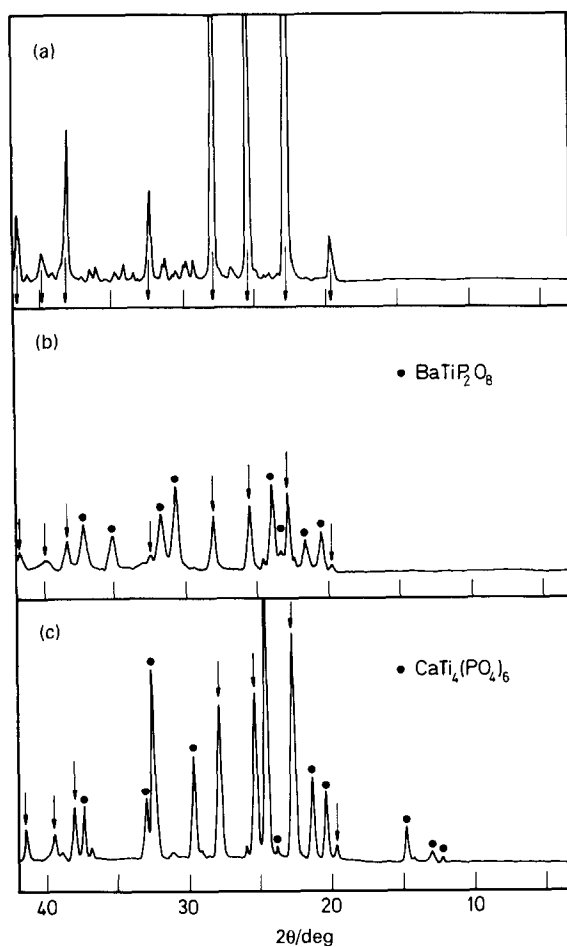
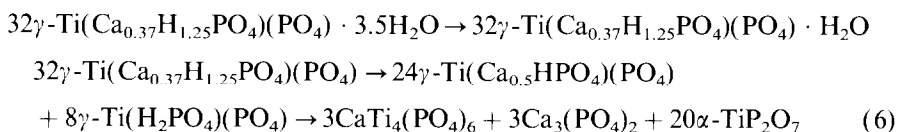
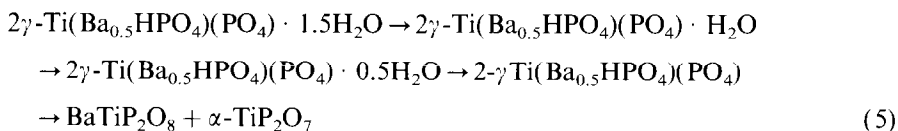


Fig. 4. X-ray patterns of samples heated at 900°C: (a)  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>) · 2H<sub>2</sub>O, (b)  $\gamma$ -Ti(Ba<sub>0.5</sub>HPO<sub>4</sub>)(PO<sub>4</sub>) · 1.5H<sub>2</sub>O, and (c)  $\gamma$ -Ti(Ca<sub>0.37</sub>H<sub>1.25</sub>PO<sub>4</sub>)(PO<sub>4</sub>) · 3.5H<sub>2</sub>O.

reflection characteristic of the basal spacing of the material decreases as the treatment temperature increases. This fact can be attributed to a high deformation of the  $\gamma$ -layers by the presence of barium. A similar situation is observed in the anhydrous single-layer silicates in which the  $[\text{SiO}_4]$  layers are deformed to a variable extent owing to the presence of cations of various sizes between the layers [26].

When the  $\gamma$ -TiP is heated at  $900^\circ\text{C}$ ,  $\alpha$ - $\text{TiP}_2\text{O}_7$  is formed (Fig. 4(a)). The treatment at this temperature of the  $\gamma$ - $\text{Ti}(\text{Ba}_{0.5}\text{HPO}_4)(\text{PO}_4) \cdot 1.5\text{H}_2\text{O}$  phase produces a mixture of  $\text{BaTiP}_2\text{O}_8$  (low temperature form, JCPDS-ICDD no. 25-81) and  $\alpha$ - $\text{TiP}_2\text{O}_7$  (Fig. 4(b)). The barium phase dehydration process is summarized in (5).



The  $\gamma$ - $\text{Ti}(\text{Ca}_{0.37}\text{H}_{1.25}\text{PO}_4)(\text{PO}_4) \cdot 3.5\text{H}_2\text{O}$  phase was formed when  $\gamma$ -TiP was treated with  $\text{CaCl}_2$  plus  $\text{HCl}$  solutions [16]. The special thermal behaviour of this phase at temperatures below  $300^\circ\text{C}$  (splitting of the 37.5% phase after the loss of crystallization water from mixtures of dihydrogen and half-exchanged phases) was used for quantitative analyses of crystalline phases [27], but the behaviour of the phase at higher temperatures was studied. When this phase is heated at  $900^\circ\text{C}$ , a solid is formed containing a mixture of two crystalline phases (Fig. 4(c)):  $\text{CaTi}_4(\text{PO}_4)_6$  (JCPDS-ICDD No. 35-740) and  $\alpha$ - $\text{TiP}_2\text{O}_7$  and one phase not detected by X-ray diffraction,  $\text{Ca}_3(\text{PO}_4)_2$ . The calcium phase dehydration process is summarized in (6), above. The decomposition route is a function of the type of metal and the amount present in the layered metal(IV) phosphate.

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