

STRUCTURAL AND THERMAL PROPERTIES OF ALKALINE EARTH METAL PHOSPHATES *

R.G. SARAWADEKAR **

Explosives Research and Development Laboratory, Pashan, Pune 411021 (India)

S.B. KULKARNI

National Chemical Laboratory, Pune 411008 (India)

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ABSTRACT

A series of alkaline earth metal orthophosphates $M_3(PO_4)_2 \cdot X H_2O$ ($M = Mg, Ca, Sr$ and Ba) is studied by DTA, TG and DTG techniques followed by X-ray diffraction and IR spectroscopy. The activation energies for the dehydration of the various phosphates are evaluated, and the structural changes occurring in the phosphates on calcination at different temperatures are discussed in the light of X-ray diffraction and IR data.

INTRODUCTION

Phosphorus compounds, especially metal orthophosphates, are increasingly being used as catalysts for a variety of industrially important reactions. Tricalcium phosphate has a high selectivity and activity for the dehydrogenation of 2-propanol to acetone [1]. Alkaline earth metal orthophosphates have been used as catalysts for the dehydration of ethanol to ethylene [2–4]. The thermal analysis of a few orthophosphates has been reported by Ben-Dor and Felnar [5]. In the present work the preparation, structural and thermal properties of these phosphates are reported.

MATERIALS

Aqueous solutions of metal chlorides and phosphoric acid (1:1 mole) were mixed and ammonia (14% v/v) was added to control the pH (~ 5) of the resulting mixtures. The solutions were stirred for about 2 h at room

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** To whom correspondence should be addressed.

temperature and then allowed to stand for a further period of 24 h. The precipitates were filtered, washed with distilled water, and dried in air at 100°C for 8 h.

CHEMICAL ANALYSIS

The percent metal oxide and phosphorus pentoxide of the synthetic phosphates was determined by wet chemical analysis [6]. The compositions of metal oxide, phosphorus pentoxide and water are compared with theoretically calculated values in Table 1.

THERMAL ANALYSIS

The thermoanalytical curves were recorded on a MOM derivatograph (type 00-102B) [7] in the temperature range ambient to 1000°C using 200 mg samples and a heating rate of 10°C min⁻¹ in air. Calcined α -alumina was used as reference material.

X-RAY DIFFRACTION

The X-ray powder diffraction patterns of all the phosphates were recorded on a Philips X-ray diffractometer (model PW 100) using nickel filtered CuK α radiation.

IR SPECTRA

Infrared spectra were recorded on a Perkin-Elmer IR spectrophotometer (model No. 457) in KBr matrix at room temperature.

TABLE 1
Chemical analysis of metal phosphates

Metal phosphate	Theoretical %			Observed %		
	MO	P ₂ O ₅	H ₂ O	MO	P ₂ O ₅	H ₂ O
Mg ₃ (PO ₄) ₂ ·19 H ₂ O	19.97	23.47	56.52	19.91	23.39	56.67
Ca ₃ (PO ₄) ₂ ·H ₂ O	51.22	43.29	5.49	51.12	43.15	5.73
Sr ₃ (PO ₄) ₂ ·H ₂ O	66.03	30.16	3.89	65.89	29.95	4.24
Ba ₃ (PO ₄) ₂ ·H ₂ O	73.13	22.58	4.29	73.02	22.45	4.53

RESULTS AND DISCUSSION

DTA

Figure 1 shows the DTA profiles of $M_3(PO_4)_2 \cdot X H_2O$, where $M = Mg, Ca, Sr$ and Ba . The curve of magnesium phosphate [$Mg_3(PO_4)_2 \cdot 19 H_2O$] shows two well-formed endotherms with peak maxima at $112^\circ C$ and $260^\circ C$ and an exotherm with the peak maximum at $510^\circ C$. The endotherms are attributed to dehydration while the exotherm is associated with the phase transition from amorphous to crystalline state. Calcium phosphate does not show a distinct dehydration endotherm. The strontium and barium phosphates show endotherms at 300 and $360^\circ C$ for dehydration. Barium phos-

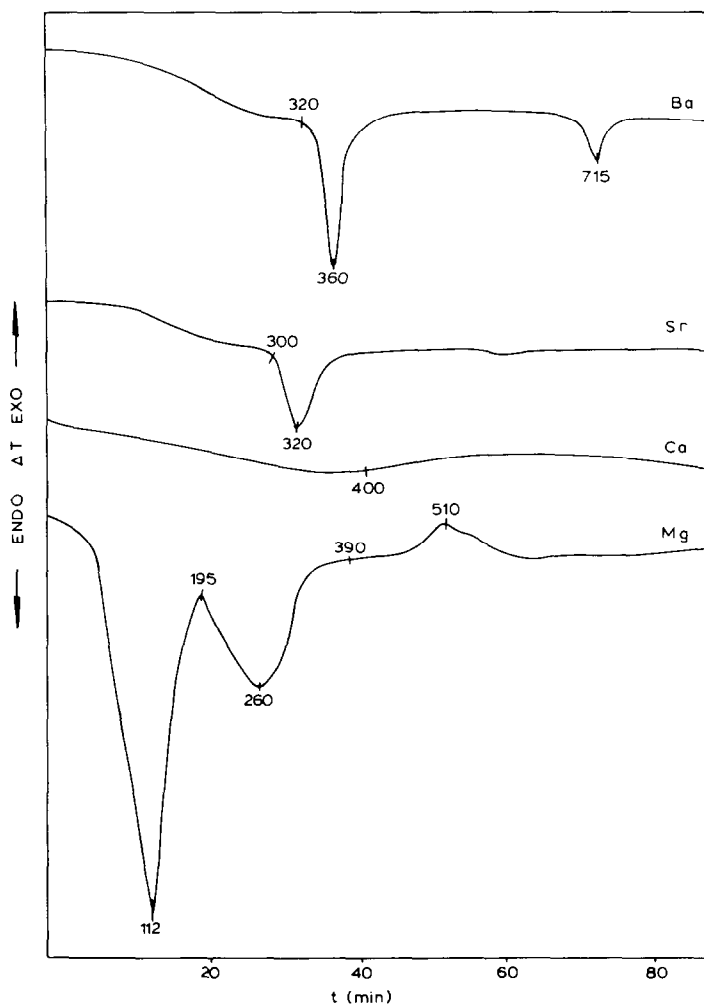


Fig. 1. DTA curves of the phosphates.

phate shows another endotherm at 775°C which corresponds to phase transition.

Thermogravimetry

Figure 2 shows the TG and DTG curves of the alkaline earth phosphates. $\text{Mg}_3(\text{PO}_4)_2 \cdot 19 \text{H}_2\text{O}$ shows 56.5% weight loss in two steps; the first step is sharp while the second is broad. In the first step dehydration starts at 100°C and reaches a maximum at 110°C and corresponds to the removal of 12 molecules of water; the second step commences at 260°C with the loss of the remaining seven molecules of water. The thermal analysis of $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ reported earlier [8,9] showed the dehydration to occur in three steps at

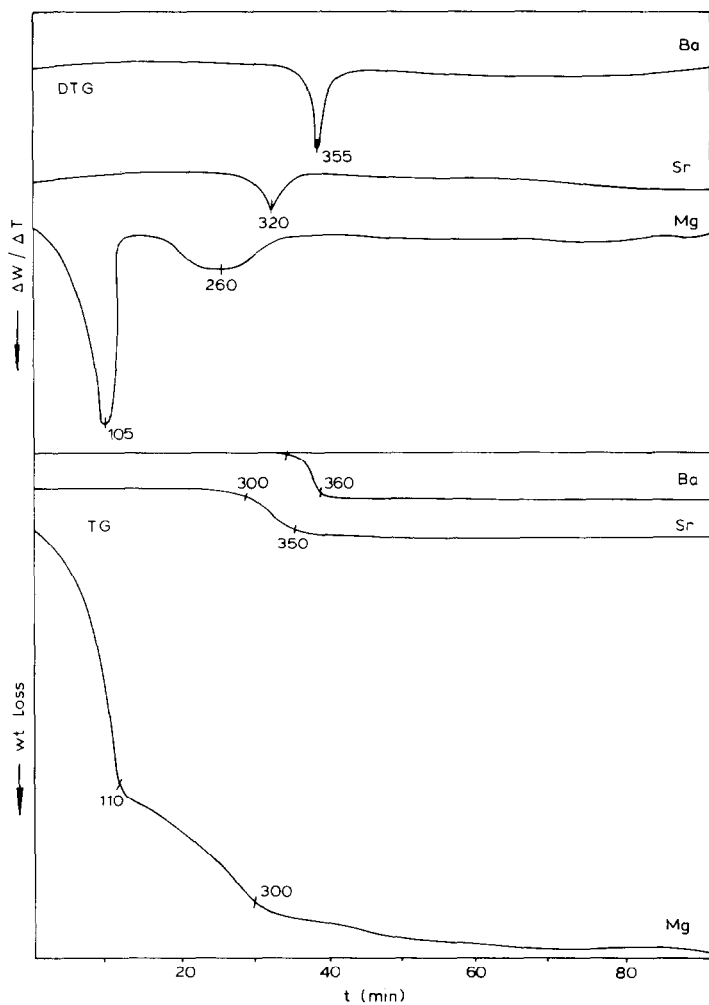


Fig. 2. TG and DTG curves of the phosphates.

temperatures higher than observed in the present work.

Calcium phosphate monohydrate shows a total weight loss of 5.2% up to 800°C while up to about 400°C half of the water is lost. This is in good agreement with reported data [10,11]. Strontium phosphate hydrate loses water molecules in a single step in the temperature range 310–350°C, the total weight loss being 4.5%. In the case of barium phosphate the dehydration starts at 320°C and is complete at 360°C. The DTG peak is sharp and the total weight loss is 4.2% which corresponds to a loss of 1.5 molecules of water.

Kinetics of dehydration

The kinetic parameters for the dehydration process were calculated using the equations of Piloyan [12] and Coates and Redfern [13]. The activation energy values for dehydration for the first step in magnesium phosphate are

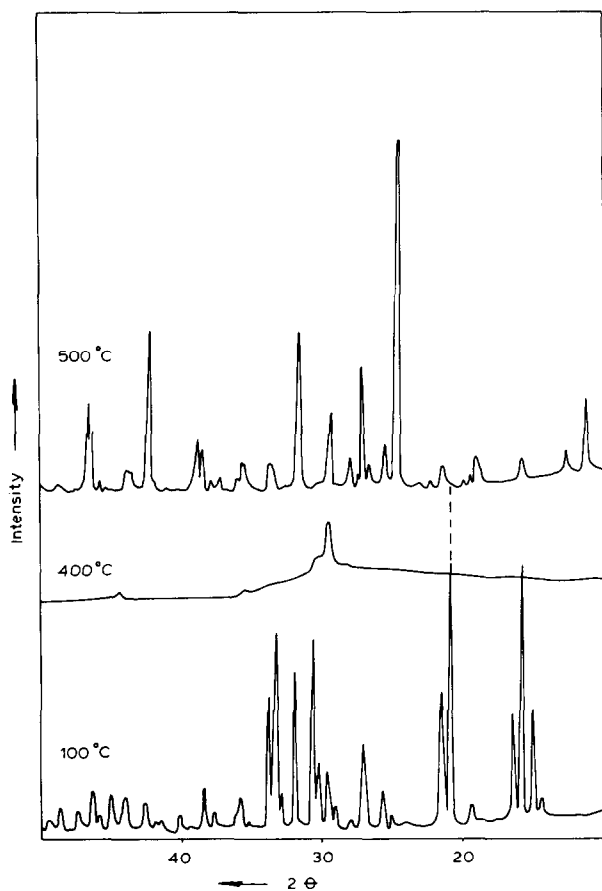


Fig. 3. X-Ray diffraction patterns of $Mg_3(PO_4)_2$ at different calcination temperatures.

17.2 and 20.1 kcal mole⁻¹ employing DTA and TG data, respectively. The order of reaction is nearly 1.0 as evaluated by shape index method [14]. For the second step, the energy of activation is 33.64 kcal mole⁻¹ and n is 1.18. In the case of strontium phosphate the energy of activation is 38.85 kcal mole⁻¹ and $n = 1.1$. It is clear that the dehydration of the phosphates follows first order kinetics. The dehydration of phosphates proceeds with lower energy to remove physically adsorbed water molecules. On the other hand, a higher activation energy is required to remove chemisorbed water.

X-Ray diffraction

Figure 3 shows the X-ray diffraction patterns of magnesium phosphate calcined at various temperatures. Magnesium phosphate [$\text{Mg}_3(\text{PO}_4)_2 \cdot 19 \text{H}_2\text{O}$] shows a perfectly crystalline pattern. After calcination at 400°C all the water molecules are lost and the phosphate becomes amorphous (Fig. 3). DTA indicated a phase transition at 510°C from the amorphous to crystalline state, the phosphate calcined at 500°C shows a crystalline pattern which corresponds to a monoclinic structure and is comparable with reported data [15].

Figure 4 shows the X-ray diffraction patterns of calcium phosphate which

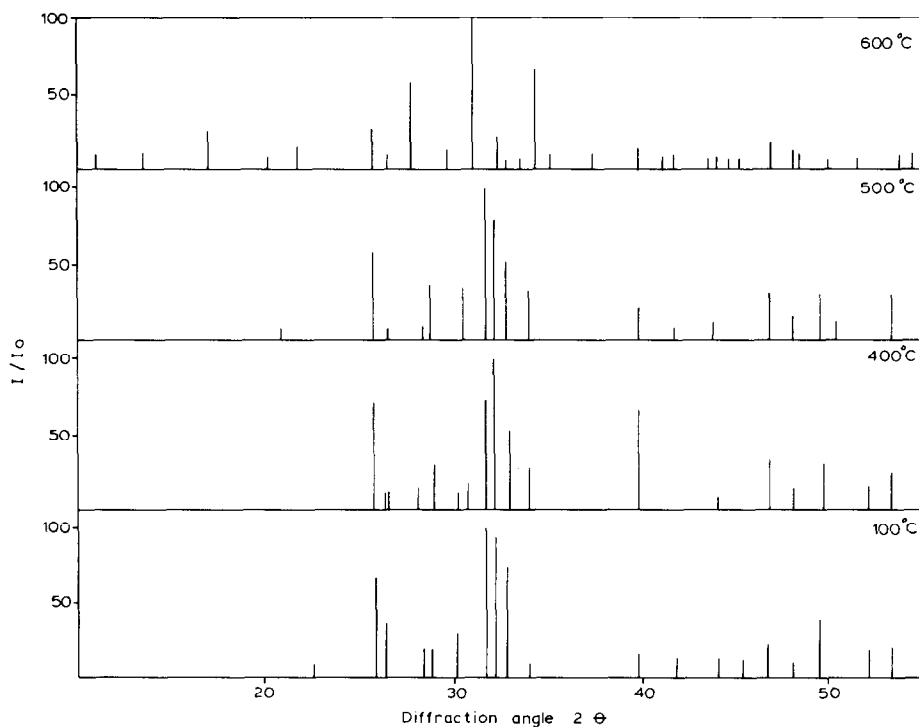


Fig. 4. X-Ray intensities of calcium phosphate.

was calcined at different temperatures. As the calcination temperature increases, the crystallinity increases and finally at 600°C it shows a hexagonal structure. The structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ is in good agreement with that reported in the literature [16]. Calcium phosphate exists in three polymorphic forms [17,18] of which the β form is reported to be stable up to 1180°C.

The X-ray diffraction patterns of strontium and barium phosphates calcined at 400°C show rhombohedral structure which is comparable with reported work [19]. Figure 5 shows the IR spectra of alkaline earth phosphates calcined at 400°C. The hydrated forms show absorption bands at 3400 and 1650 cm^{-1} for the free hydroxyl group and chemically bound water, respectively. The phosphates calcined at 400°C show IR bands at 937 and 420 cm^{-1} and 1080 and 562 cm^{-1} , assigned to the stretching and deformation frequencies of PO_4 groups, respectively [20,21].

From the present work it is concluded that these phosphates are thermally

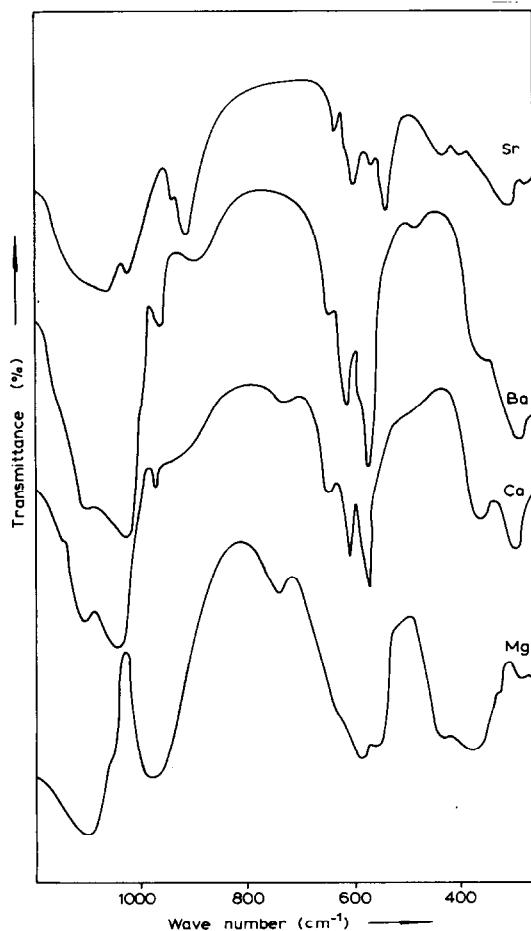


Fig. 5. IR spectra of the phosphates

stable and do not undergo structural transformations up to about 700°C. The alkaline earth phosphates show good crystallinity and can be used as catalysts. The IR spectra did not show any distortion of the PO₄ tetrahedra.

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