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Materials Research Bulletin 42 (2007) 165–170
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Synthesis and characterization of a new layered magnesium zinc phosphate hydrate

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Received 28 February 2006; received in revised form 13 April 2006; accepted 28 April 2006
Available online 22 May 2006

Abstract

A new layered magnesium zinc phosphate hydrate, $MgZn(HPO_4)_2{\cdot}H_2O$, with a zinc phosphate framework isostructural with the one of $Na_2Zn(HPO_4)_2{\cdot}4H_2O$, was prepared by the direct ambient pressure and temperature reaction between zinc 2,4-pentanedionate, phosphoric acid and hexahydrated magnesium chloride. The as-prepared sample is monoclinic ($a = 8.780(7)$ Å, $b = 13.240(7)$ Å, $c = 11.123(0)$ Å and $\beta = 116.21(2)^\circ$). The prepared solid undergoes two thermal transformations when it is heated from 110 to 600 °C. The first transformation is due to the release of intercalated water molecules and the second one is due to the $HPO_4^{2-} \rightarrow P_2O_7^{4-}$ transition.

Keywords: A. Inorganic compounds; A. Layered compounds; B. Chemical synthesis; C. Differential scanning calorimetry; C. X-ray diffraction

1. Introduction

Layered acid phosphates are of continuing academic and industrial interest because of their extensive use as heterogeneous catalysts [1–3]. Some of them can undergo ion exchange and reversible hydration in the same way as zeolites. In the past few years, we developed a new room temperature synthetic route for the preparation of layered acid phosphates of magnesium. The interlayer species were water [4,5], ethanol and ethylene glycol [6]. The water-intercalated magnesium phosphate can undergo reversible dehydration–rehydration provided it is not heated beyond 200 °C. There is a growing interest in the preparation of new non-aluminosilicate framework materials with structures that include very large pores. Indeed, some of the zinc phosphate structures exhibit channels with diameters exceeding 14 Å [7–9].

Recently, we reported the synthesis and characterization of a new layered zincophosphate material isostructural with $Na_2Zn(HPO_4)_2{\cdot}4H_2O$ [10]. These materials exhibit a two-dimensional structure containing a network of layers of bifurcated tetrahedral 12-rings connected by sodium cations and H-bonds [11]. This paper reports the synthesis and characterization of $MgZn(HPO_4)_2{\cdot}H_2O$ a new member of this family, using a simple ambient conditions synthetic method. The prepared solid was characterized by X-ray powder diffraction and IR spectroscopy. The thermal

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0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2006.04.039

transformations were investigated by thermogravimetric (TG), differential thermal (DT) measurements and X-ray powder diffraction.

2. Experimental

The compound was prepared by mixing in distilled water zinc 2,4-pentanedionate $Zn(C_5H_7O_2)_2{\cdot}H_2O$ (Johnson Matthey Electronics) with phosphoric acid (99.999%, 85 wt.%, Aldrich Chemical Co.) and hexahydrated magnesium chloride (Aldrich Chemical Co.) in a ratio of $Zn(C_5H_7O_2)_2{\cdot}H_2O$:$2H_3PO_4$:$MgCl_2{\cdot}6H_2O$. Then with rapid stirring, the formation of a white gelatinous precipitate was initiated by raising the pH to 6.0 using potassium hydroxide (Aldrich Chemical Co.). This precipitate was recovered by filtration and dried at 110 °C for 2 h. The dry white powder was analyzed by:

- X-ray powder diffraction (XRD) using a SCINTAG automated PAD-X diffractometer utilizing monochromatic Cu Kα radiation. The diffraction patterns were taken in the range of $5^\circ < 2\theta < 70^\circ$. The 2θ step size was 0.04° and the count time was 1 s. Quartz was used as an internal standard. Cell parameters were obtained from a least square

Table 1
X-ray powder data of the as-prepared sample

h k l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)	I/I_0 (%)
1 1 −2	5.02366	5.03088	−0.00722	23
1 1 1	4.79716	4.81705	−0.01989	20
2 0 −1	4.38381	4.38435	−0.00054	19
0 2 2	3.96999	3.98465	−0.01466	11
2 1 0	3.80488	3.77538	0.02950	14
1 0 −3	3.71706	3.70681	0.01025	13
1 0 2	3.58712	3.56340	0.02372	11
1 1 2	3.44505	3.44097	0.00408	24
1 3 1	3.36322	3.35714	0.00608	26
1 2 2	3.14047	3.13775	0.00272	43
3 1 −2	2.83902	2.84587	−0.00685	100
1 4 1	2.80822	2.78795	0.02027	10
0 4 2	2.77094	2.75837	0.01257	21
3 2 −1	2.63860	2.63368	0.00492	21
1 1 3	2.61575	2.61799	−0.00224	12
2 0 2	2.60098	2.58571	0.01527	22
2 4 0	2.52685	2.53414	−0.00729	18
0 0 4	2.50615	2.49481	0.01134	25
3 3 0	2.26089	2.25671	0.00418	16
1 5 −3	2.14746	2.15476	−0.00730	19
1 5 2	2.13390	2.12548	0.00842	18
3 0 2	1.99603	1.98964	0.00639	19
4 1 0	1.94110	1.94801	−0.00691	18
3 3 2	1.81762	1.81385	0.00377	21
4 2 1	1.72632	1.72613	0.00019	11
3 1 3	1.69321	1.70938	−0.01617	21
4 5 −2	1.68630	1.68865	−0.00235	12
3 2 3	1.66930	1.66819	0.00111	12
4 5 −1	1.66261	1.65405	0.00856	14
3 5 2	1.59084	1.59069	0.00015	11
4 2 2	1.56234	1.56042	0.00192	22
3 4 3	1.52354	1.52892	−0.00538	18

	As-prepared sample	$Na_2Zn(HPO_4)_2{\cdot}4H_2O$
a (Å)	8.780(7)	8.947(2)
b (Å)	13.240(7)	13.254(2)
c (Å)	11.123(0)	10.098(2)
β (°)	116.21(2)	116.35(8)