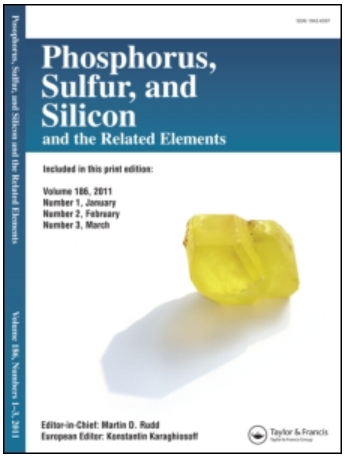

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The Solid Solutions of $(Cu_{1-Y}M_Y)_2(OH)PO_4$ (M-Zn, Co, Ni)

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THE SOLID SOLUTIONS OF $(Cu_{1-Y}M_Y)_2(OH)PO_4$ (M–Zn, Co, Ni)

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Solid solutions of $(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ ($0 \le Y \le 0.26$), $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ ($0 \le Y \le 0.10$), and $(Cu_{1-Y}Ni_Y)_2(OH)PO_4$ ($0 \le Y \le 0.08$) were prepared. Phosphoric acid and mixtures of hydroxide carbonates were used as starting materials. The solid solutions crystallize in the orthorhombic system, space group Pnnm. The unit cell parameters of solid solution are close to those of $Cu_2(OH)PO_4$. The IR spectra of synthesized hydroxide phosphates are similar, indicating that they have the same structure. The significant Mg, Mn substitution for Cu was not observed. The thermal decomposition of $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ was studied.

Keywords Hydroxide phosphate; isomorphic substitution; libethenite; solid solution; synthesis

INTRODUCTION

Copper forms three hydroxide phosphates that are known as natural minerals: $Cu_2(OH)PO_4$ (libethenite), $Cu_5(OH)_4(PO_4)_2$ (pseudomalachite), and $Cu_3(OH)_3PO_4$ (cornetite). The first two compounds were also synthesized from phosphoric acid and copper hydroxide carbonate.[1–3] In the last few years, libethenite has attracted attention in the organic synthesis of fine chemicals.[3–5] Copper (II) oxide phosphate $Cu_4O(PO_4)_2$ is an electrode material.[2] It is usually prepared by the calcination of $Cu_2(OH)PO_4$.

Libethenite, $Cu_2(OH)PO_4$, crystallizes in the orthorhombic system, space group Pnnm.[6] The libethenite structure contains anion polyhedra around the copper and phosphorus atoms. There are two types of Cu sites with different geometries: Cu(1) and Cu(2).[7] The Cu(1) atoms are octahedrally surrounded by six oxygen atoms. These octahedra are distorted and form chains running parallel to the *c* axis. The linkage between the chains is formed by nearly regular PO_4 tetrahedras. The Cu(2) atoms lie in channels that runs parallel to the *c* axis. The Cu(2) sites are five-coordinated with the oxygen atoms around them forming trigonal bipyramids.

Zinc hydroxide phosphate, $Zn_2(OH)PO_4$, usually crystallizes in the triclinic system.[8] The modifications of $Zn_2(OH)PO_4$ and $Co_2(OH)PO_4$, which are isostructural with libethenite, were also known, but they can be formed only in the presence of tetraethylammonium hydroxide under hydrothermal conditions.[9] Hydroxide phosphates of nickel, magnesium, and manganese do not form modifications that crystallize in a libethenite-type structure. Therefore, the Zn, Co, Ni, Mg, or Mn substitution into the lattice of $Cu_2(OH)PO_4$ would not be unlimited.

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The mineral $CuZn(OH)PO_4$ is known.[10] The Zn-substituted libethenite with maximum molar ratio $Zn/(Cu + Zn) = 0.46$ was prepared from Cu and Zn sulfates and trisodium phosphate.[11] On the other hand, $Cu_2(OH)AsO_4$ and $Zn_2(OH)AsO_4$ are isostructural with libethenite. An unlimited solid solution exists between these arsenates.[10,12]

One of the ways to synthesize new materials is the preparation of substitutional solid solutions on the base of known phases, for example, libethenite. This article is a part of a systematic investigation of an isomorphous substitution in bivalent metal phosphates.

We report the synthesis of solid solutions of $(Cu_{1-Y}M_Y)_2(OH)PO_4$ (M–Zn, Co, or Ni) from phosphoric acid and mixtures of metal hydroxide carbonates. It was shown that the libethenite structure is unwilling to accommodate significant Mn and Mn substitution for Cu. The samples obtained were characterized by chemical analysis, XRD, IR, and thermal analysis (DTA and DTG).

EXPERIMENTAL

The samples were prepared from a 6.5% solution of H_3PO_4 and mixtures of hydroxide carbonates of Cu and Zn, Co, Ni, Mn, or Mg. For the starting materials, the P/(M + Cu) molar ratio was 1.00. The molar ratio of W = M/(M + Cu) 100% was varied from 0 to 100 mol. % (where M = Zn, Co, Ni, Mn, or Mg). The reaction was carried out at a temperature of 80°C for 7–30 days. A small amount of H_2O_2 was added to reduce the impurities of Co(III), Mn(III), and Mn(IV). Then the precipitates were filtrated, washed by water, and dried.

The synthesized samples and starting materials were analyzed by chemical methods. The total contents of Cu and Co, Ni, or Zn (as well as content of Cu in the presence of Mg) were determined by back complexometric titration. Co, Ni, or Zn were analyzed with the same method, but after masking of Cu by $Na_2S_2O_3$. Iodometric titration was used to determine Cu in the presence of Mn. Magnesium was analyzed by a gravimetric method (in the form of magnesium-ammonium phosphate), and Mn was determined by photometry (in the form of MnO_4^-). The phosphorous was determined by gravimetric method (precipitation of quinoline salt of phosphorus-molybdenum heteropolyacid). Water content was found from weight loss after calcination at 800°C for 1 h.

X-ray powder diffraction (XRD) patterns were recorded on a DRON-4-07 diffractometer (CoK_α radiation, single-step mode), and SiO_2 and NaCl were used as external standards. The lattice parameters of the compounds were calculated and refined by least-squares method. Infrared spectra were recorded at room temperature on a UR-20 spectrometer using KBr pellets. Thermogravimetric analysis was performed on Q-1500 analyzer with a heating rate 5°C/min from 20 to 1000°C. The samples were heated in open platinum crucibles.

RESULTS

The reaction of H_3PO_4 with Cu and Zn hydroxide carbonates at W $\leq$ 35 mol. % gave the phosphates with the P/(M + Cu) and H_2O/P molar ratios close to 0.50 and 0.60–0.70, respectively (Table I). These values were determined by analysis. They agreed with theoretical calculated ratios for $M^{II}_2(OH)PO_4$, (where M^{II} = bivalent metal). However, the interaction of the reagents at W > 35 mol. % led to precipitation of solids with P/(M + Cu) > 0.50 and H_2O/P > 0.70. Therefore, increasing Zn content in the starting materials above 35 mol. % resulted in coprecipitation of $M^{II}_2(OH)PO_4$ and nonstoichiometric zinc phosphate.

Table I The chemical composition of synthesized samples

Starting materials		Composition of the prepared samples						
Cu	M	P	Cu	M	H_2O	$\frac{P}{Cu+M}$	$\frac{H_2O}{P}$	
mol. %		wt. %.				mol. ratios		Obtained phases
				M−Zn				
100	0	12.90	52.77	—	4.90	0.502	0.65	$Cu_2(OH)PO_4$
90	10	13.00	49.26	3.58	4.46	0.507	0.59	$(Cu_{0.94}Zn_{0.06})_2(OH)PO_4$
80	20	13.01	45.09	7.61	4.46	0.509	0.59	$(Cu_{0.86}Zn_{0.14})_2(OH)PO_4$
70	30	12.90	40.05	12.51	4.47	0.507	0.60	$(Cu_{0.77}Zn_{0.23})_2(OH)PO_4$
65	35	12.99	38.82	13.83	4.42	0.510	0.59	$(Cu_{0.74}Zn_{0.26})_2(OH)PO_4$
60	40	12.99	35.53	16.65	5.45	0.514	0.72	$(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ with zinc phosphate.
0	100	13.84	—	47.54	9.07	0.614	1.13	Zinc phosphate.
				M−Co				
100	0	12.90	52.77	—	4.90	0.502	0.65	$Cu_2(OH)PO_4$
90	10	12.91	51.79	1.02	5.05	0.502	0.67	$(Cu_{0.98}Co_{0.02})_2(OH)PO_4$
80	20	12.94	49.84	2.48	5.09	0.505	0.68	$(Cu_{0.95}Co_{0.05})_2(OH)PO_4$
70	30	12.98	47.18	5.02	4.55	0.506	0.60	$(Cu_{0.90}Co_{0.10})_2(OH)PO_4$
65	35	13.03	44.76	6.92	5.82	0.511	0.77	$(Cu_{1-Y}Co_Y)_2(OH)PO_4$ with cobalt phosphate.
60	40	13.77	39.37	9.39	7.09	0.566	0.88	
				M−Ni				
100	0	12.90	52.77	—	4.90	0.502	0.65	$Cu_2(OH)PO_4$
90	10	12.86	52.35	0.44	5.07	0.495	0.67	$(Cu_{0.99}Ni_{0.01})_2(OH)PO_4$
80	20	12.93	50.29	1.95	5.38	0.506	0.72	$(Cu_{0.96}Ni_{0.04})_2(OH)PO_4$
75	25	13.03	48.00	4.08	5.54	0.510	0.73	$(Cu_{0.92}Ni_{0.08})_2(OH)PO_4$
70	30	12.54	45.54	5.64	7.10	0.498	0.97	$(Cu_{1-Y}Ni_Y)_2(OH)PO_4$ with $Ni_3(PO_4)_2 \cdot 8H_2O$
60	40	12.67	37.50	9.48	11.47	0.544	1.56	
0	100	12.15	—	34.03	28.82	0.675	4.08	$Ni_3(PO_4)_2 \cdot 8H_2O$

In case of copper-cobalt and copper-nickel hydroxide phosphates, similar results were obtained. Precipitation of the cations of Cu and Co at W $\leq$ 30 mol. % as well as Cu and Ni at W $\leq$ 25 mol. % led to products with molar ratios of P/(M + Cu) and H_2O / P that were close to same for libethenite (Table I). But in both systems, increasing of W above these values resulted in an increase of P/(M + Cu) and H_2O/P ratios in the solids. Thus, at higher Co or Ni contents in starting materials (above 30 or 25 mol. %, respectively), other phases were formed. For example, the sample, prepared from pure nickel hydroxide carbonate (W = 100 mol. %), had the composition of $Ni_3(PO_4)_2 \cdot 8H_2O$. In the case of Zn and Co, the nonstoichiometric phosphates were obtained at W = 100 mol. %.

The XRD patterns of the phosphates, synthesized by precipitation of cation of Cu and Zn at W $\leq$ 35 mol. %; Cu and Co at W $\leq$ 30 mol. %; and Cu and Ni at W $\leq$ 25 mol. %, were similar to that of libethenite (Figure 1). The XRD data showed that all these samples were single-phase. The unit cell parameters were also close (Table II). The values of parameters found for pure $Cu_2(OH)PO_4$ agree with JCPDS data.[6]

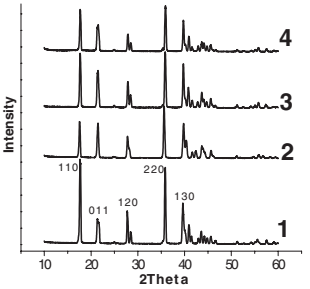

Figure 1 XRD powder patterns of $Cu_2(OH)PO_4$ (1), $(Cu_{0.74}Zn_{0.26})_2(OH)PO_4$ (2), $(Cu_{0.90}Co_{0.10})_2(OH)PO_4$ (3), and $(Cu_{0.92}Ni_{0.08})_2(OH)PO_4$ (4).

When the values of $W = M/(M + Cu)\cdot 100\%$ were more than 35 mol. % for Zn, 30 mol. % for Co, or 25 mol% for Ni, there were XRD peaks assigned to libethenite and other phosphates. It showed the formation of mixtures of two different phases. The coprecipitation of libethenite with other phosphates could be observed visually, as the phases have different colors.

Therefore, the precipitation of Cu and Zn at $W \leq 35$ mol. %; Cu and Co at $W \leq 30$ mol. %; and Cu and Ni at $W \leq 25$ mol. % resulted in formation of substitutional solid solutions $(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ $(0 \leq Y \leq 0.26)$, $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ $(0 \leq Y \leq 0.10)$, and $(Cu_{1-Y}Ni_Y)_2(OH)PO_4$ $(0 \leq Y \leq 0.08)$. These phases crystallize in the orthorhombic system, space group Pnnm. The unit cell parameters of the solid solutions are close to those of $Cu_2(OH)PO_4$. Using starting materials with higher Zn, Co, or Ni contents led to precipitation of mixtures of different phosphates.

A significant Mn or Mg substitution for Cu was not observed for the structure of $Cu_2(OH)PO_4$. It was found that Mn and Mg can substitute for Cu up to 0.03 and 0.01 molar parts (or 3 and 1 mol. %), respectively.

IR spectra are often used to determine the degree of homogeneity of solids. The spectra of solid solutions usually demonstrate bands that present in the spectrum of unsubstituted compounds. But the mechanical mixtures give spectra that can be derived by linear combination of the spectra of the components. The IR spectra obtained are illustrated in Figure 2, in which $Cu_2(OH)PO_4$ and all solid solutions show the same bands. Particularly, all spectra were similar in the area of bending [($\delta_s(PO_4)$: 410–490 and $\delta_{as}(PO_4)$: 510–670 cm^{-1}] as well as stretching [($\nu_s(PO_4)$: 930–990 and $\nu_{as}(PO_4)$: 975–1140 cm^{-1}]

Table II The unit cell parameters of synthesized solid solutions (orthorhombic system, space group Pnnm)

Chemical composition	*a*	*b*	*c*	V
	nm			nm^3
$Cu_2(OH)PO_4$	0.8070	0.8405	0.5894	0.3998
$(Cu_{0.95}Co_{0.05})_2(OH)PO_4$	0.8080	0.8397	0.5896	0.4000
$(Cu_{0.90}Co_{0.10})_2(OH)PO_4$	0.8091	0.8372	0.5898	0.3995
$(Cu_{0.94}Zn_{0.06})_2(OH)PO_4$	0.8090	0.8405	0.5894	0.4008
$(Cu_{0.74}Zn_{0.26})_2(OH)PO_4$	0.8195	0.8365	0.5890	0.4038
$(Cu_{0.96}Ni_{0.04})_2(OH)PO_4$	0.8069	0.8391	0.5896	0.3992
$(Cu_{0.92}Ni_{0.08})_2(OH)PO_4$	0.8067	0.8375	0.5900	0.3986

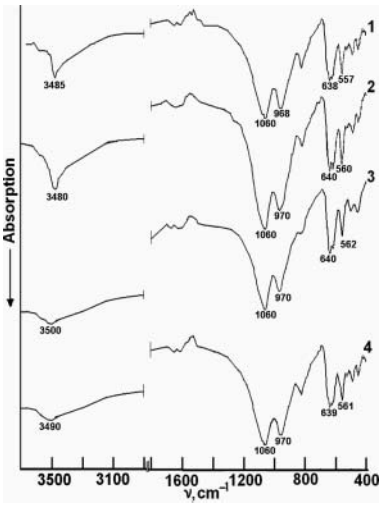

Figure 2 IR spectra of: $Cu_2(OH)PO_4$ (1), $(Cu_{0.90}Co_{0.10})_2(OH)PO_4$ (2), $(Cu_{0.74}Zn_{0.26})_2(OH)PO_4$ (3), and $(Cu_{0.92}Ni_{0.08})_2(OH)PO_4$ (4).

vibrations of the phosphate anion.[13] In the case of $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.10$), the ν(OH) band (about 3500 cm^{-1}) was also close to the same for libethenite independent of cobalt content (Y). On the other hand, for $(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.26$) and $(Cu_{1-Y}Ni_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.08$), the band of stretching OH vibrations was broadened with significant Zn or Ni contents (Figure 2).

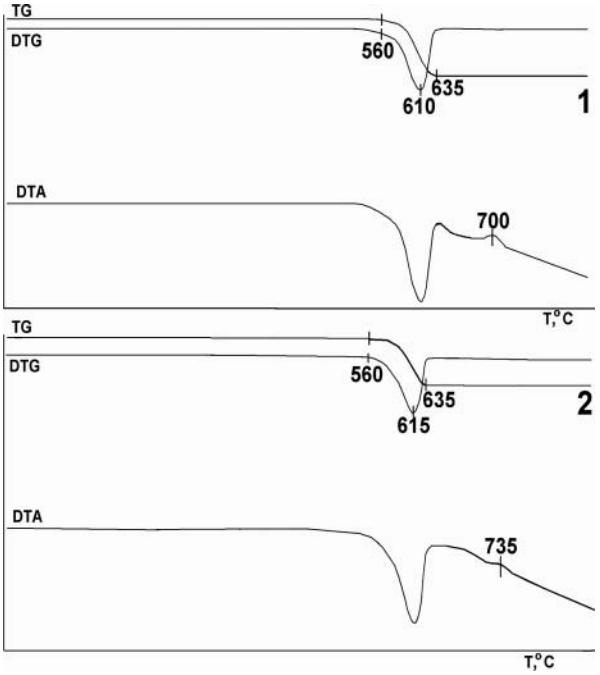

Figure 3 DTG and DTA curves of $Cu_2(OH)PO_4$ (1) and $(Cu_{0.90}Co_{0.10})_2(OH)PO_4$ (2).

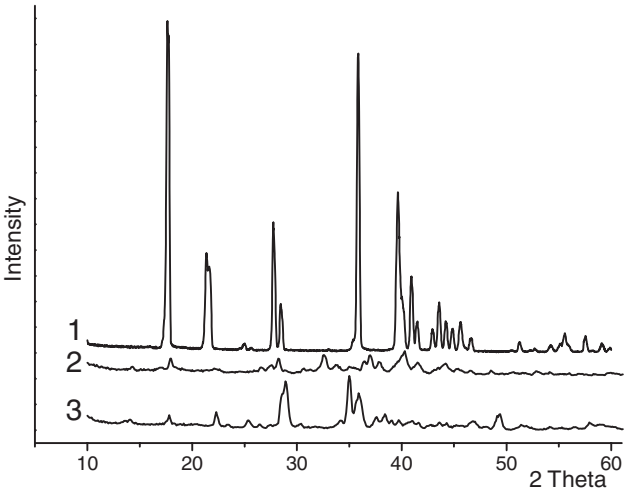

Figure 4 The XRD patterns for $Cu_2(OH)PO_4$ (1) and the product of its calcination at 630°C (2) and 750°C for 1 h.

The samples of $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.10$) were used to investigate the thermolysis of synthesized solid solutions (Figure 3). The DTG curve showed one effect that was accompanied by an endothermic peak in the DTA. The effect was attributed to loss of all water (0.6–0.7 mol). This value is close to theoretical water content (0.5 mol H_2O). For end-members of the solid solution (with $Y = 0$ and $Y = 0.10$), the temperatures of this effect were very close (610°C and 615°C, respectively). Calcination of the $Cu_2(OH)PO_4$ sample at 630°C for 1 h resulted in disappearance of the initial peaks in the XRD pattern (Figure 4).

The DTA curve also demonstrated the exothermic effect (700°C for $Y = 0$ and 735°C in case of $Y = 0.10$). The XRD pattern of libethenite calcinated at 750°C for 1 h showed weak peaks, indicating the start of crystallization. Therefore the exothermic effect can be attributed to heat of crystallization.

However, XRD data showed that a high-crystallinity sample of $Cu_4O(PO_4)_2$ formed at 850–900°C. The XRD pattern of copper oxide phosphate obtained at 850–900°C agreed with JCPDS data.[14]

The ionic radii of Zn^{2+}, Co^{2+}, and Ni^{2+} are close. Thus, the maximum values of Co and Ni substitution for Cu are close. But $(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.26$) solid solution has a wider area of homogeneity than those for Co and Ni analogs, which cannot be explained by existence of rhombic modification of $Zn_2(OH)PO_4$ (isostructural with libethenite). Such a phase is known for cobalt hydroxide phosphate also.

CONCLUSIONS

The substitutional solid solutions of $(Cu_{1-Y}Zn_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.26$), $(Cu_{1-Y}Co_Y)_2(OH)PO_4 \cdot xH_2O$ ($0 \leq Y \leq 0.10$), and $(Cu_{1-Y}Ni_Y)_2(OH)PO_4 \cdot xH_2O$ ($0 \leq Y \leq 0.08$) were synthesized. An increase of molar parts of Zn, Co, or Ni in starting materials [$W = M/(M + Cu)$ 100%] leads to precipitation of mechanical mixtures. Synthesized

solid solutions crystallize in the orthorhombic system, space group Pnnm. Their unit cell parameters and IR spectra are similar.

The DTA curves of $(Cu_{1-Y}Co_Y)_2(OH)PO_4$ ($0 \leq Y \leq 0.10$) demonstrate one exothermic and one endothermic effect. The first effect is assigned to the dehydration of the hydroxide phosphates; the second is explained by the start of crystallization.

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