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Journal of Solid State Chemistry 178 (2005) 1308–1311

JOURNAL OF SOLID STATE CHEMISTRY

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Rapid communication

Room temperature synthesis and solid-state structure of $Ni_2P_2O_6 \cdot 12H_2O$

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Received 3 November 2004; received in revised form 30 November 2004; accepted 2 December 2004

Abstract

The synthesis and crystal structure of $Ni_2P_2O_6 \cdot 12H_2O$ are reported. The compound was synthesized from aqueous solutions of nickel chloride and sodium hypodiphosphate at room temperature. The space group is orthorhombic, *Pnnm*. Unit cell dimensions are $a = 11.2418(5)$ Å, $b = 18.5245(8)$ Å, and $c = 7.3188(3)$ Å, $Z = 4$. The product is unstable with respect to dehydration above room temperature.

Keywords: Metal hypodiphosphate; Room temperature synthesis

1. Introduction

The transition metal hypodithiophosphates, $M_2P_2S_6$ (e.g. $M =$ Mn [1], Fe [1], Co [1], Ni [1], Cd [1], Sn [2]) have received considerable attention because of the interesting structural, chemical, and magnetic behavior demonstrated by this class of compounds [3]. Several reports of the room temperature preparation of transition metal hypodithiophosphates have been published. Bourdon et al. [4] reported the room temperature synthesis of $Sn_2P_2S_6$, with an estimated particle size of ca. 20 nm. Fragnaud et al. [5] reported the synthesis of a highly disordered $Ni_2P_2S_6$. Huang et al. [6] also reported the room temperature synthesis of $Ni_2P_2S_6$, but their product appears to be non-crystalline.

The corresponding hypodiphosphates, $M_2P_2O_6$, have received considerably less attention, in spite of their useful properties (e.g. in situ Ni metal deposition) [7]. One reason may be the difficulty in preparing metal hypodiphosphates. In both of these classes of compounds, the phosphorus assumes the unusual oxidation state of IV and is susceptible to disproportionation (vide infra) [8].

In this communication, we report the synthesis and solid-state structure of high quality crystalline $Ni_2P_2O_6 \cdot 12H_2O$ grown from aqueous solution.

2. Experimental section

2.1. Synthesis

Single crystals of $Ni_2P_2O_6 \cdot 12H_2O$ were prepared by mixing two aqueous solutions: nickel chloride and sodium hypodiphosphate. The nickel chloride solution was prepared with $NiCl_2 \cdot 6H_2O$ (2.37 g, 9.97 mmol) and deionized (DI) water (10 mL, 17 MΩ) forming a clear green solution. Sodium hypodiphosphate was prepared using a modified procedure reported by Leininger and Chulski [9]. Sodium chlorite (8.19 g, 90.6 mmol) was mixed with DI water (12 mL) for 15 min resulting in a light yellow creamy colored mixture. Red phosphorus (1.84 g, 59.4 mmol) was mixed with DI water (~20 mL) in a separate beaker forming a reddish brown mixture. The sodium chlorite solution was then slowly added to

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doi:10.1016/j.jssc.2004.12.005

the red phosphorous mixture. The reaction between the two mixtures was violent and exothermic, resulting in the evolution of a yellow gas and the solvent boiling. The color of the mixture changed from reddish brown to a bright yellow as the sodium chlorite was added. After all of the sodium chlorite was added, the mixture was filtered (medium) yielding a bright yellow solution with a pH near 0. The pH was raised to 10 by the addition of 3 M NaOH(aq). At a pH of ca. 8, crystals of $Na_4P_2O_6 \cdot 10H_2O$ began falling out of solution. After all of the NaOH(aq) was added, the crystals were isolated with a Buchner funnel and allowed to air dry. The crystals were redissolved in H_2O/D_2O and the resulting solution analyzed using ^{31}P NMR spectroscopy. The solution showed a single ^{31}P resonance peak between 10 and 14.5 ppm (relative to 85% H_3PO_4(aq)) depending on the pH of the solution [10]. The crystals were also analyzed with thermogravimetric analysis (TGA), which showed a weight loss consistent with the dehydration of ten water molecules per formula unit.

Nickel chloride hexahydrate (99%) and sodium chlorite (80%) were purchased from Aldrich. The amorphous red phosphorous (99%, 100 mesh) was purchased from Alfa Aesar. All reagents were used as received.

$Na_4P_2O_6 \cdot 10H_2O$ (0.066 g, 0.154 mmol) was dissolved in DI water (20 mL) forming a clear and colorless solution. This solution was poured into a vial containing the $NiCl_2$ solution. The combined solutions were a slightly lighter green than the initial nickel solution and no visible reaction had occurred. After 3 h, crystals could be seen at the bottom of the vial and below the meniscus. After 24 h, a large quantity of light green $Ni_2P_2O_6 \cdot 12H_2O$ crystals were produced and isolated. When the reaction was allowed to proceed for one week, a yield of 60.1% (based on $Na_4P_2O_6 \cdot 10H_2O$) was realized.

2.2. *Single crystal X-ray diffraction*

Crystals of compound 1 were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 292(2) K using a Bruker/Siemens SMART APEX instrument (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.77 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [11] software and refined using SAINTPlus [12] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [13]. The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package [14]. The structure was solved in the space group *Pnnm* (# 58) by analysis of systematic absences. All atoms were refined anisotropically. Hydrogen atoms were located on the difference map and their positions were fixed, in spite of some close intermolecular distances. Hydrogen thermal parameters were refined with a riding model with $U_{iso} = 1.5U_{eq}$ of the parent atom. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1 [15].

Table 1
Crystal data and structure refinement for $Ni_2P_2O_6 \cdot 12H_2O$

Empirical formula	$H_{24}Ni_2O_{18}P_2$
Formula weight	491.55
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pnnm*
a (Å)	11.2418(5)
b (Å)	18.5245(8)
c (Å)	7.3188(3)
Volume (Å^3)	1524.13(11)
Z	4
Density calc. (mg/m^3)	2.142
μ (mm^{-1})	2.771
Crystal color and habit	Light green needle
Index ranges	$-14 \leqslant h \leqslant 14$, $-24 \leqslant k \leqslant 24$, $-9 \leqslant l \leqslant 9$
Reflns (collected/independent)	22951/1891 ($R_{int} = 0.0378$)
Data/restraints/parameters	1891/0/117
GOF	1.153
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0358$, w$R_2 = 0.0793$

$R_1 = \sum |F_o| - |F_c| \sum |F_o|$; w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

3. Results and discussion

One reason for the paucity of hypodiphosphate materials is the instability of the $P_2O_6^{4-}$ species. Under acidic conditions, it is thermodynamically unstable with respect to disproportionation [8]

$$H_4P_2O_6 + H_2O \rightarrow H_3PO_4 + H_3PO_3.$$

Nevertheless, in our experiments, the $P_2O_6^{4-}$(aq) moiety remained intact long enough (several hours) to react with Ni^{2+}(aq) to produce $Ni_2P_2O_6 \cdot 12H_2O$(s). In similar experiments with hypodithiophosphate, $P_2S_6^{4-}$(aq), we have been unable to obtain a crystalline material that can be characterized by single crystal X-ray diffraction.

The structure of $Ni_2P_2O_6 \cdot 12H_2O$ is shown in Figs. 1a and b. There is considerable strong hydrogen bonding between the cations and the anions ranging from 2.606(2) Å (O5–H5b…O10) at the closet to 2.837(2) Å (O1–H1a…O11). This links the whole structure into a