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Synthesis and characterization of multi-functional material MoBP$_3$O$_{12}$

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ABSTRACT

New metal borophosphate compound MoBP$_3$O$_{12}$, as a potential candidate of nonlinear optical material, was obtained by hydrothermal method. The title compound was synthesized from the mixture of MoO$_3$, B$_2$O$_3$, and (NH$_4$)$_2$HPO$_4$ with the molar ratio 1:0.5:3, by heating at 200 °C for 3 days. The powder X-ray diffraction data was indexed in tetragonal system with the refined unit cell parameters, a = b = 5.302 (8), c = 21.538 (4) Å and Z = 1. Stoichiometric chemical analysis of molybdenum was done by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and boron content was analysed by spectrophotometric azomethine H method. The indexed powder X-ray diffraction (XRD) data with POWD program, fourier transform infrared spectroscopy (FTIR) spectrum and thermal analysis of MoBP$_3$O$_{12}$ are also given in the paper.

1. Introduction

In the last decades, metal borates have drawn world attention because of their excellent physical and unique optical nature [1-3]. On the other hand, phosphate compounds have been taken an interest due to their magnetic, optic and electro-optic properties [4-6]. In the borate structure, boron atoms can connect with oxygen atoms in two different ways; trigonal sp^2 bonds or tetrahedral sp^3 bonds to form BO$_3$ and BO$_4$, respectively [7]. In addition to these two simple groups, borates contain complex groups, such as symmetrical B$_3$O$_6$ boroxol ring, unsymmetrical B$_3$O$_7$ ring and infinite chain (BO$_2$)$_n$ [8, 9]. In the phosphate structure, relatively simple tetrahedral PO$_4$ and complex P$_2$O$_7$ are mainly available [9]. The diversity of linkage of boron and phosphorus atoms with oxygen atoms lead to the formation of new compounds called 'borophosphates' with different partial anionic structures [10]. Borophosphates are described by the existence of "BPO$_7$ group" including four-fold coordinated B and P, and bridging oxygens occurring silica-like network [11]. Borophosphate compounds are promising new class of functional materials, particularly nonlinear optics, because of having a huge structural diversity [12].

There is much information for the industrial applications of metal borophosphate compounds. For example; alkaline earth metal borophosphates, especially CaBPO$_5$, are used for corrosion protection of metal surfaces. Moreover, different types of metal borophosphates are being used as antioxidant, fire proofing agent (sodium, potassium borophosphate) and also as a binder (aluminium borophosphate as binder for clays and phosphates) [13]. Strontium borophosphate is reported as light sensitive material and can be used in solar energy research [14]. As the other group, rare earth borophosphate compounds have found wide application area for laser and luminescence materials and can be called "self-active lasers". Borophosphate glass ceramic compositions are being used for sealing cathode ray tubes, plasma display panels and fluorescent character display tubes [15]. Alkaline, alkaline earth and rare earth metal borophosphate compounds have been studied and investigated in detail in recent years. But, to our knowledge, there is few reports deal with transition metal borophosphates.

Generally, conventional solid state synthesis is used to obtain metal borophosphates. Anhydrous borophosphates as M[BPO$_5$] (M=Ca, Sr), M$_3$[BP$_3$O$_{12}$] (M=Ba, Pb) and Na$_5$[B$_2$P$_3$O$_{13}$] are the basic borophosphates synthesized by high temperature furnaces at about 1100-1400 °C [16-19]. However, such high temperature can lead to glassy product not possible to get optical quality crystals [20]. Therefore, more mild applications like hydrothermal method must be explored. To synthesize single crystal and polycrystalline compounds, hydrothermal synthesis is an excellent method. Lots of chromate, phosphate, borate, and borophosphate

compounds are produced with hydrothermal synthesis [21]. The most common arrangement required for such crystallization is the temperature gradient that helps to transport the material from the zone of high solubility. This method has some significant advantages over other chemical techniques. Many materials can be produced directly in the desired crystalline phase at relatively low temperatures (under 350 °C) with eliminating any need for the calcination treatment prior to sintering.

Herein, the hydrothermal synthesis and structural analysis of molybdenum borophosphate, $MoBP_3O_{12}$ is reported. This compound is characterized by powder X-ray diffraction (XRD), fourier transform infrared spectrophotometry (FTIR), inductively coupled plasma/optical emission spectroscopy (ICP/OES) and azomethine H spectrophotometric method.

2. Materials and methods

2.1 Synthesis of $MoBP_3O_{12}$

The chemical reagents, MoO_3, B_2O_3, $(NH_4)_2HPO_4$ and H_3PO_4 were analytical grade by Merck and Riedel. MoO_3, B_2O_3 and $(NH_4)_2HPO_4$ were mixed in 1:0.5:3 molar ratio and 6 mL H_3PO_4 (85 %) and 20 mL distilled water added to dissolve them (pH<2). The clear solution was transferred into stainless steel Teflon autoclave and heated at 200 °C for 3 days. The products were filtered off, washed with distilled water and dried at 60 °C. Experiment was repeated three times for reproducibility.

2.2 Characterization

The XRD data were collected by using Brucker Axs-Advanced-Dx type of diffractometer with Cu-K_a radiation (40 kV, 20 mA, I=1.54056 Å). Infrared spectrum was obtained using Perkin Elmer BX-2 FTIR spectrophotometer in the 4000-400 cm^{-1} range. The thermal property was defined by Perkin Elmer Diamond thermogravimetric analysis (TGA).

2.3 Chemical analysis

The elemental boron analysis was determined by using the azomethine H spectrophotometric method with high and good sensitivity. Elemental boron analysis was performed using the azomethine-H spectrochemical method with high detection power [22,23], Lange Cadas 2800 spectrophotometer. In this method borate anions form a yellow complex which is photometrically perceptible with azomethine-H. A standard kit (LCK 307 Bor, 0.05-2.5 mg/L, supplied by Hach Lange, GmbH Willstätterstr, 11, 40549 Düsseldorf, Germany) was used for this procedure. The sample to be assayed was weighed in appropriate quantities and the appropriate dilution was carried out in the presence of a small amount (2-3 mL) of nitric acid, dissolved in water, with a boron concentration of 0.05-2.5 mg/L in

the sample. Using standard kits, the boron concentration in the sample to be assayed was measured in a spectrophotometer against the previously prepared peptide. Using mathematical transformations, it is determined how many moles of boron are present in one molar product Mo content was also determined with several necessary dilutions by using a PerkinElmer Optima 3100-XL-ICP-OES by using molybdenum standard.

2.4 Indexing of the XRD pattern

The refinement of the unit cell parameters were realized by the POWD program (an interactive Powder Diffraction Data Interpretation and Indexing Program Ver. 2.2.) [24].

3. Results and discussion

3.1 Powder X-ray diffraction results of $MoBP_3O_{12}$

The synthesized product was obtained as a white powder and stable at room temperature. Figure 1 shows the powder X-ray diffraction pattern of the product. When we compared the "d" values with ICDD (International Centre for Diffraction Data) crystal structure database and literature, there was no coupling. Therefore, we indexed the pattern via POWD program and decided that an original new XRD patterns were obtained with the product. In the indexing process, none impurity was detected. So, all reflections are indexed in the tetragonal system. After refinements, the lattice constants were calculated as a= b= 5.302(8) and c=21.538(4) Å. The experimental density of the product was obtained 1.124 g/cm^3 and Z value was calculated as 1. The observed and calculated powder XRD data of the product are listed in Table 1. So we could say high purity of this compound was obtained by hydrothermal method. The basic chemical reaction of synthesis of $MoBP_3O_{12}$ can be suggested as follows:

$$MoO_3 + 1/2B_2O_3 + 3(NH_4)_2HPO_4 \longrightarrow MoBP_3O_{12} + 6NH_3 + 9/2H_2O \quad (1)$$
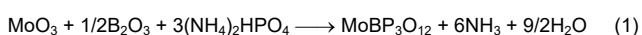
3.2 The results of chemical analysis

The mole ratio of boron was calculated 1.13 by azomethine H method. The value was very close to the theoretical stoichiometric value, resulting with a formula $MoBP_3O_{12}$. The target compound was dissolved in warm nitric acid/water solution (1:1) to obtain 1 M solution of the compound to obtain stock solution. The solution was analysed with several necessary dilutions on PerkinElmer Optima 3100 XL ICP-OES with software Winlab 32 and connected AS-90-TrayB auto sampler. The instrumentation was equipped with an echelle-based polychromator, a standard axially viewed glass torch and a cross flow nebulizer coupled to glass cyclonic spray chamber. Transport of the solutions to the nebulizer was achieved using a peristaltic pump at 1.5 mL min^{-1}. Plasma, auxiliary and nebulization gas flows were 15.0, 0.5 and 0.5 L.min^{-1}, respectively. The wavelength has been used for the Mo element was at 202.031 nm.
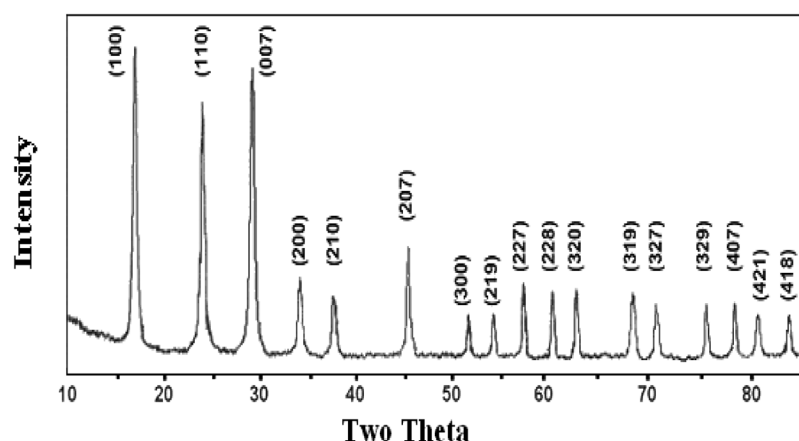
Figure 1. Powder X-ray diffraction pattern of $MoBP_3O_{12}$.

Table 1. List of diffraction intensities, d-values and the indexing results of $MoBP_3O_{12}$.

I/I_0	d_{obs}	d_{calc}	hkl
100	5.27	5.30	100
86	3.725	3.750	110
95	3.061	3.077	007 (114)
26	2.650	2.651	200
21	2.366	2.372	210
42	2.004	2.009	207
16	1.7687	1.7676	300 (224)
16	1.6836	1.6845	219
20	1.6002	1.6011	227 (314)
18	1.5365	1.5385	228
18	1.4697	1.4707	320
18	1.3722	1.3723	319
15	1.3281	1.3269	327
16	1.2526	1.2530	329
15	1.2166	1.2175	407 (334)
13	1.1842	1.1840	421
14	1.1610	1.1605	418

The obtained Mo and B concentrations in mg/L were converted to mol/L and the mole ratio of Mo/B was calculated as 1:1 molar ratio.

3.3 FTIR and thermal studies

The FTIR spectrum of $MoBP_3O_{12}$ is illustrated in Figure 2. The absorption bands around 3615, 3450 and 1670 cm^{-1} are due to the absorption of water from the air. Absorption bands at 1241 and 1377 cm^{-1} may be assigned to non-bridging P=O vibrations. Experimental and referred stretching vibrations of BO_4, BO_3, PO_4 and other functional groups have been given in Table 2 [25-27]. Since the borophosphates are consisting of simple or complex anionic structures like BO_3, BO_4, PO_4 and BOP, the IR bands support the presence of this coordination in the synthesized crystal structure.

The result of thermal analysis is displayed in Figure 3. The mass loss at about 200 °C is related to the humidity. Thermal changes at 708 and 990 °C represent phase transformations in crystal structure.
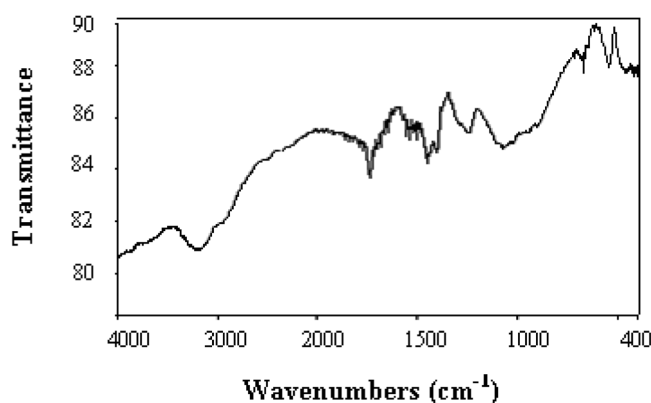

Figure 2. FTIR spectrum of $MoBP_3O_{12}$.

Table 2. The FTIR wavenumbers of $MoBP_3O_{12}$.

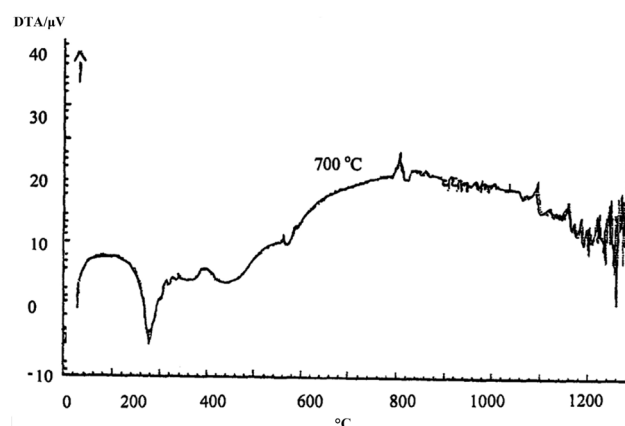| Assignments	Experimental Wavenumbers (cm^{-1})	Band Locations (cm^{-1})
ν(P=O)	1241	1216
	1370 (Broad)	1377
ν_3 (BO_3)	1241(Broad)	1200-1245
ν_3 (BPO_7)	1079	1079
ν_3 (BO_4)	1020 (Broad)	1051
ν_s (BOP)	718	749
ν_4 (PO_4)	467	467
ν_1 (BO_4)	897	882
δ (BOP)	668	655
δ (OPO)	548	561

Figure 3. The DTA curves of $MoBP_3O_{12}$.

4. Conclusions

In this work, the synthesis of molybdenum borophosphate has been achieved by hydrothermal method for the first time. The crystal structure and unit cell parameters of $MoBP_3O_{12}$ were obtained by POWD indexing program as tetragonal system and a=b=5.302(8) and c=21.538(4) Å, respectively. While indexing process, we used powder X-ray diffraction pattern. Also, we benefit from FTIR spectrum, ICP-OES analyse results, spectrophotometric method results, and thermal analysis for supporting presence of borophosphate in the crystal structure and mole ratio of the basic atoms. Also, crystal system, unit cell parameters and chemical formula of molybdenum borophosphate were described for the first time with this paper.

Acknowledgment

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