Solid State Sciences 64 (2017) 76–83

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

High-throughput syntheses of iron phosphite open frameworks in ionic liquids☆

Zhixiu Wang [a], Ying Mu [b], Yilin Wang [b], Qiming Bing [a], Tan Su [a, b, *], Jingyao Liu [a]

[a] Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130021, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 12 September 2016
Received in revised form
8 December 2016
Accepted 9 December 2016
Available online 29 December 2016

Keywords:
Ionic liquids
High-throughput
Open framework
Iron phosphite
Mössbauer measurement
Magnetic behavior

ABSTRACT

Three open-framework iron phosphites: $Fe^{II}_5(NH_4)_2(HPO_3)_6$ (**1**), $Fe^{II}_2Fe^{III}(NH_4)(HPO_3)_4$ (**2**) and $Fe^{III}_2(HPO_3)_3$ (**3**) have been synthesized under ionothermal conditions. How the different synthesis parameters, such as the gel concentrations, synthetic times, reaction temperatures and solvents affect the products have been monitored by using high-throughput approaches. Within each type of experiment, relevant products have been investigated. The optimal reaction conditions are obtained from a series of experiments by high-throughput approaches. All the structures are determined by single-crystal X-ray diffraction analysis and further characterized by PXRD, TGA and FTIR analyses. Magnetic study reveals that those three compounds show interesting magnetic behavior at low temperature.

1. Introduction

The discovery of new structures needs a large amount of experimental efforts, which can be diminished by using high-throughput approaches. In the synthesis procedure, the application of high-throughput approaches for materials science can help researchers to rapid screen the variables, raising the number of samples produced and characterized [1–3]. In 1998, Wendelbo's group [4] presented the high-throughput technique into zeolite syntheses, which has showed its formidable strength in the fast optimization of synthetic conditions of known zeolites [5–7] and in the discovery of new structures [8–10]. Many metal phosphates [11–16] have attracted much attention because of their unique physical and chemical properties in optics, electronics and magnetism, and exhibited great potential applications in the fields of separation, adsorption and catalysis [17,18] due to various metal ions doped in these compounds. Lately, using phosphite group to replace tetrahedral phosphate group to afford new metal phosphites have attracted great attention [19]. Lots of metal phosphites have been synthesized and characterized, such as zinc phosphites [20–22], vanadium phosphites [23–26], cobalt phosphites [27–33], manganese phosphites [34,35] and iron phosphites [36–57]. Among these materials, iron phosphites occupied a considerable position because of its rich diversity of structures and special magnetic properties. Notable examples includes, $|C_{10}N_2H_8|[Fe^{III}(HPO_3)(H_2PO_4)]$ [40], the first 1D iron phosphite-phosphate with an antiferromagnetic character, $|C_4H_{12}N_2|[Fe^{II}Fe^{III}(HPO_3)_2F_3]$ [43], an iron phosphite with a mixed valence nature and antiferromagnetic property, $|C_4N_3H_{14}|[Fe_3(HPO_3)_4F_2(H_2O)_2]$ [50], and a new 3D iron phosphite with an antiferromagnetic property. Typically, metal phosphites were synthesized under hydrothermal or solvothermal conditions.

In 2004, Morris and co-workers developed the ionothermal method for syntheses of inorganic open-framework materials [58] for the first time. In recent decade, a number of studies on the usage of ionic liquids as the solvent and structure-directing agent to synthesize microporous aluminum phosphate molecular sieves were reported [59–64]. Ionic liquids are a class of organic molten salts, which are completely constituted by ions at room temperature and adjacent temperature [65,66]. The reaction possess negligible vapor pressure, which in sealed autoclaves is safe [67]. There are other potential advantages of ionothermal method, such

☆ In this paper, the crystallographic data of compound **1** comes from the Cambridge Crystallographic Data Centre (CCDC reference: 1027279).

* Corresponding author. Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130021, PR China.
E-mail address: sutan_jlu@jlu.edu.cn (T. Su).

http://dx.doi.org/10.1016/j.solidstatesciences.2016.12.017
1293-2558/

as it can improve the templating effect, which can reduce the competition between solvent and template for their interaction with coordinate atoms [68], and also this route may generate a series of new structures [69–75]. For instance, Yu's group has reported the ionothermal synthesis of $5H_3O\cdot[Ni_8(HPO_3)_9Cl_3]\cdot 1.5H_2O$ [74], a nickel phosphite shows antiferromagnetic property and $|NH_4|_4[Mn_4(HPO_3)_6]$ [75], a new 2D manganese(II) phosphite with an antiferromagnetic dimer system.

To date, the ionothermal synthesis of metal doped phosphites by high-throughput technique have not been studied widely, which inspired us to use this method to synthesize innovative phosphite open-framework materials. In this manuscript, we report three iron phosphites by using high-throughput technique, named, $Fe^{II}_5(NH_4)_2(HPO_3)_6$ (**1**), $Fe^{II}_2Fe^{III}(NH_4)(HPO_3)_4$ (**2**) and $Fe^{III}_2(HPO_3)_3$ (**3**) respectively. The ionothermal syntheses, crystal structures, thermogravimetric analyses, magnetic and Mössbauer analyses of the compounds are reported.

2. Experimental section

2.1. Reagents and physicochemical characterization techniques

Phosphorous acid (AR, purity 99%, Sinopharm Chemical Reagent Co., Ltd), iron(III) oxalate hexahydrate (Alfa Aesar), ionic liquids (prepared by ourselves), deionized water, all the chemicals were used as-purchased and without further purification.

The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/MAX-IIIA diffractometer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Infrared spectra was performed using the KBr pellet method: 2 or 3 mg of each compound were mixed with KBr powder and pressed to form a pellet which was analyzed by a Nicolet Impact 410 FTIR spectrometer in the range 400–4000 cm^{-1}. Thermogravimetric measurements were performed on Perkin-Elmer TG-7 thermal analyzer in N_2 with the heating rate of 10 °C/min^{-1}. The magnetization was measured over the temperature range of 2–300 K for the title compounds, using a Quantum Design MPMS-XL SQUID magnetometer. Mössbauer measurement was made on the OXFORD MS-500 instrument at room temperature using a conventional constantacceleration spectrometer with a ^{57}Co/Pd source and the velocity of isomer shifts is calibrated by the α-Fe foil.

2.2. Synthesis

In this work, we have investigated the following issues:

1) How the gel concentrations, synthetic times and reaction temperatures affect the synthesis process. So a series of different synthesis reaction paths were designed by the high-throughput approaches. By controlling different reaction temperatures, different reaction times and different Fe/P ratios, three iron phosphites open-framework $Fe^{II}_5(NH_4)_2(HPO_3)_6$ (**1**), $Fe^{II}_2Fe^{III}(NH_4)(HPO_3)_4$ (**2**) and $Fe^{III}_2(HPO_3)_3$ (**3**) have been obtained. For each compound, we have selected the best reaction conditions which can generate the pure phase, and only one variable parameter has been changed for each specific condition. Specially, we found that the compound **1** was produced as the increase of reaction temperature but its crystallinity decreased. All the reaction results are listed in Table 1. The following is the optimal reaction conditions for our synthesis.
2) Based on the optimal reaction routes, the effects of different ionic liquids [69] on the products were also studied. The results are listed in Table 2. From this table, we can see that the use of small steric hindrance solvent ([Emim]Br) is more conducive to produce target products in the reaction, the phase of $Fe^{III}_2(HPO_3)_3$ (**3**) and amorphism are more easily generated by using other ionic liquids as solvents and template agents.

Table 1
Crystallization field diagram for all compounds.

Crystallisation time/Temp.[°C]	5d	10d	15d	20d
140	**3**	**3**	**3**	**3**
150	**3**	**2+3**	**2+3**	**2+3**
160	**1+3**	**1+3**	**1+3**	**1+3**
180	**1+3**	**1**	**1**	**1**
200	Amorphism	Amorphism	Amorphism+**1**	Amorphism

Table 2
Crystallization field diagram for all four different ionic liquids at the optimal reaction conditions.

Ionic Liquid/ Temp. [°C]	[Emim]Br	[Prmim]Br	[Bmim]Br	[Pemim]Br
140	**3**	**3**	**3**	**3**
150	**2+3**	Amorphism	**3**	**3**
160	**1+3**	Amorphism	Amorphism	**3**
180	**1+3**	Amorphism	Amorphism	**3**
200	Amorphism+**1**	Amorphism	Amorphism	Amorphism