

学校编码：10384

分类号 _____ 密级 _____

学号：20720131150069

UDC _____

厦 门 大 学

硕 士 学 位 论 文

新型过渡金属磷酸盐卤化物的合成与表征

Synthesis and Characterization of New Transition Metal
phosphate halides

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论文提交日期：2016年5月

论文答辩时间：2016年5月

学位授予日期：2016年 月

答辩委员会主席： _____

评 阅 人： _____

2016年5月

**Synthesis and Characterization of New Transition Metal
phosphate halides**



A Dissertation Submitted to the Graduate School in Partial
Fulfillment of the Requirement for the Master Degree of
Philosophy

By

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May, 2016

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厦门大学博硕士论文摘要库

摘要

随着含氟磷酸铁锂在二次锂离子电池正极材料中的应用,含氟聚阴离子型化合物受到了人们的关注,但是在合成化学上多个阴离子基团的引入存在一定的难度,使得含氟或卤素磷酸盐化合物的数目并不多,结构化学亟待丰富。同时多阴离子基团与过渡金属元素之间的协同作用规律性也有待进一步探索。因此本文旨在以含氟、含氯和含氟氯的过渡金属磷酸盐为研究对象,利用氯化物盐类自带的结晶水而尽可能少加水或不加水的水热法,探索合成新晶体,进一步丰富该类化合物的结构化学,探讨氟和氯在晶体结构中的作用,并研究其热稳定性或磁性等方面的性质。主要结果如下:

(1) 采用相同反应物却不同加水量的改进水热法合成出了含三价锰 Mn^{III} 的氟氯多阴离子磷酸盐化合物 $BaMnPO_4FCl$ 和罕见的含氟钡锰磷酸盐 $BaMnPO_4F_2$, 并对两个化合物的晶体结构、红外、热稳定性、磁性和 Mn 的化合价等进行了表征。加水量影响了两个化合物的合成。大半径 Cl 元素的引入使得 $BaMnPO_4F_2$ 中的八面体链断裂成 $BaMnPO_4FCl$ 中的岛状八面体。 $[PO_4]$ 基团的变形程度影响了化合物的分子振动模式。热分析残留的 6 mg 左右的粉末,也可用于粉末 XRD 晶体结构的测定。不同结构的两个化合物磁性也有差异。

(2) 采用改进的水热法合成出了两个含 $[CuO_4Cl]$ 五聚体的铜磷酸盐氯化物 $Li_3Cu_5(PO_4)_4Cl \cdot 4.24H_2O$ 和 $BaCu_{4.5}H_2(PO_4)_4Cl$ 及一个含孤立 $[CuO_4F]$ 的铜磷酸盐氟化物 $BaCuPO_4F$, 并对三个化合物的晶体结构、红外和热稳定性等进行了表征,探讨了 $BaCu_{4.5}H_2(PO_4)_4Cl$ 化合物的磁性和紫外可见光的吸收。两个氯化物结构类似但有差异, Cl 原子的连接方式十分罕见。热分析结果显示两个化合物中氯的分解温度不同。 $BaCuPO_4F$ 与 $BaMn^{II}[PO_4]F$ 的晶体结构有密切关系。

(3) 采用水热法合成出了含二价钴 Co^{II} 的磷酸盐氟化物 $Li_2Na_2Co_3(P_2O_7)_2F_2$, 并对该化合物的晶体结构和红外进行了表征,研究了该化合物的紫外可见的光吸收。 F 原子剪切了该晶体结构的维度。在含水体系中, Co^{II} 易稳定存在。

关键词: 氟磷酸盐; 磁性; 水热法

Abstract

Since the application of lithium iron phosphates containing fluorine in secondary lithium ion battery cathode materials, fluorine-containing polyanionic compounds have attracted a lot of interest. But there are some difficulties in introducing polyanionic groups in synthetic chemistry. So the number of phosphates having fluorine or halogens is not too much. It's urgent to rich their structural chemistry. Meanwhile synergy regularities between polyanionic groups and transition metal elements are also needed further exploration. So This thesis takes transition metal phosphates containing fluorine or chlorine as the research object. The author use chloride salts with crystal water to explore the synthesis of new crystals, further enrich the structural chemistry of transition metal phosphates containing fluorine or chlorine, research the role of fluorine or chlorine in the crystal structure, and study the magnetic properties and thermal stabilities. The main results are as follows:

(1) Two new phosphate halides, having fluorine and chlorine polyanionic $\text{BaMn}^{\text{III}}[\text{PO}_4]\text{FCl}$ and rare barium manganese phosphate $\text{BaMn}^{\text{III}}[\text{PO}_4]\text{F}_2$ containing Mn^{III} have been synthesized under improved hydrothermal conditions, which had same reactions but different amount of water. Crystal structures, IR, thermal stabilities, magnetism and the valence of Mn were characterized. The amount of water played an important role in the synthesis of the two compounds. The introduction of large radius of Cl atom realized the transformation from chainlike octahedrons in $\text{BaMnPO}_4\text{F}_2$ to isolated octahedrons in $\text{BaMnPO}_4\text{FCl}$. Molecular vibrational modes were influenced by deformation of $[\text{PO}_4]$ groups. The remaining powder after thermal decomposition was about 6 mg, which can also be used to determine the crystal structure of the powder XRD. Two different compounds have different magnetism.

(2) Two copper phosphate chlorides $\text{Li}_3\text{Cu}_5(\text{PO}_4)_4\text{Cl} \cdot 4.24\text{H}_2\text{O}$ and $\text{BaCu}_{4.5}\text{H}_2(\text{PO}_4)_4\text{Cl}$ containing $[\text{CuO}_4\text{Cl}]$, a copper phosphate fluoride BaCuPO_4F with isolated $[\text{CuO}_4\text{F}]$ have been synthesized under improved hydrothermal conditions. Crystal structures, IR and Thermal stabilities were characterized. Magnetic properties

and UV-VIS spectrum were researched. The structure of two chlorides are similar but different. Cl atoms in the two compounds are connected to five $[\text{CuO}_4\text{Cl}]$ square pyramids, which was rarely mentioned in the literatures. Thermal analysis showed that two chlorine compounds had different decomposition temperatures. The crystal structure of BaCuPO_4F is closely related to $\text{BaMn}^{\text{II}}[\text{PO}_4]\text{F}$.

(3) Cobalt phosphate fluoride $\text{Li}_2\text{Na}_2\text{Co}^{\text{II}}_3(\text{P}_2\text{O}_7)_2\text{F}_2$ has been synthesized under hydrothermal conditions. Crystal structures, IR and UV-VIS were characterized. The dimensions of the crystal structure was cut by F atom. Co^{II} exists stably in aqueous systems.

Key Words: fluorophosphate; magnetic; hydrothermal.

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