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新型无水磷酸盐氟化物以及碱土金属磷酸
盐的合成与表征

Synthesis and Characterization of Novel Anhydrous
phosphate Fluorides and Alkaline Earth Phosphates

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摘要

无水化合物对于提高锂离子/钠离子电池的性能具有至关重要的作用，但是如何在温和的水热/溶剂热合成方法中制备获得无水化合物对于科学家而言一直是一项极具挑战性的工作。近年来，研究者们发现将氟离子引入锂离子电池材料中能大大提高其理论电池容量，但在实际合成过程中化合物结构中仍存在大量羟基和氟相互取代的现象，导致化合物的热稳定性较低从而限制其实际应用。因此，本文以化合物的“多氟少水”合成工艺为切入点，旨在获得高氟取代的无水磷酸盐，并在探索过程中成功获得多个磷酸盐新化合物，主要结果如下：

1、利用改性“多氟少水”溶剂热法实现高氟取代无水磷酸盐的合成，使化合物的热稳定性得到明显提高。 本文通过将氟化物配制成高浓度矿化剂溶液，同时与三乙胺、磷酸共同作用的溶剂热法实现了 F⁻离子在结构中的高氟取代，有效减少羟基存在，成功合成了 4 个无水磷酸盐新化合物： $\text{Na}_3[\text{GeF}_4(\text{PO}_4)]$ 以及 3 个同构的化合物 $\text{K}_4[\text{Ge}_2\text{F}_9(\text{PO}_4)]$ 、 $\text{K}_2\text{Ba}_2[\text{Al}_2\text{F}_9(\text{PO}_4)]$ 、 $\text{Na}_2\text{Ba}_2[\text{Al}_2\text{F}_9(\text{PO}_4)]$ ，它们均呈现出一维单链结构，F⁻离子在结构中均作为端基原子，表现出“裁剪”效应。热分析结果表明其热稳定性明显高于结构中含水或羟基的磷酸盐化合物。

2、利用带结晶水的反应原料与三乙胺、磷酸共同作用的溶剂热法获得了多个复合阴离子型磷酸盐以及焦磷酸盐新化合物。 其中， $\text{AlF}_5@[\text{Ba}_4(\text{PO}_3(\text{OH}))_4] \cdot 2(\text{H}_5\text{O}_2)$ 属于复合阴离子型磷酸盐包合卤化物，它不同于普通的铝磷酸盐化合物， AlF_6 八面体单链不直接与 $[\text{PO}_4]$ 四面体相连，而是被 Ba 多面体包裹成一维筒状复合链，再进一步与 $[\text{PO}_4]$ 四面体连接形成与分子筛相类似的三维孔道结构，孔道直径可达 7.31 Å。此外， $\text{Ba}_5(\text{P}_3\text{O}_{10})(\text{HPO}_4)_2\text{Cl}$ 也属于聚阴离子型磷酸盐卤化物，其独特之处在于结构中同时存在着磷酸根三聚体 $[\text{P}_3\text{O}_{10}]$ 、 $[\text{HPO}_4]$ 基团以及 Cl⁻离子这三种不同的阴离子基团。

3、对含氟锆磷酸体系中 Ge 原子周围 F⁻离子的配位情况进行了归纳与总结。 发现随着 Ge 原子周围配位的 F⁻离子数量的增加，结构中的 Ge/P 比例增大，促使化合物由富磷状态向富锆状态转变。其中， $\text{K}_4[\text{Ge}_2\text{F}_9(\text{PO}_4)]$ 是目前数据库中 Ge/P 比例最高的化合物。

关键词：高氟取代；溶剂热法；复合阴离子；锆磷酸盐

Abstract

Anhydrous compounds are crucially important for many technological applications, such as achieving high performance in lithium/sodium cells, but are often challenging to synthesize under hydrothermal conditions. Moreover, there are still a large number of hydroxyl groups and fluorine substituted interaction phenomenon in the synthesis process, leading to limit its practical application for their low thermal stability. Therefore, a new method for obtaining anhydrous phosphate compounds was proposed, and more than 10 new phosphate compounds were obtained in this paper. The main results are as follows:

1. A modified solvo-/hydro-fluorothermal method with fluoride-rich and water-deficient condition is highly effective for synthesizing anhydrous compounds by the replacement of hydroxyl groups and water molecules with fluorine. Several novel anhydrous compounds $\text{Na}_3[\text{GeF}_4(\text{PO}_4)]$, $\text{K}_4[\text{Ge}_2\text{F}_9(\text{PO}_4)]$, $\text{K}_2\text{Ba}_2[\text{Al}_2\text{F}_9(\text{PO}_4)]$ and $\text{Na}_2\text{Ba}_2[\text{Al}_2\text{F}_9(\text{PO}_4)]$ were successfully prepared by the solvothermal method of high concentration fluoride mineralization solution with triethylamine and phosphoric acid. Their crystal structures exhibit a one-dimensional chain structure, All F atoms exclusively coordinated to Ge/Al do not have any further connection, which demonstrates fluoride prefers to be terminals that act like “scissors”. The results of TG-DTA tests showed that thermal stability of anhydrous phosphate compounds was significantly higher than that of aqueous or hydroxyl compounds.

2. Several novel polyanionic phosphate compounds and pyrophosphate compounds were synthesized via solvothermal synthesis of the reaction raw materials with crystalline water with triethylamine and phosphoric acid. It is worth noting that, $\text{AlF}_5@[\text{Ba}_4(\text{PO}_3(\text{OH}))_4] \cdot 2(\text{H}_5\text{O}_2)$ is a hydroxyl polyanionic phosphate, consists of per-fluorinated AlF_6 octahedral linear chains which are enwrapped in the barrel shape tubes of barium polyhedra that forming a rod shape chain. The resulting rods are interconnected to each other to form a three dimensional (3-D) framework structure with 1-D channels running along the c-axis where the

H_5O_2^+ ions resided. And it shows the similar three-dimensional framework structure to molecular sieve materials, the pore diameter was up to 7.31 Å. Besides, $\text{Ba}_5(\text{P}_3\text{O}_{10})(\text{HPO}_4)_2\text{Cl}$ also belongs to the polyanionic halide phosphate, which is unique because of three different anionic groups: $[\text{P}_3\text{O}_{10}]^{5-}$ phosphate trimer, $[\text{HPO}_4]^{3-}$ group, Cl^- exist simultaneously in the structure.

3. In the system of fluoro-germanophosphates, all F atoms exclusively coordinated to Ge were summarized. It is interesting to note that the Ge/P ratio increases with the increasing number of F^- substitutions, which leads to the transformation of the compounds from the phosphorus-rich state to the germanium-rich state. Remarkably, the anhydrous phosphate $\text{K}_4[\text{Ge}_2\text{F}_9(\text{PO}_4)]$ is the highest proportion of Ge/P in the germanophosphates database.

Keywords: High fluorine substitution; Solvothermal method; Polyanionic; Germanophosphates.

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