

*Some titanium phosphates as host materials: A Crystallographic Perspective*

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Metal phosphate compounds exhibit a galaxy of fascinating structures with different dimensionalities that include one-dimensional chain or ladder structures, two-dimensional layers and three-dimensional structures possessing channels of different sizes [1]. Because of their extraordinary properties, a great variety of potential and realized uses have been invoked. Titanium phosphate can be prepared either as gel or in intermediate stages of crystallinity, but also in several crystalline forms including  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O ( $\alpha$ -TiP) and -Ti(PO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)·2H<sub>2</sub>O (-TiP), being known that the main factors affecting the ion-exchange behavior of tetravalent metals phosphates are their structures and the degree of crystallinity.  $\alpha$ - and  $\gamma$ -TiP are layered compounds with a flexible two-dimensional structures that, although they have ion-exchange properties, display low affinity towards both transition and inner transition metal ions. The synthesis of ion-exchange phases with polyvalent cations is possible by means of an indirect route [2]. In the first stage, the reaction between the inorganic solid acid ( $\alpha$ - or  $\gamma$ -TiP) and the vapor of an organic base (e.g., n-alkylamine), produced an essentially non-porous intercalation compound, usually with strong preferential orientation effects and thermal disorder of the alkyl chains. In a second step, the intercalation compound reacts with an aqueous solution of the desired metal salt, and the substitution of intercalated organic cation by the inorganic metal cation takes place. On the other hand, two Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O 3D-polymorphs (-TiP and n-TiP) were prepared hydrothermally, and the crystal structure of two polymorphs were solved ab initio from synchrotron X-ray powder diffraction data [3]. The topology of two fibrous materials consists of a Ti/P/O framework enclosing two different linear channels parallel to the direction of fibers growth, both containing water molecules coordinated to only one of two octahedral-coordinated independent titanium atoms. Despite of their neutral network, these compounds exhibit ion-exchange properties in aqueous media, and their reaction with metal salts originates fibrous phases. Herein, we give an overview of some of our ongoing research, for instance, propylamine intercalated in  $\alpha$ -TiP has been selected to investigate its sorption of Eu(III), including TEM studies and the photoluminescence behavior of these new materials. Moreover, the structural modeling of a hypothetical full ion-exchange phase, [Eu(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>/3Ti(PO<sub>4</sub>)<sub>2</sub>·[(H<sub>2</sub>O)<sub>6</sub>]<sub>1/3</sub>, has been also proposed on the basis of DFT calculations. In addition, we describe the crystal structure of n-Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O and the crystal features of the thermal transformation of -Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O to its anhydrous phase, -Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>, where the coordination of the hydrated titanium atom changed from octahedral to distorted tetrahedral and the unusual behavior of this compounds family. Also, we report the synthesis of europium-based photoluminescent materials and the surprising ability for gas-adsorption at both high (N<sub>2</sub> and H<sub>2</sub>) and ultra-low (H<sub>2</sub>) temperatures. In all cases, the observed fascinating properties can only be explained after the elucidation of the crystallographic features of these materials. Acknowledgments. This work was financially supported by Spanish MINECO (MAT2013-40950-R, MAT2016-78155-C2-1-R) and Gobierno del Principado de Asturias (GRUPIN14-060), and ERDF.

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