Magnetic cooling materials, Pesticides detoxification

Formation of lanthanide clusters in crystal lattice using ionic crystals

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Abstract

It is well known that lanthanide hydroxide clusters show intriguing photophysical, magnetic, and catalytic properties. However, the controlled synthesis of this class of clusters is still challenging due to the high pH responsibility and the geometrical flexibility of lanthanide ions. In this study, we developed a simple synthetic method to obtain lanthanide hydroxide clusters using the post-synthetic installation of lanthanide ions inside ionic crystals. Soaking ionic crystals of $K_6[Rh_4Zn_4O(L\text{-cysteinate})_6]$ in a solution of late lanthanide acetate led to the exchange of potassium ions by lanthanide ions to form lanthanide hydroxide clusters in the crystal lattice. In addition, the crystals installed by lanthanide clusters showed potential applications for magnetic cooling and catalytic hydrolysis of phosphate esters.

Background & Results

The post-synthetic modification (PSM) of crystalline materials is one of the methods to synthesize new compounds that are difficult to synthesize by conventional processes. In this study, we found the formation of lanthanide cubane clusters inside ionic crystals of coordination compounds through the PSM process.

We used ionic crystals of $K_6[Rh_4Zn_4O(L\text{-cysteinate})_6]$ that have recently been synthesized by us as the host crystals, which showed superionic conduction due to potassium ions. Immersing the host crystals in an $EtOH/H_2O$ solution containing excess $Ln(OAc)_3$ (Ln = Gd^{III}, Tb^{III}, Dy^{III}, Er^{III}, Ho^{III}, Tm^{III}, Yb^{III}, Lu^{III}) at room temperature gave new crystals containing cubane-type lanthanide hydroxide clusters $Ln_4(OH)_4$ via single-crystal-to-single-crystal transformation. In the crystal, each lanthanide cubane cluster is bound by free carboxylate groups of the $[Rh_4Zn_4O(L\text{-cysteinate})_6]^{6-}$ anions to construct an infinitely connected MOF structure. A preliminary magnetic cooling experiment indicated that crystals containing Gd^{3+} cubane clusters were cooled down from 2.6 K to 1.8 K by reducing the magnetic field from 5T to 2T. The magnetic cooling below 2 K is very remarkable because the cooling below 2 K is achieved only by the use of ^3He that is a rare and expensive resource. Moreover, all the crystals containing Ln^{3+} cubane clusters showed good heterogeneous catalytic activities for the hydrolysis of phosphate esters in an aqueous media. Since phosphate esters are used as a pesticide in agriculture, which is a cause of water pollution in many countries, the crystals synthesized in this study are applicable for the detoxification of agricultural wastewaters and products.

Significance of the research and Future perspective

The present study revealed that the lanthanide hydroxide clusters are easily synthesized inside the pore of ionic crystals of the coordination compound via soaking crystals in a solution containing lanthanide acetate at room temperature. The resulting lanthanide clusters are tightly fixed in the crystal lattice to construct a MOF-type framework that is insoluble in solution. The crystals containing lanthanide clusters showed an excellent magnetic cooling and an effective catalytic ability for esters hydrolysis, contributing to the development of magnetic cooling devices and detoxification agents of pesticides.

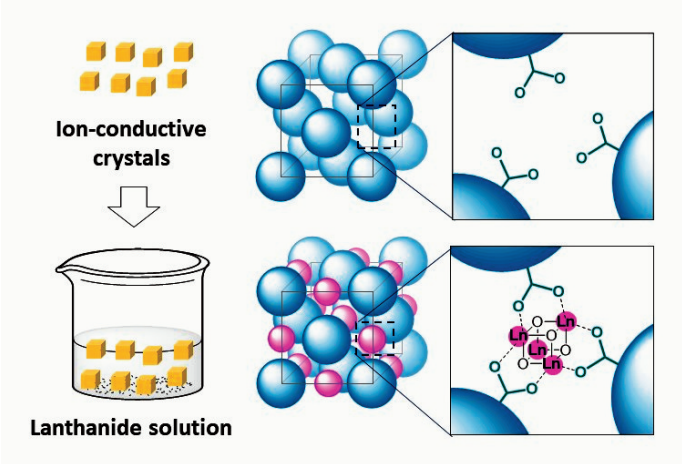

Figure 1. Schematic illustration of the synthesis of lanthanide hydroxide clusters in crystal

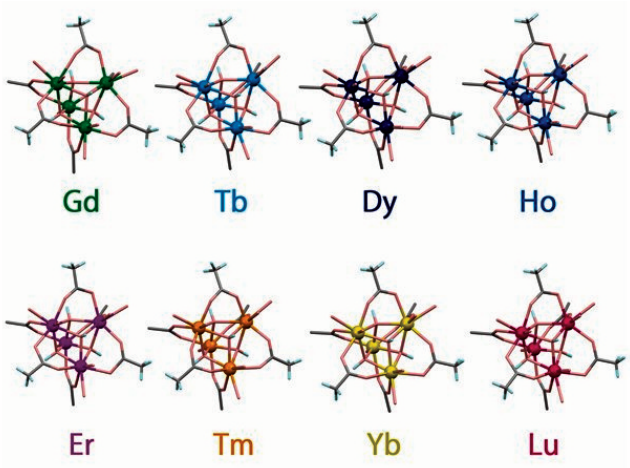

Figure 2. Structures of a series of lanthanide hydroxide clusters.

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