Synthesis of boehmite-type GaOOH: A new polymorph of Ga oxyhydroxide and geochemical implications

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ABSTRACT

Gallium (Ga) and aluminum (Al) belong to group IIIA elements in the periodic table. They show a coupled geochemical behavior in most natural systems and are considered as “geochemical partners.” However, compared with the principal oxyhydroxides of Al in nature, gibbsite [Al(OH)]3, boehmite (γ-AlOOH), and diasporite (α-AlOOH), only the analogs söhngeite [Ga(OH)]3 and tsumgalite (α-GaOOH) were reported. In this work, boehmite-type GaOOH (γ-GaOOH), a new polymorph of GaOOH, was synthesized for the first time using boehmite (γ-AlOOH) as a template. The synthesized γ-GaOOH was characterized by a series of techniques, including X-ray diffraction (XRD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and selected area electron diffraction (SAED). Furthermore, a model based on the boehmite structure was successfully applied to define the γ-GaOOH structure by the Rietveld method. Results from sample characterization and structural refinement support the successful synthesis of boehmite-type GaOOH, and thus it is referred to as γ-GaOOH. The synthesis of γ-GaOOH in the laboratory is valuable to understanding the Ga geochemistry and its enrichment process in Ga-rich boehmite in coal and bauxite.

Keywords: Gallium, boehmite analog, γ-GaOOH, template synthesis, Ga geochemistry

INTRODUCTION

Gallium (Ga) is an important strategic resource and has been widely used in the manufacturing of semiconductor devices (Ji et al. 2021), such as integrated circuits (Zhan et al. 2020), optoelectronics (Sutter et al. 2020), photovoltaic solar cells (Ramanujam and Singh 2017), and many modern high-tech fields, including 5G communication (Lv et al. 2019) and the internet of things (Braniste et al. 2020), etc. The global Ga demand is projected to increase twelvefold by 2050 (Eheliyagoda et al. 2019). Thus, the prospecting and exploitation of Ga resources in nature have become ever important for meeting the increasing demand for Ga (Gladyshev et al. 2015). However, Ga usually occurs as a trace element in a range of minerals (e.g., bauxite and Zn ores), and therefore, no mines endowed with Ga as main commodities have been discovered so far (Shao et al. 2018; Ji et al. 2020; Zhan et al. 2020). As a consequence, the bulk of global Ga derived from bauxite (e.g., karst-type bauxites) and Zn ores (e.g., Mississippi Valley Type) is exploited as a by-product from Al and Zn production (Lu et al. 2017; Xu et al. 2019; U.S. Geological Survey 2021). According to Seredin et al. (2013), the average Ga contents in bauxite are ~50 μg·g⁻¹, with a total amount estimated over 1 billion kg (Lu et al. 2017), which contribute almost 90% of the annual global Ga supply (Maarefyan et al. 2020). The identified worldwide Zn ores account for about 0.1 billion kg of Ga (Corathers and Manganese 2017), which correspond to nearly 10% of the global production of Ga (Frenzel et al. 2016). As the by-product of Zn and Al production, Ga production is inevitably affected by the exploitation of the main commodity (Frenzel et al. 2016). Nevertheless, in the past two decades, the enrichment of Ga was also discovered in coal, with some of them far higher than the industrial grade (30 μg·g⁻¹) (Dai et al. 2006a, 2006b, 2008, 2012; Zhou et al. 2010; Zhao et al. 2009; Wang et al. 2011; Mastalerz and Drobnik 2012; Sun et al. 2013; Qin et al. 2015; Qiao et al. 2016; Saikia et al. 2015; Shao et al. 2018). According to a rough estimate, coal deposits account for ~10 billion kg of Ga (Zhao et al. 2020), which represents almost 10 times the amount of Ga estimated in bauxite and Zn ores. However, so far, reports about Ga exploitation from coal are rare, and the yield is not high (Bielowicz 2020).

In natural systems, Ga is found primarily in a trivalent oxidation state (Schulz et al. 2017). Ga³⁺ can exist in the form of Ga(OH)₃ due to its metastability, which would spontaneously transform into α-GaOOH (Wang et al. 2011). Ga and Al have similar geochemical behavior resulting from similarities in oxidation state, amphotericity, coordination, and ionic radius (Rytuba et al. 2003). Therefore, during weathering of aluminosilicate-rich rocks (e.g., tephra and granite), they both behave as immobile ele-

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