



Transformation of birnessite into hollandite under the influence of silver cations in aqueous medium



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ABSTRACT

Silver hollandite or argentine cryptomelane constituted by edge-sharing double $[\text{MnO}_6]$ octahedral chains forming (2×2) tunnel structure has attracted an increased interest in the field of mining, electric and catalytic material. In this study, we report the formation of silver hollandite by transformation from birnessite under hydrothermal conditions. We compare the effects of the type of birnessite precursor, the temperature, the concentration of Ag^+ cation, the filling volume and the reaction time on the product phases, morphology and compositions of silver hollandite. Silver hollandite phase forms when 1 g birnessite reacts with 20 ml 0.08–0.1 M AgNO_3 solutions for more than 0.5 h at above 300 °C. Otherwise in the lower temperature, silver concentration or filling volume conditions, bixbyite, hausmannite or manganite would coexist as major by-products. Ag-hollandite nanofibers are observed by TEM with diameters of 15–30 nm and lengths of 40–800 nm in Ag-K-OMS-400 °C sample and 40–100 nm width and 100–800 nm lengths in Ag-Na-OMS-400 °C sample. They show the characters of Type IV N_2 adsorption isotherms that indicate the presence of the mesoporous structure nature. The average pore size and BET surface of Ag-hollandites are 8.3 nm, 57.4 m^2/g in Ag-K-OMS-400 °C and 16.5 nm, 63.7 m^2/g in Ag-Na-OMS-400 °C respectively. The silver species in Ag-hollandites are assumed to be a combination of both Ag^+ and Ag^0 by XPS examination. Silver cations can be exchanged into the layers of birnessite, and in the high temperature and pressure hydrothermal conditions silver cations can prevent the phase from decomposing, but help the birnessite pillars to form the vertical set of octahedral sheets of hollandite structure, which yields the 2×2 tunnel structure.

1. Introduction

Hollandite type minerals (OMS-2), as one class of the most common and active occurring Mn oxide in soils and sediments, have garnered much interest due to their unique structure and reactive properties [1,2]. These manganese oxides are constituted by edge-sharing double $[\text{MnO}_6]$ octahedral chains forming (2×2) tunnel structure [3,4]. The tunnels are filled with metal ions such as Ba^{2+} (defined as hollandite), Pb^{2+} (coronadite), Na^+ (manjiroite) and K^+ (cryptomelane) [5–8]. By incorporation of these cations within the center of the tunnel coordinated with oxygen anions, hollandite type minerals can be accommodated by mix-valence manganese in the framework. They are further noted for large specific surface area [9], high redox potential [10], as well as low point of zero charge [11]. Their physical and chemical characteristics provide these minerals with high reactivity with respect to sorption and redox reactions, explaining their critical application in oxidation catalysts [12], adsorbents [13], rechargeable battery materials [14] and radioactive waste immobiliza-

tions [15]. Thereby, many studies are focused on ways to obtain hollandite minerals and improve the activities.

The widely used synthetic methods of manganese oxide materials include hydrothermal refluxing, sol-gel process, co-precipitation and solid state reaction. Because morphology of molecules and materials has significant impact on properties and functions, recently this accounts focuses on the synthesis technology for morphology control and surface modification. The structure-guided combustion waves (SGCWs), which is induced by incomplete combustion through the chemical fuel-wrapped materials, is proposed for synthesizing multiple-core-shell nanoparticles of MnO_2 with carbon coating and their good application in supercapacitor electrodes [16,17]. The fabrication of 3D novel MnO_2 structure has also been reported in recent years. Tan et al. [18,19] reported 3D MnO_2 porous hollow microspheres with high adsorption and catalytic ozonation performance were synthesized by a self-template process. Rong et al. [20] demonstrated that a simple organic and template-free approach to fabricate 3D MnO_2 network structure by freeze-drying aqueous solutions of the MnO_2 nanosheets

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and nanowires. Furthermore, Oaki [21,22] developed a novel approach, namely crystal-controlled polymerization including morphology control of organic and inorganic polymers by using the interspace, surface and structure of crystals, which is reverse with the traditional polymer-controlled crystallization. These strategies can be applied to MnO_2 materials with enhanced performance and unprecedented properties in the future.

Moreover, numerous studies have proven that the incorporation of transition metals (Fe, Co, Ni, Cu, Zn) [12,23,24] or noble metals (Ag, Au, Pt, Pd, Ru) [25–28] into the tunnel or in the structural of hollandite can promote the generation of defects and enhance lattice oxygen mobility to improve their application performance, so the synthesis of different metal doped or modified hollandite have attracted an increased interest. Among them silver-doped MnO_2 such as hollandite ($\text{Ag}_x\text{Mn}_8\text{O}_{16}$, where $1 \leq x \leq 1.8$) is considered a promising alternative to electric and catalytic material. It attributes to the high activities for CO, NO and ethanol catalytic oxidation, SO_2 absorbent and high rechargeable capacity [29–35].

The chemical methods to synthesize silver hollandite are divided into three groups. The first method is based on the silver ion-exchange treatment to potassium cryptomelane in AgNO_3 solution or melt [29,34]. Cryptomelane is very effective for selective adsorption of Ag^+ , and elevated temperatures in excess silver nitrate are required to achieve the structural conversion of cryptomelane to silver hollandite. The second way to obtain silver hollandite relies on the oxidation of Mn^{2+} by AgMnO_4 in aqueous acidic medium at temperature of 100–200 °C [33]. AgMnO_4 is firstly synthesized by the reaction of KMnO_4 with AgNO_3 in aqueous solution. The temperature and the $\text{AgMnO}_4/\text{Mn}^{2+}$ molar ratio affect the crystalline structure, silver content and the morphology of the Ag-hollandite. Silver hollandite with equivalent silver content ($\text{Ag}_{1.4}\text{Mn}_8\text{O}_{16}$) can be prepared by a low-temperature co-precipitation method with aqueous solutions of AgMnO_4 , MnSO_4 and HNO_3 [36]. The third process is based on high temperature solid reaction of AgMnO_4 and Ag_2O in the molar ratio 1:1 at 970 °C under 5 kbar oxygen over 7 days. Needlelike crystals with dimensions $0.1 \times 0.4 \times 1.0 \text{ mm}^3$ are obtained [37,38].

In recent decades, silver nanoparticle and MnO_2 polymeric nanocomposites have also attracted great interest owing to their well-defined structures as a unique and special functional material. Mesoporous- MnO_2 or MnO_2 nanowires/ hybrid polymers are used as support to incorporate silver nanoparticles to prepare materials with high dielectric permittivity or anti-microbial and anti-cancer activity [39,40]. $\text{Ag}_x\text{Mn}_8\text{O}_{16-y}\cdot z\text{Ag}_2\text{O}$ composites with variable silver ion content are prepared by a co-precipitation method allows for coating silver oxide on silver hollandite nanorods [41]. Hollow Ag/ MnO_2 structures with different shell architectures— a monolayered shell composed of evenly mixed silver and MnO_2 and a double-layered shell composed of an inner MnO_2 layer and an outer silver layer— are designed and obtained [42].

When we transfer our attention from synthetic silver hollandite, cryptomelane is also found as the most naturally abundant and important silver-bearing mineral in natural world especially in Mn-Ag deposit. Argentian cryptomelane is reported to contain a few ppm to 3.15 wt% Ag in the Silver Cliff mining district of Colorado and Xiangguang deposit, which is generated in hydrothermal solution [43,44]. These silver-bearing cryptomelane are closely associated with ranciéite, chalcophanite which are birnessite-type manganese oxides consisting of layers of edge-sharing MnO_6 octahedra separated by planes of hydrated cations such as Na^+ , K^+ , Zn^{2+} , Ca^{2+} and water molecules. However, the phase relationship between silver-bearing cryptomelane and layer-structured birnessite is still not clear.

Hollandite type minerals can be produced from layer-structured birnessite by thermal and hydrothermal methods. K-, Ba-, Sr-exchanged birnessite precursors can transform to cryptomelane or hollandite-type structures at calcination temperature between 400 °C and 600 °C [45,46]. First synthesized cryptomelane via K-birnessite are

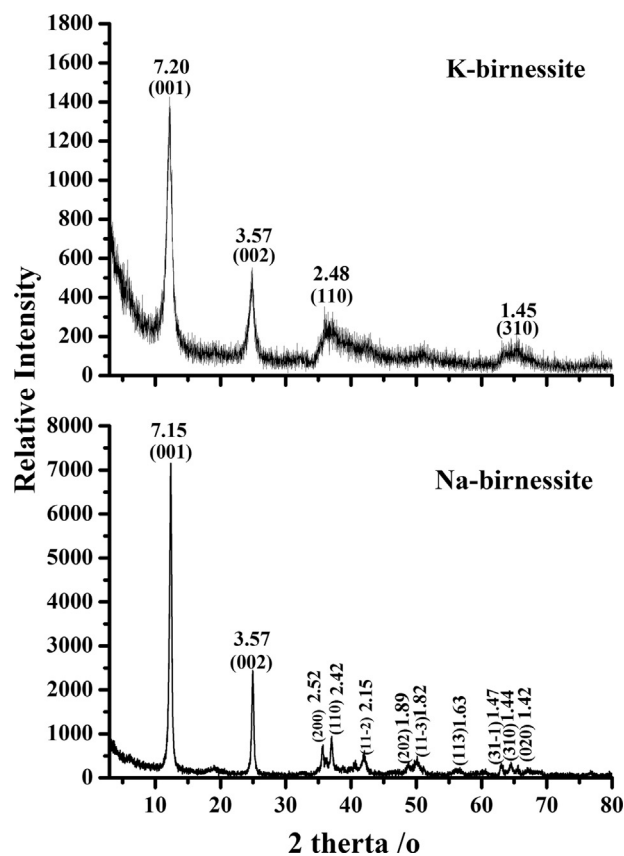


Fig. 1. The X-ray diffraction patterns (d value: Å) of birnessite precursors. –samples named K-Bir and Na-Bir.

reported by Giovanili using hydrothermal treatments to transform the layered structure to the tunnel structure at 120–250 °C for 2 days [47]. Other alkali metals such as Li^+ , Na^+ , Rb^+ and NH_4^+ are also used as cation templates for this transformation under hydrothermal conditions at 120–200 °C for a few hours to a few days [48]. The product is some dependent on the ion size and the basicity of the hydrothermal solution [3]. The formation of cryptomelane from birnessite in contact with aqueous solution is favored by the removal of ions from the layered phase [49]. The large size of ion templates may have helped prevent the birnessite layers from collapsing during the heating process, but excessive ions will make the structure unstable due to repulsive forces between the cations if the entire tunnel sites are filled [6,45,50,51]. Structural transformations appear to occur more readily in neutral to acidic solutions, however with some exceptions [3].

In this study, we report the synthesis of silver hollandite by transformation from birnessite under hydrothermal conditions. The effects of the type of birnessite precursor, the temperature, the concentration of Ag^+ cation, the reaction time and the filling volume on the product phases and morphology of silver hollandite are investigated. The formation mechanism of transformation from birnessite to hollandite under the influence of silver cations in aqueous medium is proposed through X-ray powder diffraction, transmission microscopy, scanning microscopy, N_2 adsorption and X-ray photoelectron spectroscopy measurements. The aim of this study is to explore the phase transition relationship between birnessite and hollandite with the participation of silver ions in the simulated hydrothermal conditions and also provide a new approach to synthesize the silver-hollandite for further material application research.

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