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Structural and magnetic properties of hydrothermally synthesized β -MnO₂ and α -K_xMnO₂ nanorods



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1. Introduction

Manganese dioxides have a relatively long history in applications for batteries [1], but they are still attracting considerable attention due to their wide applications in different fields, such as catalysis, lithium-ion batteries and Mg batteries, electrochemical supercapacitors, ionic or molecular sieves [2-9]. Such a great interest in manganese dioxides is due to their low price and low toxicity, particularly when compared to other metal oxides, such as nickel oxides and cobalt oxides. As a general class of materials, manganese dioxides exhibit a very rich chemistry and can be synthesized in many crystalline and disordered forms; moreover, they are very often non-stoichiometric, due to the presence of additional metal cations, physisorbed and structural water and/or structural vacancies. It is well-known that manganese dioxide forms a variety of polymorphs with chain-like tunnel, layered, and three-dimensional structures, since its basic structural units (MnO₆ octahedra) can be linked in different manners. The crystals of tunnelled polymorphs consist of single, double or triple edgeshared MnO₆ octahedral chains, which are corner-connected to form tunnels. Among these polymorphs, chain-like tunnel

ABSTRACT

Hydrothermal synthesis was applied for obtaining different manganese dioxide polymorphs whose morphology, structure and magnetic properties were thoroughly investigated. Variations in the synthesis pathways lead to the formation of tetragonal rutile-type β -MnO₂ and two tetragonal hollandite-type α -K_xMnO₂ samples with different concentration of potassium cations (x = 0.15 and 0.18). SEM images showed nanorod shape of all specimens, while microstructure characterization done by XRD measurements revealed that crystallites have an elongated rod-like shape and, hence, it confirmed the anisotropic morphology. Magnetic ordering of β -MnO₂ is antiferromagnetic below 93 K, while both α -K_xMnO₂ samples possess more complicated low-temperature behaviour of the reentrant spin-glass type: the onset of the spin-glass like state occurs at temperatures below the weak ferromagnetic ordering.

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structures with regular lattice such as pyrolusite or β -MnO₂, ramsdellite or *R*-MnO₂, hollandite or α -MnO₂, romanechite and todorokite can be distinguished.

Among a variety of MnO₂ polymorphs the pyrolusite β -MnO₂, which has tetragonal rutile-type symmetry, is the most stable one. β -MnO₂ is composed of single chains of edge-sharing MnO₆ octahedral units which form a tunnel with a diameter of 2.3 Å [10] that is the narrowest among the tunnel-type manganese dioxide family (Fig. 1a). The structure of a hollandite-type α -MnO₂ consists of MnO₆ structural units that share edges to form straight double zigzag chains, which are corner-connected to form tunnels with a diameter of 4.6 Å [10] (Fig. 1b). These tunnels are stabilized by large cations, such as K⁺, Na⁺, Ba²⁺, Pb²⁺, Li⁺, NH⁴⁺ or a water molecule. The presence of tunnel cations as impurities leads to mixed-valence Mn^{4+}/Mn^{3+} compounds with composition A_xMnO_2 (A denotes the tunnel cations). It is difficult to determine exact composition of such compounds, especially concerning the water content. This uncertainty in the composition introduces a difficulty in studying the electronic and magnetic properties of these compounds, as they depend on the type and concentration of a dopant.

Very complex electronic and magnetic properties of manganese oxides are interesting from a fundamental point of view to understand their unique properties. They display a number of different magnetic ordered phases, from antiferromagnetic to helical order. It has been known that β -MnO₂ have a screw type incommensurate



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Fig. 1. Polyhedral representations of the crystal structures of (a) pyrolusite and (b) hollandite.

magnetic ordering along the *c* axis with the moments lying in the basal plane below the Néel temperature of about 92 K [11]. The origin of the helical ordering is the competition between the firstand second-neighbour interactions with opposite sign. α -MnO₂ materials show various magnetic ordered phases whose nature are still poorly understood. Different magnetic ordered phases are probably the result of both magnetic frustration due to the triangular ladder that connects the manganese cations in the double zigzag chains and the presence of large cations in the tunnels. The most studied case is that with potassium cations (so-called cryptomelane). Yamamoto et al. reported antiferromagnetic ordering below 24.5 K for hydrothermally synthesized α -K_xMnO₂ (x < 0.070) [12] and Strobel et al. also reported AFM ordering bellow 18 K for single crystals $K_{0.166}MnO_2$ grown by an electrolytic technique [13]. The exact origin of this AFM phase is still unknown. In works of Suib et al. the spin-glass behaviour has been observed in synthetic cryptomelane K₀₁₂₅MnO₂ having a typical freezing temperature that is frequency dependent near 12-13 K [14]. Sato et al. in Refs. [15,16] reported that the hollandite-type $K_{0.187}(H_3O)_{\nu}MnO_2$ exhibits a ferromagnetic transition at 52 K and this weak ferromagnetism persist down to 20 K. When the temperature is further lowered, the ferromagnetism disappears and the anisotropic measurements of the susceptibility suggest the occurrence of a helical magnetism below 20 K. In the works of Luo et al. [17.18], it has been experimentally shown that a lower concentration of K^+ cations (bellow half occupancy, x < 0.125) induces spin-glass behaviour of α -K_xMnO₂ samples. Above the half occupancy (x > 0.125) of the K⁺ site, the spin-glass behaviour vanishes due to the appearance of the antiferromagnetism. Recently, Tseng et al. investigated hydrothermally synthesized α -K_xMnO₂ with different doping concentration [19]. They found that for doping concentration lower than 12 at% α -K_xMnO₂ samples showed ferromagneticlike ordering at low temperature (<50 K), while antiferromagnetic coupling dominated for doping concentration above 12 at%.

The above listed results show that rich varieties in magnetic properties of α -MnO₂ materials come from differences in composition and structure which are provoked by distinct synthesis pathways. Investigations on the impact of the synthesis parameters on the properties of manganese dioxide materials is of crucial importance in tailoring certain application required features. In this paper, we present a study performed on two hollandite-type α -K_xMnO₂ samples and one rutile-type β -MnO₂ sample, each of them obtained by a different hydrothermal synthesis route, but all three grown in the shape of nanorods. Detailed investigations of their morphology, structure and magnetism reveal the distinction in their properties determined by an applied synthesis route.

2. Experimental

2.1. Sample preparation

All starting reagents were of analytical grade (Sigma–Aldrich, purity of \geq 98–99%) and all were used directly without further purification. The hydrothermal syntheses were done in a 32 ml Teflon-lined stainless steel autoclave.

Sample β -MnO₂ was synthesized hydrothermally by a redox reaction between manganese(II) sulphate with ammonium persulphate as the oxidizing reagent. With respect to the literature data, by this redox reaction different polymorphs were obtained: α -MnO₂ nanowires [20], epsilon, gamma and ramsdellite polymorphs of MnO₂ [21], β -MnO₂ nanorods [22]. In our preparation route, 0.9656 g of MnSO₄·H₂O was dissolved in 25 ml of distilled water while stirring at room temperature for 15 min. Ammonium persulphate (NH₄)₂S₂O₈ (1.304 g) was added and the solution was stirred to form a clear solution. The solution was then placed in a sealed autoclave and heated at 135 °C for 12 h.

Sample α -K_xMnO₂(A) was prepared by direct hydrothermal decomposition of potassium permanganate under acidic conditions involving no templates or surfactants [23]. In a typical synthesis, potassium permanganate (KMnO₄, 0.2808 g) and 0.88 ml concentrated sulphuric acid (H₂SO₄) were added to 20.44 ml distilled water while stirring to form a solution that was then transferred into an autoclave and heated at 150 °C for 8 h.

Sample α -K_xMnO₂(B) has been prepared by a liquid-phase comproportionation method which involves no catalysts or templates and where potassium permanganate was used as the oxidizing reagent for manganese(II) sulphate [24]. Potassium permanganate (KMnO₄, 0.2589 g) was dissolved in 23 ml of distilled water and 0.1117 g of manganese(II) sulphate monohydrate (MnSO₄·H₂O) was added while stirring. The solution was transferred into an autoclave, followed by a thermal treatment at 180 °C for 16 h.

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