



# Synthesis, crystal structure and electrical properties of A-site cation ordered BaErMn<sub>2</sub>O<sub>5</sub> and BaErMn<sub>2</sub>O<sub>6</sub>

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## ABSTRACT

In this paper, we report on a synthesis procedure, structural and electrical properties of BaErMn<sub>2</sub>O<sub>5</sub> and BaErMn<sub>2</sub>O<sub>6</sub>, A-site double perovskites having layered arrangement of Ba and Er cations. These materials belong to a family of BaLnMn<sub>2</sub>O<sub>5+δ</sub> oxides, which up to now were successfully synthesized for Ln=Y and La–Ho lanthanides. Up to our knowledge, this is the first report on the successful synthesis of BaErMn<sub>2</sub>O<sub>5</sub> and BaErMn<sub>2</sub>O<sub>6</sub>, yielding > 95 wt% of the considered compounds. Structural characterization of the materials is given at room temperature, together with *in situ* XRD studies, performed during oxidation of BaErMn<sub>2</sub>O<sub>5</sub> in air, at elevated temperatures up to 500 °C. A complex structural behavior was observed, with oxidation process of BaErMn<sub>2</sub>O<sub>5</sub> occurring at around 300 °C. The oxidized BaErMn<sub>2</sub>O<sub>6</sub> shows a structural phase transition at about 225 °C. Results of structural studies are supported by thermogravimetric measurements of the oxidation process, performed in air, as well as reduction process, performed in 5 vol% of H<sub>2</sub> in Ar. Additionally, isothermal oxidation/reduction cycles were measured at 500 °C, showing interesting properties of BaErMn<sub>2</sub>O<sub>5+δ</sub>, from a point of view of oxygen storage technology. Electrical conductivity of BaErMn<sub>2</sub>O<sub>5</sub> is of the order of 10<sup>−4</sup> S cm<sup>−1</sup> at room temperature and shows activated character on temperature with activation energy  $E_a=0.30(1)$  eV. Positive sign of Seebeck coefficient for this material indicates holes as dominant charge carriers. Oxidized BaErMn<sub>2</sub>O<sub>6</sub> possesses much higher electrical conductivity, almost 0.2 S cm<sup>−1</sup> at room temperature. Additional, about 10-fold increase of electrical conductivity, occurring in the vicinity of 225 °C for this material, can be associated with phase transition from charge/orbital-ordered insulator COI(CE) to paramagnetic metal PM phase. The highest conductivity for BaErMn<sub>2</sub>O<sub>6</sub> was measured near 500 °C and is almost equal to 40 S cm<sup>−1</sup>, while negative sign of Seebeck coefficient can be associated with electrons being dominant charge carriers.

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## 1. Introduction

BaLnMn<sub>2</sub>O<sub>5+δ</sub> oxides (Ln=Y and La–Ho lanthanides) belong to a group of cation-ordered perovskites. Ordering in these materials occurs in A-site and originates from a large difference between ionic radii of Ba<sup>2+</sup> and Ln<sup>3+</sup> cations. These materials exhibit interesting physical properties, including colossal magnetoresistance, structural transitions, as well as metal–insulator transitions accompanied by charge/orbital order [1–5]. Moreover, the electronic phase diagram for cation-ordered compounds was found to be different, comparing to the one for respective, unordered analogues [1,3–5]. Recently, BaYMn<sub>2</sub>O<sub>5</sub>–BaYMn<sub>2</sub>O<sub>6</sub> system was found to possess very good oxygen storage-related properties [6,7]. According to [1], up to now it was possible to synthesize pure BaLnMn<sub>2</sub>O<sub>5+δ</sub> with Ln

cations as small as Dy<sup>3+</sup>, Ho<sup>3+</sup> and with Y<sup>3+</sup>, while synthesis for Er<sup>3+</sup> and Tm<sup>3+</sup> yielded materials with significant amount of impurities.

Aristotype space group for A-site ordered perovskites with layered arrangements of cations is tetragonal *P4/mmm* [8], which can be visualized as a stacking of two primitive, perovskite unit cells along *c*-axis, giving such layered-type structure. Alternating layers of BaO<sub>12</sub> and LnO<sub>12</sub> cubo-octahedra are present in the structure of fully oxidized BaLnMn<sub>2</sub>O<sub>6</sub>. In the mentioned space group all Mn sites are equivalent. Also, all manganese cations are located in the octahedral coordination (MnO<sub>6</sub>) in the oxidized BaLnMn<sub>2</sub>O<sub>6</sub>, while in the reduced BaLnMn<sub>2</sub>O<sub>5</sub>, oxygen sites in Ln-related layer are completely empty, giving square pyramidal coordination of manganese cations (MnO<sub>5</sub>). Typically, the considered materials are synthesized in the reduced form, i.e. BaLnMn<sub>2</sub>O<sub>5</sub>, while the oxidized, BaLnMn<sub>2</sub>O<sub>6</sub> compounds can be easily obtained at relatively low temperatures by oxidation process, performed in air (or oxygen) [4]. It seems that the direct

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synthesis of oxidized  $\text{BaLnMn}_2\text{O}_6$  is either very difficult or even impossible for many Ln cations. While an explanation of this effect needs further studies, we believe that it is related to a strong tendency of formation of  $\text{BaMnO}_3$  and  $\text{LnMnO}_3$ , while the synthesis is performed in the oxidizing atmospheres, as confirmed by XRD analysis of materials obtained in such experiments. Another reason is that smaller  $\text{Ln}^{3+}$  cations (especially  $\text{Er}^{3+}$ ) seems to be too small for 12-fold coordination in  $\text{BaLnMn}_2\text{O}_6$ , which can be stated that they occupy volume smaller than available in such void. Calculated ratio of ionic radii of small  $\text{Ln}^{3+}$  and  $\text{O}^{2-}$  rather points to cubic coordination (not cubo-octahedral). In the reduced  $\text{BaLnMn}_2\text{O}_5$  coordination of Ln cations is eight fold.

Interestingly, partially reduced  $\text{BaLnMn}_2\text{O}_{5.5}$  can be obtained, as shown for  $\text{BaYm}_2\text{O}_{5.5}$ , in which every other oxygen position is occupied in the mentioned Ln-related layer [9]. It is not known, if  $\text{BaLnMn}_2\text{O}_{5.5}$  compounds can be obtained for all considered lanthanides.

As mentioned above, such ordered manganites exhibit interesting electrical and magnetic properties. Phase diagram for oxidized  $\text{BaLnMn}_2\text{O}_6$  is known for  $\text{Ln}=\text{Y}$  and La–Ho lanthanides, and the compounds can be classified into three groups showing different behavior, depending on the ionic radius of  $\text{Ln}^{3+}$  [1]. Materials with small cations ( $\text{Ho}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$ ) exhibit three separated phase transitions: structural, charge order-related and antiferromagnetic one. For compounds with larger cations ( $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ), no structural transition occurs, while in the third group ( $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$  and  $\text{La}^{3+}$ ) ferromagnetic transition occurs in the vicinity of 300 K [1]. In the first mentioned group, temperature of structural transition, as well as temperature of charge-order transition were found to increase considerably with decreasing size of  $\text{Ln}^{3+}$ ; however until now, the phase diagram was shown down to  $\text{Ho}^{3+}$  only. Successful synthesis of  $\text{BaErMn}_2\text{O}_6$  and  $\text{BaErMn}_2\text{O}_5$  presented in this work allow to expand knowledge about the system for materials containing significantly smaller  $\text{Er}^{3+}$  cations.

As reported by Motohashi et al.,  $\text{BaYm}_2\text{O}_{5+\delta}$  exhibits excellent oxygen storage properties, with the measured reversible oxygen storage capacity almost equal theoretical one (3.85 wt% change between  $\text{BaYm}_2\text{O}_5$  and  $\text{BaYm}_2\text{O}_6$ ), low temperatures of reduction and oxidation processes and fast kinetics of changes of  $\delta$  at 500 °C [6]. Currently, there are no information available about oxygen storage-related properties for whole series of  $\text{BaLnMn}_2\text{O}_{5+\delta}$ . While the expected reversible capacity will be definitely smaller, due to substitution of lighter  $\text{Y}^{3+}$  by heavier  $\text{Ln}^{3+}$  elements, the effect of such substitution on the kinetics of oxidation and reduction processes is yet to be studied.

In this work, we report on structural properties, including high-temperature *in situ* XRD measurements, electrical conductivity and Seebeck coefficient, as well as oxygen storage-related properties of  $\text{BaErMn}_2\text{O}_{5+\delta}$ . Studied  $\text{BaErMn}_2\text{O}_{5+\delta}$  exhibits similar behavior to  $\text{BaYm}_2\text{O}_{5+\delta}$  during reduction and oxidation; however, due to its higher molar mass, the recorded reversible oxygen storage capacity is smaller.

## 2. Experimental

$\text{BaErMn}_2\text{O}_5$  was synthesized by a *soft chemistry* method followed by a series of consecutive oxidations and reductions performed at 500 °C. In order to obtain a precursor, respective nitrates were dissolved in a minimal amount of deionized water, in stoichiometric proportions. Ammonia salt of ethylenediaminetetraacetic acid (EDTA) was added as a complexing agent. Prepared solution was heated in quartz container in air up to about 400 °C, which resulted in evaporation of water, followed by decomposition of ammonium nitrite and oxidation of residual carbon. This method allows to one obtain homogeneous mixing of cations,

which are effectively trapped by strong complexing agent, making high-quality precursor for the main synthesis. The obtained precursor was thoroughly grinded and pressed into pellets. The actual synthesis was performed at 1200 °C for 8 h in 5 N Ar atmosphere, with flow of gas about  $100 \text{ cm}^3 \text{ min}^{-1}$ . Attempts to synthesize the considered material at different temperatures and/or at different oxygen partial pressures were unsuccessful.

Structural studies of the materials were carried out in 10–110 deg range with  $\text{CuK}\alpha$  radiation, using Panalytical Empyrean diffractometer, equipped also with Anton Paar HTK 1200N oven-chamber for high-temperature measurements. Temperature-dependent sample's height correction was automatically applied during high-temperature studies. Rietveld analysis of XRD data were done using GSAS/EXPGUI set of software [10,11]. Crystallite size of the powders was determined from Scherrer's equation. Initial, room temperature (RT) structural studies indicated formation of A-site double perovskite having layered arrangement of Ba and Er cations; however, reflections belonging to  $\text{Ba}_3\text{Er}_4\text{O}_9$  phase, as well as several small unidentified peaks were also observed. The pristine material was afterwards oxidized and reduced five times, respectively in air and in 5 vol%  $\text{H}_2$  in Ar mixture, by heating with  $5 \text{ deg min}^{-1}$  rate up to 500 °C, and fast cooling to room temperature. After such cycling, a substantial decrease of intensity of the unidentified reflections was observed, while peaks related to  $\text{Ba}_3\text{Er}_4\text{O}_9$  phase remained almost unchanged. XRD data shown in Fig. 1 were collected after cycling experiments. High temperature structural measurements were performed in air up to 500 °C, with data collected every 25 °C on heating and cooling for about 1 h.

Oxidation and reduction experiments, related to oxygen storage properties of  $\text{BaErMn}_2\text{O}_{5+\delta}$ , were evaluated by thermogravimetric (TG) method on TA Q5000IR apparatus. Measurements were done on powdered samples, obtained after grinding of sinters and sieving on 100  $\mu\text{m}$  sieve. For reduction, 5 vol%  $\text{H}_2$  in Ar mixture was used, while oxidation process was studied in air flow. Gas flow of  $100 \text{ cm}^3 \text{ min}^{-1}$  and heating rate of  $5 \text{ deg min}^{-1}$  were selected as experimental conditions. Isothermal oxidation and reduction experiments were done at 500 °C. These measurements were followed by non-isothermal studies of oxidation and reduction, which were performed from RT up to 500 °C, similarly, in air and in 5 vol%  $\text{H}_2$  in Ar atmosphere. Buoyancy effect was established on the basis of runs performed without material, and appropriate correction was applied for calculation of reversible oxygen storage capacity. Theoretical oxygen storage capacity of  $\text{BaErMn}_2\text{O}_{5+\delta}$  was calculated assuming complete change of  $\delta$  between 0 and 1 for reduced and oxidized material.

Microstructural images of  $\text{BaErMn}_2\text{O}_5$  and  $\text{BaErMn}_2\text{O}_6$  powders were recorded on FEI Nova NanoSEM 200 microscope equipped with low vacuum detector.

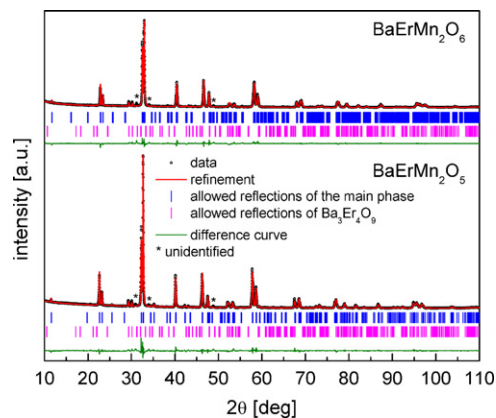


Fig. 1. X-ray diffractograms with Rietveld analysis for  $\text{BaErMn}_2\text{O}_5$  and  $\text{BaErMn}_2\text{O}_6$ .

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