



# Subsolidus phase equilibria in the $\text{La}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--Sb}_2\text{O}_5$ system and characterization of layered ternary oxide $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$

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## ABSTRACT

Phase equilibria in the  $\text{La}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--Sb}_2\text{O}_5$  system have been studied. The isothermal section was constructed at  $T=900^\circ\text{C}$ . The existence of the ternary oxide  $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$  was confirmed. The structure of this compound was solved using Rietveld refinement of synchrotron radiation-based powder XRD data.  $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$  crystallizes in a trigonal layered structure relating to  $\text{PbSb}_2\text{O}_6$  type (space group  $P\bar{3}1m$ ,  $a=b=5.2446(3)\text{Å}$ ,  $c=5.1930(3)\text{Å}$ ,  $Z=1$ ). The fine powder of  $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$  was prepared by molten salt synthesis. The compound was characterized by diffuse reflection and Mossbauer spectroscopy, magnetic measurements, scanning electron microscopy and photocatalytic tests. The magnetic behavior of  $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$  in the applied magnetic field  $H=5000\text{Oe}$  is entirely paramagnetic. By contrast, in the small magnetic field  $H=100\text{Oe}$  the magnetic data of  $\text{LaFe}_{0.5}\text{Sb}_{1.5}\text{O}_6$  indicates an unusual critical behavior near phase transition at  $T < 2\text{K}$ .

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## 1. Introduction

The chemistry of layered transition metal oxides is one of the most extensively studied subjects of material science. Layered oxides exhibit a number of functional properties including superconductivity [1], colossal magnetoresistance [2], photocatalytic activity [3] and also conduction band properties which have promising application as n-type transparent conductors [4]. On a fundamental level the layered oxides with magnetic ions have received great interest due to their ability to adopt unusual magnetic ground states which remain poorly understood [5]. Indeed, the lattice of trigonal structure type layered oxides consists of interleaved layers of edge-sharing octahedra containing magnetic and nonmagnetic cations respectively. Thus the magnetic structure of these compounds is based on isolated triangular plaquettes with magnetic ions in the vertexes of triangles. In the case of antiferromagnetic short-range exchange interactions between neighbor ions the 2-D magnetic sublattice composed of these triangles is geometrically frustrated. Depending on spin configurations this frustrated system can undergo phase transition to long range ordered state or may result in the emergence of non-Neel ground states like spin glass or spin ice [5–7].

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Layered antimonates with the general formula  $\text{MSb}_2\text{O}_6$ , form a variety of crystal structures based on a double-layered hexagonal close packed array of oxygen anions with cations occupying octahedral voids: ( $\text{MnSb}_2\text{O}_6$  (space group  $P321$ ) [8],  $\text{MSb}_2\text{O}_6$  ( $M=\text{Pb}$  [9],  $\text{Cd}$  [10],  $\text{Ca}$ ,  $\text{Sr}$  and  $\text{Ba}$  [11] space group  $P\bar{3}1m$ ) and  $\text{NaSbO}_3$  (or  $\text{Na}_2\text{Sb}_2\text{O}_6$ , space group  $R\bar{3}$ ) [12]. The only two magnetic phases of this antimonate family,  $\text{MnSb}_2\text{O}_6$ , (space group  $P321$ ) [8,13,14] and  $\text{MnSb}_2\text{O}_6$  (space group  $P\bar{3}1m$ ) [15], have been investigated and recently reported. The layered crystal structure (of both  $\text{MnSb}_2\text{O}_6$  trigonal structure types) consists of manganese triangles with intra-connecting  $\text{SbO}_6$  octahedra. The difference between two phases lies in the  $\text{Sb}$  positions, which move by  $c/2$  from the  $\text{Mn}$  layer to the empty octahedral of the  $\text{Sb}$  layer and in much more regular  $\text{MnO}_6$  and  $\text{SbO}_6$  octahedra [15]. Magnetic properties for both phases appeared to be similar but not identical and showed evidence for short-range magnetic correlations below  $T=200\text{K}$  and long-range antiferromagnetic order below  $T_N=12.5\text{K}$  [13] and  $T_N=8.5\text{K}$  [15] respectively. An increase in the magnetization at  $T=41.5\text{K}$  associated with a weak ferromagnetic component was revealed in the  $\text{MnSb}_2\text{O}_6$  phase (space group  $P\bar{3}1m$ ) [15]. Functional density analysis of the magnetic structure confirmed that the main spin exchange interactions in  $\text{MnSb}_2\text{O}_6$  are antiferromagnetic thereby forming a spin-frustrated lattice of  $\text{Mn}^{2+}$  triangles [15].

Some  $\text{MSb}_2\text{O}_6$  layered antimonates have been identified as good photocatalysts under UV light irradiation. Indeed,  $\text{CaSb}_2\text{O}_6$

and NaSbO<sub>3</sub> have been reported to photochemically split water [16]. PbSb<sub>2</sub>O<sub>6</sub>, CdSb<sub>2</sub>O<sub>6</sub> and ZnSb<sub>2</sub>O<sub>6</sub> have been known to decompose methylene blue dye [17,18].

Earlier Blasse and Pauw [19] studied the possibility of a joint heterovalent substitution in PbSb<sub>2</sub>O<sub>6</sub> (space group *P*-31*m*). Among the other compounds the complex oxide LaFe<sub>0.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> has been found. It was shown that this compound is of PbSb<sub>2</sub>O<sub>6</sub> structure and the lattice parameters were calculated. However the detailed structure study has not been performed and magnetic properties have not been studied. Thereafter LaFe<sub>0.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> has not been referenced to in the literature, as well as the information about this compound in crystallographic databases being absent.

To confirm the LaFe<sub>0.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> existence we studied the phase relations in the La<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>5</sub> system. Here we report the results of this study and also structural, magnetic and photocatalytic data for this layered oxide.

## 2. Experimental section

### 2.1. Sample preparation

The sample compositions for phase equilibria study in the La<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>5</sub> were chosen according to the cross-sections method. As the initial components we used high-purity grade reagents La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Sb<sub>2</sub>O<sub>3</sub>. The samples were synthesized by solid-state reaction in platinum crucibles in a muffle furnace in air at 900–1200 °C. Taking into account the possibility of the metastable phase formation during melt crystallization, the sintering temperature of the initial mixtures was chosen from the subsolidus region. Duration of synthesis including intermediate grindings varied from 6 up to 16 days. The accomplishment of the reaction was evaluated using the X-ray diffraction method. Equilibrium is considered to be reached when the X-ray diffraction patterns of the samples do not show changes with subsequent heating.

Fine powders of the LaFe<sub>0.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> compound were prepared using molten salt synthesis. Two eutectic mixtures of salts, KCl–KBr and K<sub>2</sub>SO<sub>4</sub>–Na<sub>2</sub>SO<sub>4</sub>, were used as a solvent. The stoichiometric amounts of La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub> oxides were added to salts at a weight ratio of 1:1 and finely ground with an agate mortar and pestle. A mixture of the reactants and KCl–KBr was heated above the melting temperature of the salt at 700 °C for 7 days, while the reactant mixture with K<sub>2</sub>SO<sub>4</sub>–Na<sub>2</sub>SO<sub>4</sub> was kept at 900 °C for 3 h. Hereafter the reactant mass was cooled to room temperature and washed with distilled water to remove the salt. The complex oxide powder was obtained after drying at 50 °C over 24 h.

### 2.2. Research technique

X-ray powder diffraction patterns were recorded using a Bruker D8 Advance diffractometer (Bragg–Brentano geometry) with Ni-filtered CuKα radiation and a LYNXEYE detector. The diffraction data was collected in the 2θ range from 10° to 80° with a step of 0.02° and collection time of 0.3 s/step. Phase identification was carried out in reference to JCPDS Research Associateship. Structure parameters were refined by synchrotron radiation-based X-ray diffraction. The measurements were performed at the Structural Materials Science beamline of the Kurchatov Synchrotron Radiation Source (NRC “Kurchatov Institute”, Moscow) in the transmission mode using a 2D MarCCD detector at a wavelength λ = 1.19546 Å in the 2θ range from 6° to 63°. For the angular scale calibration, a polycrystalline silicon powder (NIST SRM 640c) sample was used. The Rietveld refinement was performed using the Jana2006 code [20].

The <sup>57</sup>Fe Mössbauer spectra were recorded on an

electrodynamic spectrometer Wissel (Germany). <sup>57</sup>Co (Rh) was used as a radiation source with activity of 1.1 GBq. Isomer shifts were taken from the center HFS lines of metallic iron. Mössbauer spectra fitting was carried out by the standard least square minimization programs (Loren, Win-Normos) assuming Lorentz line shape.

Magnetic properties were characterized using an automated physical characterization system, Quantum Design PPMS-9. Zero-field cooled (ZFC) and field cooled (FC) data were collected between 2 and 300 K using an applied field of 100 Oe and 5000 Oe. The temperature dependence of the AC-susceptibility at low temperatures within 500–10000 Hz frequency range was also measured.

The UV–Vis diffuse reflectance data was collected over the spectral range 300–800 nm with a PerkinElmer Lambda 650S (Waltham, MA) spectrometer on powder samples.

Photocatalytic experiments were carried out using the degradation reaction of crystal violet aqueous solution. A typical experiment of degradation was performed as follows: catalyst suspension (2 mL, 1 g/l) was mixed with aqueous solution of crystal violet (40 μL, 400 mg/l). Prior to irradiation, suspension of the catalyst and dye solution was stirred in darkness for 30 min, aiming at providing the equilibrium adsorption. Hereafter, the cuvettes were irradiated by a halogen 391 lamp for 15 h. The solutions were centrifuged and dye concentration was determined by measuring absorbance at the crystal violet band maximum (λ<sub>max</sub> = 591 nm). The concentration of the dye was monitored directly during the course of the photocatalytic reaction by use of OceanOptics HPS-2000 spectrometer in the λ = 200–900 nm spectral region. The specific surface area was determined by low temperature nitrogen adsorption using an ATK06 (KATAKON, Russia) analyzer. Before the measurements, the samples were degassed in a dry helium flow at 150 °C for 30 min. The specific surface area of the powders was calculated by the five point Brunauer–Emmett–Teller, BET, model. The morphology of the products was examined using a high resolution scanning electron microscope (Carl Zeiss NVision 40, equipped with an Oxford Instruments X-Max detector at 1 kV acceleration voltage).

## 3. Results and discussion

### 3.1. Phase relationships in the La<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>5</sub> system

The phase relations in the La<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>5</sub> system were not investigated earlier. Ternary oxides existing in this system were not referenced to in the literature except for LaFe<sub>0.5</sub>Sb<sub>1.5</sub>O<sub>6</sub> [19]. However the boundary binary systems have been studied in detail. In the La<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> system two compounds LaFeO<sub>3</sub> and LaFe<sub>12</sub>O<sub>19</sub> are realized [21]. Perovskite structure type compound LaFeO<sub>3</sub> (space group *Pm*-3*m*) melts congruently at T ~ 1900 °C. LaFe<sub>12</sub>O<sub>19</sub> is of magnetoplumbite hexagonal structure (space group *P*6<sub>3</sub>/*mmc*) and exists in the narrow temperature interval 1380–1420 °C. Several compounds were revealed in the La–Sb–O system however, only three of them La<sub>3</sub>SbO<sub>7</sub>, LaSbO<sub>4</sub> and LaSb<sub>3</sub>O<sub>9</sub> arise at ambient conditions [22–24]. Orthorhombic phase LaSb<sub>3</sub>O<sub>9</sub> (space group *Cmcm*) is stable only up to 1100 °C and melts incongruently above this temperature forming LaSbO<sub>4</sub> [23]. LaSbO<sub>4</sub> is of monoclinic (space group *P*12<sub>1</sub>/*c*1) structure and exists up to T = 1450 °C and then decomposes, forming orthorhombic La<sub>3</sub>SbO<sub>7</sub> (space group *Cmcm*) [22,24]. It should be noted, that in all listed above compounds antimony is in 5+ oxidation state. Earlier phase equilibria in the La<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>3</sub> system in vacuum within the temperature range up to 900 °C have been studied [25]. Phase equilibria in the La<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>3</sub> system in air have not been studied because the annealing in the air at T > 360 °C gives rise to the oxidation of

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