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Protonic transport in oxyfluorides Ba_2InO_3F and $Ba_3In_2O_5F_2$ with Ruddlesden–Popper structure

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ABSTRACT

Oxyfluorides with Ruddlesden–Popper structure Ba_2InO_3F and $Ba_3In_2O_5F_2$ were synthesized, and their structure, thermal properties, hydration behaviour and electrical properties have been investigated. It was proved that the oxyfluorides are capable to water uptake and can exhibit proton transport.

1. Introduction

Complex oxides with perovskite structure ABO_3 have wide variety in physicochemical properties due to the ability of the A- and B-sites to adopt various metal cations. While the majority of studies have concentrated on the influence of cation doping, much less research has been done to control the structural and physicochemical properties by the anion substitution. The suitable anion for introduction in oxygen sublattice should have a close ionic radius and electronegativity, from this point of view fluorine is a good candidate for substitution.

Oxyfluorides and F^--substituted solid solutions with perovskite related structure represent promising class of compounds because of the ability to improve the original properties and discover new effects. There are studies describing oxyfluorides as a high temperature superconductors, dielectrics, piezoelectrics, electrolytes etc. For example, high temperature superconductivity was discovered for copper oxyfluoride $Sr_{2-x}M_xCuO_2F_{2+\delta}$ (M = Ca, Ba) [1–4]. It was found that introduction of fluorine-ions in the anion sublattice leads to an increase T_c. Piezoelectric properties were studied for the phases with elpasolite structure, such as $A_2BM^{+4}OF_5$, $A_2BM^{+5}O_2F_4$, and $A_2BM^{+6}O_3F_3$, where A- and B-alkali metals; M^{+4} = Ti, V; M^{+5} = V, Nb, Ta; M^{+6} = Mo, W [5–10]. Catalytic and photocatalytic properties were described for oxyfluorides of alkali metals K_2TiOF_4, K_3TiOF_5, $K_7Ti_4O_4F_7$ and K_2TiF_6 [11]. It was shown that the presence of F^--ions in the anion sublattice effects beneficially on the photocatalytic activity. Oxyfluorides of rare earth elements $Ln_2Ln'_2O_3F_6$ (where Ln = Nd, La; Ln′ — rare earth metals) were described as an oxygen-ion conductors [12].

Solid solutions based on substitution of O^{2-} by F^- in complex oxides can also be prepared. The dielectric properties of fluorine-doped perovskites $SrTiO_3$ and $BaTiO_3$ were described [13]. It was shown that the introduction of fluorine led to improving some characteristics (the ferroelectric Curie temperature, the distortion lattice). Fluorine-doped phases, such as $SrCo_{0.5}Fe_{0.5}O_{2.5}F_{0.5}$ and $SrCoO_{2.5}F_{0.5}$, based on brownmillerites Sr_2CoFeO_5 and $Sr_2Co_2O_5$ exhibited ferromagnetic transition at the temperatures below 150 K [14].

Unfortunately the investigations of the transport properties (in particular proton transport) in the systems with two kinds of hetero anions are still scarce. The two F^--substituted solid solutions $Ba_{2-0.5x}In_2O_{5-x}F_x$ ($0 \le x \le 0.30$) and $Ba_2In_2O_{5-0.5y}F_y$ ($0 \le y \le 0.25$), based on brownmillerite $Ba_2In_2O_5$, were prepared [15–18]. It was established that small F^--concentrations can improve the oxide-ion and the proton conductivities [15,17,18]. The hydration process of brownmillerite structure resulting in the occupation of oxygen vacancies by OH^--groups is accompanied by phase transition and formation of new oxyhydroxide phase. From crystallochemical point of view this hydration process is accompanied by the transformation of indium tetrahedra (unsaturated coordination polyhedra) into octahedra. The ability of indium to adopt various coordinations provides a reversibility of hydration–dehydration process.

There are examples of complex oxides [19] and oxyfluorides [20,21] where indium adopts five-fold coordination. The oxyfluorides Ba_2InO_3F

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($n = 1$) [20] and $Ba_3In_2O_5F_2$ ($n = 2$) [21] with Ruddlesden–Popper structure $AX(ABX_3)_n$ consist of perovskite-type structural units ABX_3, separated by the layers of rock salt AX. For the composition Ba_2InO_3F [20] indium shows a square based pyramidal arrangement [InO_5], and the rock salt regions are alternating BaF and BaO layers. The structure of $Ba_3In_2O_5F_2$ can be considered to consist of double layers of vertex-sharing [InO_5] square pyramids separated by BaF layers [21]. It can be assumed that due to transformation of unsaturated coordination polyhedra [InO_5] into octahedra upon hydration (by analogy with brownmillerite structure with alternating sequence of octahedral and tetrahedral layers) the proton conduction can arise. In order to check this thesis we have investigated oxyfluorides Ba_2InO_3F and $Ba_3In_2O_5F_2$ as potential proton conductors.

In this work the crystal structure, the water uptake and the electrical properties of oxyfluorides Ba_2InO_3F and $Ba_3In_2O_5F_2$ were investigated.

2. Experimental

The samples Ba_2InO_3F and $Ba_3In_2O_5F_2$ were prepared by a solid state method from preliminary dried stoichiometric amounts of high-purity powders of $BaCO_3$ (99.9999% purity, VEKTON, Ukraine), BaF_2 (99.99% purity, VEKTON, Ukraine), and In_2O_3 (99.99% purity, REACHIM, Russia).

The starting reagents were mixed in agate mortar and then calcined at 1050 °C (the synthesis regime was determined in accordance with the literature data presented in [20,21]). Reactions between starting materials can be expressed by the following equations:

$$1.5BaCO_3 + 0.5In_2O_3 + 0.5BaF_2 \rightarrow Ba_2InO_3F + 1.5CO_2 \quad (1)$$

$$2BaCO_3 + In_2O_3 + BaF_2 \rightarrow Ba_3In_2O_5F_2 + 2CO_2. \quad (2)$$

The X-ray powder diffraction (XRD) measurements were made on a Bruker Advance D8 diffractometer with Cu K_α radiation. The crystal structures of dried and hydrated samples were determined through Rietveld refinement using FULLPROF software.

The surface morphology of the samples and the concentration distribution of elements were studied using a JEOL JSM 6390LA scanning electron microscope equipped with a JEOL JED 2300 energy-dispersive detector. The detection limit at usual energies (5–20 kV) was 0.5 at.%, and concentration measurement error was ±2%.

Thermogravimetric analysis was carried out on a STA (Simultaneous Thermal Analyzer) 409 PC analyzer (Netzsch) coupled with a quadrupole mass spectrometer QMS 403 C Aëolos (Netzsch). The hydrated forms of the samples were heated at the rate of 10 °C/min in a corundum crucible under a flow of argon. For the preparation of hydrated forms of specimens the powder samples were hydrated at slow cooling from 900 to 100 °C (1 °C/min) under a flow of wet air ($pH_2O = 2 \cdot 10^{-2}$ atm).

The ceramic samples used for the electrical measurements were prepared in tableted form and sintered at 1050 °C for 10 h in dry air. The relative densities of all the sintered samples were calculated to be ~85% of the theoretical density. The platinum paste electrodes were fired at 900 °C for 3 h. The conductivity measurements were carried out under dry and wet air by varying the temperature. The *ac* conductivity of the samples (2-probe method) was measured using an impedance spectrometer IM6 (Zahner Electric) within the frequency range of 1–10^6 Hz. The bulk resistance was calculated from a complex impedance plot using the Zview software fitting. The measurements of the temperature dependencies of conductivities were performed from 1000 °C to 200 °C every 10–20 °C with a cooling rate of 1 °C/min. Before the measurements the samples were equilibrated up to constant values of resistance (0.5 h for high temperatures and 1–2 h for low temperatures $T < 600$ °C).

The conductivity measurements were performed in air and N_2. The "wet" atmospheres were obtained by bubbling the gas at room temperature first through distilled water and then through saturated solution of KBr ($pH_2O = 2 \cdot 10^{-2}$ atm). The "dry" atmospheres were produced by flowing the gas through P_2O_5 ($pH_2O = 3.5 \cdot 10^{-5}$ atm). The "Honeywell" HIH-3610 humidity sensor was used for measuring the humidity of gases.

3. Results and discussions

The XRD results for the samples Ba_2InO_3F and $Ba_3In_2O_5F_2$, prepared under dry air and cooled to room temperature, showed that they were single phase and had a tetragonal structure. The lattice parameters for Ba_2InO_3F ($a = b = 4162(4)$ Å, $c = 13{,}948(3)$ Å, space group $P4/nmm$) and for $Ba_3In_2O_5F_2$ ($a = b = 4185(2)$ Å, $c = 22{,}823(1)$ Å space group $I4/mmm$) are in good agreement with previously reported data [20, 21]. Hydrated samples $Ba_2InO_3F \cdot nH_2O$ and $Ba_3In_2O_5F_2 \cdot nH_2O$ were characterized by XRD, and upon water incorporation the oxyfluorides transformed into an orthorhombic structure with lattice parameters $a = 3761(1)$ Å, $b = 15{,}447(2)$ Å, $c = 20{,}311(6)$ Å and $a = 3751(4)$ Å, $b = 15{,}421(6)$ Å, $c = 20{,}279(6)$ Å, respectively (space group $Cmma$). The examples of treatment by the Rietveld method are shown in Fig. 1a, b.

The surface morphology of the samples was examined by scanning electron microscopy (SEM). SEM image of the powder sample Ba_2InO_3F is given in Fig. 2. As it can be seen, the grain size was

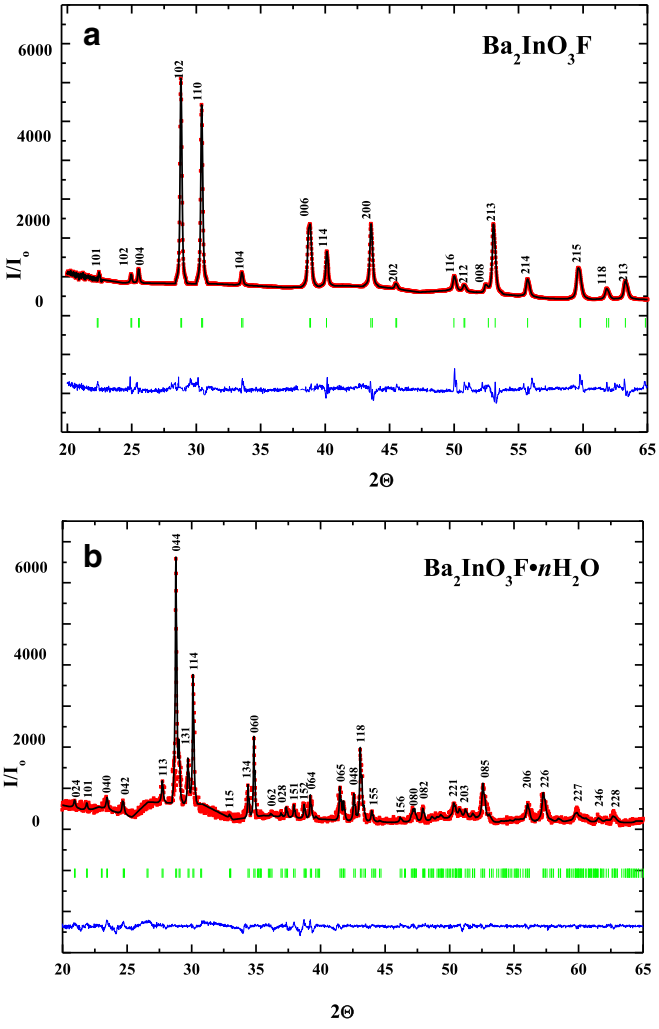

Fig. 1. X-ray powder diffraction patterns of Ba_2InO_3F (*a*) and $Ba_2InO_3F \cdot nH_2O$ (*b*). The lower curve represents the difference between the observed diffraction pattern and the calculated fit. Vertical bars show the Bragg angle positions for the perovskite phase ((*a*): $R_p = 5.91$, $R_{wp} = 7.64$, $R_{exp} = 2.62$, $\chi^2 = 2.88$; (*b*): $R_p = 5.75$, $R_{wp} = 7.21$, $R_{exp} = 2.41$, $\chi^2 = 2.65$).