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The influence of fluorine doping on short-range structure in brownmillerite $Ba_{1.95}In_2O_{4.9}F_{0.1}$

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ABSTRACT

The composition $Ba_{1.95}In_2O_{4.9}F_{0.1}$ from homogeneity range $Ba_{2-0.5x}In_2O_{5-x}F_x$ with $x = 0.1$ was obtained by a solid state method, the crystalline structure and local structure have been investigated (X-ray, infrared and Raman spectroscopy, NMR). The introduction of fluorine in oxygen sublattice is accompanied by decreasing some In–O distances. The phase is capable of dissociative dissolution of water, and as a result the nonequivalent OH^--groups are formed. The fluorine doping leads to the increase of hydrogen bonds of OH^--groups and this reflects increase in some O–H distances. For F^--doped sample the protons are weaker coupled to the lattice and become more mobile compared to $Ba_2In_2O_4(OH)_2$.

1. Introduction

Complex oxides with perovskite and perovskite-related structure have been widely investigated because of their various applications [1,2]. The oxygen deficient structures are studied as oxide-ion and proton conductors and can be used in different electrochemical devices [3,4].

The most oxygen-deficient compositions (among the perovskite-related structure) correspond to the general formula $A_2BB'O_5$ or $A_2B_2O_5$ and have a brownmillerite structure. The best investigated brownmillerite is the barium indate $Ba_2In_2O_5$ — a vacancy ordered analog of the perovskite. In order to modify the structure and to improve the ion conduction, some methods, based on *cationic* doping, are used. There are many investigations of its structure, electrical properties and spectroscopic characteristics [5–19]. Recently we have investigated an alternative doping strategy — heterogeneous doping of the *anionic* subblattice in barium indate $Ba_2In_2O_5$ [20]. Introduction of one F^- instead of one O^{2-} in $Ba_2In_2O_5[V_o]_1$ leads to the formation of vacancies in Ba-sublattice and the concentration of oxygen vacancies is not changed. This process can be expressed by the quasi-chemical simplified reaction:

$$\begin{matrix} BaF_2 \leftrightarrow Ba_{Ba}^{\times} + 2F_o^{\bullet} + V_{Ba}'', \\ \rightarrow BaO \end{matrix} \quad (1)$$

where $F_o^{\bullet}$ represents the fluorine in the oxygen sublattice, V''_{Ba} — barium vacancy.

Conductivity and TG measurements of the solid solution $Ba_{2-0.5x}[V_{Ba}]_{0.5x}In_2O_{5-x}F_x[V_o]_1$ ($0 \le x \le 0.3$) were studied earlier [20]. It was found [20] that small additives of F^--ions promote an increase in oxygen mobility as a result of additional effects of repulsion of ions of different nature in the same sublattice. This effect was named as a *mixed anion effect*. Moreover, small concentrations of fluoride lead to an increase in mobility of proton carriers. This fact is due to an increase in oxygen mobility. It is well known that the dynamics of the oxygen sublattice determines mobility of protons [21].

In continuation of these investigations [20] the present work is focused on the effect of fluorine on the local structure for the composition of $Ba_{1.95}In_2O_{4.9}F_{0.1}$ with a highest oxygen-ion and proton conductivity in the homogeneity region of the solid solution $Ba_{2-0.5x}In_2O_{5-x}F_x$. In order to better understand the influence of fluorine on the state of the oxygen–hydrogen groups and proton mobility the infrared, Raman and NMR spectra were studied.

2. Experimental

2.1. Materials

$BaCO_3$ (99.9999% purity, VEKTON, Ukraine), BaF_2 (99.99% purity, VEKTON, Ukraine) and In_2O_3 (99.99% purity, REACHIM, Russia).

2.2. Synthesis

The samples $Ba_{1.95}In_2O_{4.9}F_{0.1}$ and $Ba_2In_2O_5$ were prepared by a solid state method from preliminary dried stoichiometric amounts of starting compounds. The sample $Ba_2In_2O_5$ has been prepared and described

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previously [22–27], and was synthesized here for comparison. The starting reagents were mixed with ethanol in agate mortar and then calcined in accordance with the time–temperature regime: 800 °C–24 h, 1000 °C–24 h, 1100 °C–24 h, 1200 °C–24 h; intermediate grindings were made after each stage. Reactions between starting materials can be expressed with the following equations:

$$2\,BaCO_3 + In_2O_3 \rightarrow Ba_2In_2O_5 + 2CO_2 \quad (2)$$

$$1.9\,BaCO_3 + In_2O_3 + 0.05BaF_2 \rightarrow Ba_{1.95}In_2O_{4.9}F_{0.1} + 1.9CO_2. \quad (3)$$

Different partial water vapor pressures were used for preparation of the dried and hydrated samples. The "wet" atmospheres were obtained by bubbling the air at room temperature first through distilled water and then through saturated solution of KBr ($pH_2O = 1.42\ 10^{-2}$ atm). The "dry" atmospheres were produced by flowing the gas through P_2O_5 ($pH_2O = 4.5\ 10^{-4}$ atm). The humidity of gases was controlled by H_2O-sensor ("Honeywell" HIH-3610). For 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. According to TG-measurements [25] the water uptake for $Ba_2In_2O_5$ was close to 1 mol H_2O, i.e. the formation of hydroxo-phase $Ba_2In_2O_4(OH)_2$ takes place. The hydration degree for the sample $Ba_{1.95}In_2O_{4.9}F_{0.1}$ achieves 0.8 mol H_2O, for simplicity we'll denote the hydrated state as $Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot xH_2O$.

The treatment under dry air (cooling from 900 to 100 °C) allows preparation of dried forms of the samples ("dry" samples).

2.3. X-ray measurements

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.

2.4. Infrared, Raman and NMR spectroscopies

The IR spectra were recorded using a Fourier spectrometer Nicolet 6700 (ambient temperature, mid-IR region 450–4000 and far-IR region 50–600 cm^{-1}). Raman spectra were obtained using spectrometer Renishaw 1000, capacity of the laser 20 mW, scan range of 15–1000 cm^{-1}.

The IR and Raman spectra up to 900 cm^{-1} are expected to be related to the host-lattice vibration and reflect the short-range structure of the investigated samples. The frequencies of the O–H stretch vibrations fall into the range of 2500 to 3500 cm^{-1} and demonstrate the presence of protons in the structure.

MAS NMR spectra were obtained on the Agilent 400 spectrometer operating at Larmor frequencies of 400.0 MHz for ^1H and 376.4 for ^{19}F. All the MAS NMR spectra were recorded using a 4-mm double bearing MAS probe (Agilent) at spinning frequency of 10 kHz. For the variable temperature MAS NMR experiments, an Agilent VT unit was used. The ^1H and ^{19}F spectra were referenced to a TMS and $CFCl_3$ respectively set at 0 ppm. Analysis of spectra was carried out with Dmfit program.

3. Results and discussions

3.1. Structural characterization

Room temperature X-ray diffraction (XRD) results show that all prepared materials were single phase. The lattice parameters for $Ba_2In_2O_5$ are in good agreement with previously reported values [27], the sample belongs to space group *Ibm*2 with $a = 6.094(1)$ Å, $b = 16.740(0)$ Å, $c = 5.959(3)$ Å, and $\alpha = \beta = \gamma = 90°$. The XRD patterns for the fluorine-doped sample $Ba_{1.95}In_2O_{4.9}F_{0.1}$ can be indexed to body-centered orthorhombic unit cells of brownmillerite-type structure and the lattice parameters are very close to $Ba_2In_2O_5$: $a = 6.074(1)$ Å, $b = 16.741(0)$ Å, $c = 5.952(3)$ (space group *Ibm*2), but some decrease in *a*-parameter was observed. The X-ray diffraction patterns for both samples are presented in Fig. 1.

The hydrated samples were also characterized by XRD, and upon water incorporation the structure of both undoped and F^--doped samples transformed into a tetragonal symmetry similar to that of $Ba_2In_2O_4(OH)_2$ [26]. The lattice parameters for hydrated barium indate are $a = b = 4.177(2)$ Å, and $c = 8.977(6)$ Å and for fluorine-doped composition $Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot xH_2O$, respectively, $a = b = 4.191(5)$ Å, and $c = 8.975(4)$ Å ($\alpha = \beta = \gamma = 90°$, space group *P*4/mmm). The XRD patterns for hydrated samples are presented in Fig. 2.

The lattice parameters and crystal structure were also refined by Rietveld analysis. Fig. 3 shows the result of Rietveld fit. A good agreement between the calculated profiles and the experimental data was observed as confirmed by the reliability factors ($R_{wp} = 6.03$, $R_e = 3.92$, $\chi^2 = 1.96$). The determination of the specific positions of the F^- ions was not possible since fluorine is not ordered in the brownmillerite structure and the superstructure lines on the diffraction patterns were absent. Therefore the study of the local structure is most important.

3.2. Infrared spectroscopy

The IR spectra of "dry" samples in far-IR region are shown in Fig. 4. There are three areas of well visible bands, which are typical for perovskite-related structures. The lowest frequency bands can be assigned to vibrations mainly involving Ba^{+2} ions: the band at around 145 cm^{-1} is associated to the Ba–[InO_x] stretching vibration and the bands located at lower frequencies are related to bending vibration; the band at around 390 cm^{-1} and the broad band extending from 500 to 570 cm^{-1} can be assigned to the O–In–O bending modes and In–O stretching vibration, respectively. The IR-spectrum of $Ba_2In_2O_5$ agrees well with previously reported results [28].

The substitution of O-atoms for F leads to some changes of the spectrum. The low-frequency side of broad band shifts to higher frequencies (500 to 535 cm^{-1}), while high-frequency part (570 cm^{-1}) is not changed. These changes may reflect the decrease in some In–O distance. The 390 cm^{-1} band, assigned to the O–In–O bend, is not changed.

A new band at 435 cm^{-1} can be resolved and probably this is due to the presence of fluorine in the crystal lattice. Comparing the data on metal–O and metal–F distances in perovskite-related oxyfluorides [29–33], a general relationship may be detected: as a rule, the metal–F distance is longer than the metal–O distance. Thus, the metal–O stretching modes correspond to higher frequency region in comparison with metal–F. Moreover, based on the vibration spectroscopy investigations of the InF_3-containing glasses [34,35], it can be concluded that the In–F vibrational modes correspond to the range 450–500 cm^{-1}. So, we

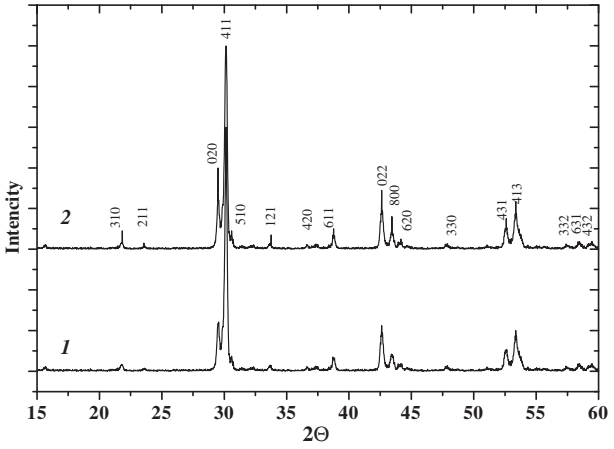

Fig. 1. XRD patterns of $Ba_2In_2O_5$ (1) and $Ba_{1.95}In_2O_{4.9}F_{0.1}$ (2) prepared under dry air.