



# Ion mobility and transport properties of bismuth fluoride-containing solid solutions with tysonite-type structure



V.Ya. Kavun<sup>a,\*</sup>, N.F. Uvarov<sup>b</sup>, A.B. Slobodyuk<sup>a</sup>, E.B. Merkulov<sup>a</sup>, M.M. Polyantsev<sup>a</sup>

<sup>a</sup> Institute of Chemistry FEB RAS, 159, Pr. 100-letiya Vladivostoka, Vladivostok 690022, Russia

<sup>b</sup> Institute of Solid State Chemistry and Mechanochemistry, SB RAS, 18, Kutateladze Str., Novosibirsk 630128, Russia

## ARTICLE INFO

### Keywords:

BiF<sub>3</sub>  
Solid solutions of tysonite-type structure  
Ion mobility  
Conductivity  
NMR spectra

## ABSTRACT

The ion mobility and conductivity of solid solutions with tysonite-type structure obtained by doping bismuth trifluoride with lead (II) fluoride, and zirconium and bismuth oxides have been studied using <sup>19</sup>F NMR, X-ray diffraction analysis, and impedance spectroscopy. The types of ionic motions in the fluoride sublattice of the synthesized solid solutions in the temperature range 150–450 K have been determined and the energy of their activation has been estimated. Due to high ionic conductivity, above 10<sup>-2</sup> S/cm at 570 K, these solid solutions can be considered as superionic conductors.

## 1. Introduction

One of the focuses in fluoride systems research consists in studies of ionic mobility and ionic transport. Ionic conductors characterized with high conductivity are promising materials for various electrochemical devices, chemical sensors etc. [1–3]. Heavy metals fluorides, such as LaF<sub>3</sub>, CeF<sub>3</sub>, PbF<sub>2</sub>, SnF<sub>2</sub>, BiF<sub>3</sub>, and SbF<sub>3</sub> and materials based on them, can be attributed to fluorine-containing compounds with high ionic conductivity [1,4–12]. The latter is explained by high polarizability of large-size cations (low ionization energy), which results in the decrease of the energy of activation of ionic transfer. Among numerous fluorine-containing compounds and solid solutions, a certain interest is related to solid electrolytes based on BiF<sub>3</sub> [1,5,7,13]. Depending on the dopant concentration, solid solutions in BiF<sub>3</sub>-containing systems can have fluorite as well as tysonite structure. Here, as a rule, high conductivity is characteristic for solid solutions in both cases [1,7,14]. Formation of tysonite phases is observed in anion-depleted fluoride systems, such as BiF<sub>3</sub>-MF (M – an alkaline cation) [1,15], BiF<sub>3</sub>-MeF<sub>2</sub> (Me – Ba, Pb) [1,14], BiF<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub> [1] etc. [12]. At studies of the phase diagram of BiF<sub>3</sub>-PbF<sub>2</sub>, the formation of solid solutions Bi<sub>1-y</sub>Pb<sub>y</sub>F<sub>3-y</sub> with the tysonite structure was established at 0.05 < y < 0.25 [16]. From the data of X-ray diffraction studies, solid solutions Bi<sub>1-x</sub>Pb<sub>x</sub>F<sub>3-x</sub> (x = 0.075 – 0.175) crystallize in the structural type of tysonite with the disordered hexagonal structure [14]. We have not found the data on studies of solid solutions with the tysonite-type structure in the system BiF<sub>3</sub>-ZrO<sub>2</sub> in the available literature. The formation of solid solutions of BiO<sub>y</sub>F<sub>3-2y</sub> with the structure of the LaF<sub>3</sub> type [17–21] was established from the data of physical-chemical studies in the system BiF<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub>.

The objective of the present work was to study the effect of doping BiF<sub>3</sub> with lead(II) fluoride and zirconium and bismuth(III) oxides on the character of ionic mobility and conductivity in the formed solid solutions of the tysonite-like structure. Solid solutions 90BiF<sub>3</sub>-10PbF<sub>2</sub> (I), 94BiF<sub>3</sub>-6ZrO<sub>2</sub> (II), 96BiF<sub>3</sub>-4Bi<sub>2</sub>O<sub>3</sub> (III) have been obtained and investigated. The NMR spectroscopy was employed as an efficient method of studying fluoride ionic motions in compounds of the tysonite-like structure [22–25].

## 2. Experimental

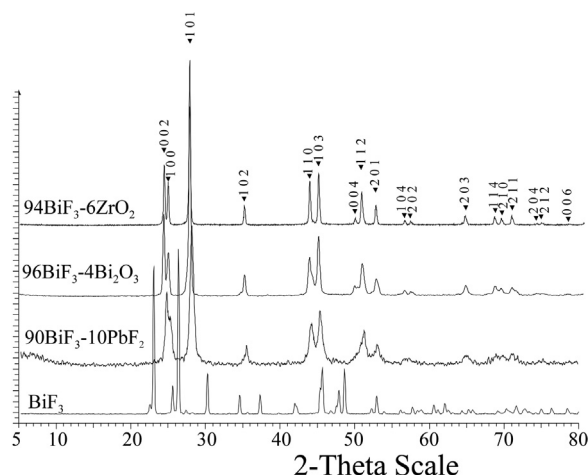
### 2.1. Synthesis

Solid solutions of the tysonite-like structure were obtained through doping BiF<sub>3</sub> with small amounts of lead(II) fluoride and zirconium and bismuth oxides under mild conditions at room temperature. The following compounds were used for the synthesis: orthorhombic BiF<sub>3</sub> obtained through precipitation by hydrofluoric acid from bismuth nitrate solution with subsequent drying at 60 °C in a vacuum oven; PbF<sub>2</sub> of the special purity grade heated up to 400 °C in the presence of NH<sub>4</sub>F to remove oxygen-containing impurities; and Bi<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> of the analytical grade preliminarily annealed at 400 °C.

The synthesis was performed by the mechanochemical method in a Fritsch Pulverisette 7 Premium line mill using 20 mL grinding cartridges coated with ZrO<sub>2</sub> and 10 grinding balls of a diameter of 10 mm made of similar material with a total weight of 35 g for each cartridge. 5 g mixture of initial substances was used for each load; the ratio of the weight of the sample to the mass of the grinding balls was 1–7.

\* Corresponding author.

E-mail address: [kavun@ich.dvo.ru](mailto:kavun@ich.dvo.ru) (V.Y. Kavun).



**Fig. 1.** X-ray diffraction patterns of the  $94\text{BiF}_3\text{-}6\text{ZrO}_2$ ,  $96\text{BiF}_3\text{-}4\text{Bi}_2\text{O}_3$ ,  $90\text{BiF}_3\text{-}10\text{PbF}_2$  solid solutions and  $\text{BiF}_3$  obtained by the mechanochemical method that underwent sintering at  $400^\circ\text{C}$ . The  $hkl$  indexes on the figure correspond to the tysonite-like phase.

Grinding was carried out at a speed of 800 rpm for 4 h in cycles of 10 min each out with 20-min breaks and reverse motion application. As compared to the conventional technique of many-hour sintering at  $400^\circ\text{C}$ , in the course of synthesis, pyrohydrolysis accompanied by HF release does not occur, and the composition of the produced samples corresponds to that of the initial charge. To exclude the atmospheric effect, samples were additionally heated in a labyrinth crucible up to  $300\text{--}400^\circ\text{C}$  in a Q-1500 derivatograph: here, no noticeable changes in the samples masses were observed (less than 0.5 wt%). Heating resulted in the increase of the samples crystallinity degree, which is manifested in narrowing of XRD reflections. All the obtained samples have the hexagonal tysonite-like structure (Fig. 1)

## 2.2. NMR study

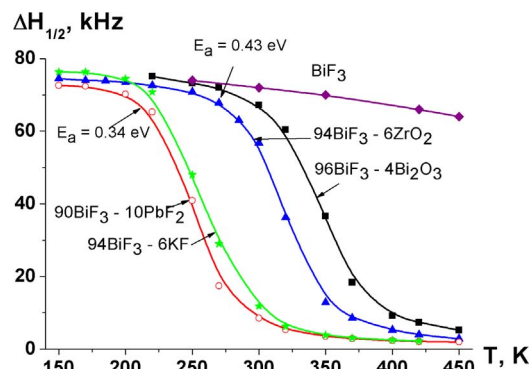
The  $^{19}\text{F}$  NMR spectra of the solid solutions were recorded using a Bruker AVANCE-300 spectrometer at Larmor frequency 282.4 MHz at temperatures  $(150\text{--}450\text{ K}) \pm 2\text{ K}$ . The method for measuring the parameters of the NMR spectra is described in [26]. The chemical shifts (CS, $\delta$ ) of  $^{19}\text{F}$  NMR signals were measured relatively to the standards ( $\text{C}_6\text{F}_6$ ) with an error of not higher than 1–2 ppm. Computer simulation of experimental NMR spectra (the deconvolution of the spectrum into individual components) was carried out with an accuracy of 2–5%. The activation energy  $E_{\text{NMR}}$  of local (diffusion) motions was estimated by the Waugh–Fedin equation  $E_{\text{NMR}} = 0.0016 \cdot T_c$  (eV) with an accuracy of 0.03 eV [27].  $T_c$  was taken as the onset temperature (absolute scale) for a decrease of the second moment  $S_2$  (or width  $\Delta H_{1/2}$ ) of  $^{19}\text{F}$  NMR spectra.

## 2.3. X-ray study

X-ray diffraction data (XRD) were obtained for the powdered solid solutions using a Bruker D8 ADVANCE diffractometer with the filtered  $\text{CuK}_\alpha$  radiation.

## 2.4. Conductivity study

Conductivity was studied on pellets compacted at 400 MPa with silver pressed-in electrodes. Densities of pellets were determined from values of the mass, diameter, and thickness of the pellets and were typically of 85–90% of the theoretical densities. Such a density was enough to avoid the contribution of grain boundary resistance into the overall impedance of the samples and to determine their bulk conductivity with an accuracy of 10–15%. AC electrical measurements were carried out in accordance with a two-terminal scheme in vacuum



**Fig. 2.** Temperature dependences of the  $^{19}\text{F}$  NMR spectrum width  $\Delta H_{1/2}$  for studied solid solutions and  $\text{BiF}_3$ .

in the temperature range  $(300\text{--}570\text{ K}) \pm 2\text{ K}$  using a HP-4284A Precision LCR at frequencies 20 Hz–1 MHz. The temperature was varied stepwise and controlled by a "Termodat 11E" thermostat. Measurements were carried out in an isothermal mode, prior to each measurement the sample was held at a predetermined temperature for 15 min. The details of conductivity measurements ( $\sigma$ ) have been reported in [26].

## 3. Results and discussion

### 3.1. NMR data

Doping  $\text{BiF}_3$  with specific amounts of lead(II) fluoride and zirconium and bismuth(III) oxides yielding the formation of solid solutions of the tysonite-type structure affects significantly the character of temperature dependence of the width of  $^{19}\text{F}$  NMR spectra of  $\text{BiF}_3$  (Fig. 2). The  $^{19}\text{F}$  NMR data for solid solutions indicate a dramatic decrease of the energy of activation of local motions in the fluoride sublattice in comparison with  $\text{BiF}_3$ , which is corroborated by the analysis of temperature dependencies of  $\Delta H_{1/2}(\text{F})$  (Fig. 2). The observed transformation of  $^{19}\text{F}$  NMR spectra upon temperature variations (Fig. 3) results from changes in the dynamic state of resonating nuclei in the fluoride sublattice. The most intensive dynamic processes are observed in fluoride sublattice of solid solution  $90\text{BiF}_3\text{-}10\text{PbF}_2$ . In the temperature range 150–220 K, the  $^{19}\text{F}$  NMR spectra of the solid solutions under study consist of an asymmetric line with half-width of  $\approx 76\text{--}70\text{ kHz}$  (second moment of  $^{19}\text{F}$  NMR spectra  $\approx 78 \pm 5\text{ G}^2$  for **I** and  $\approx 100\text{ G}^2$  for **II**, **III**). The parameters of  $^{19}\text{F}$  NMR spectra in the temperature range 150–220 K and the observed dependence of  $\Delta H_{1/2}(\text{F})$  at these temperatures (Fig. 2) indicate the absence of ionic motions in the fluoride sublattice of solid solution **I** with frequencies higher than  $10^4\text{ Hz}$  at temperatures below 220 K ("rigid lattice" in NMR terms [27]). For solid solutions  $94\text{BiF}_3\text{-}6\text{ZrO}_2$  and  $96\text{BiF}_3\text{-}4\text{Bi}_2\text{O}_3$ , the rigid lattice is observed below 270 K. The  $^{19}\text{F}$  NMR spectrum of solid solutions **I–III** at 150–200 K can be simulated by two components  $p_1$  and  $p_{23}$  (Fig. 4), which must be attributed (taking into consideration the data of [1,7,14,28,29]) to the different sublattices. First of the sublattices contain ions belonging to F1 structural positions and the second includes F2 and F3 ions. The ratio of areas of  $p_1$  and  $p_{23}$  components in NMR spectra of solid solutions  $96\text{BiF}_3\text{-}4\text{Bi}_2\text{O}_3$  and  $94\text{BiF}_3\text{-}6\text{ZrO}_2$  at 200 K equals to  $\approx 67:33$  and is in good agreement with the occupancies of respective structural positions 12:(4+2) in tysonite [1,7,28,30]. More intensive component in NMR spectra of solid solutions corresponds to fluoride ions of the F1 sublattice, whereas less intensive one – to total signal from fluoride ions of the F2 and F3 sublattice. Note that, based on the  $^{19}\text{F}$  NMR data and taking into account an insignificant difference in structural positions of F2 and F3 from X-ray diffraction analysis results, the authors of [7,27] concluded that the noticeable manifestation of the structural none-

Download English Version:

<https://daneshyari.com/en/article/7757730>

Download Persian Version:

<https://daneshyari.com/article/7757730>

[Daneshyari.com](https://daneshyari.com)