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Ion Mobility in the Fluorite Solid Solutions 50PbF$_2$–30BiF$_3$–20K(Na)F According to ^{19}F, ^{23}Na NMR Data

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ABSTRACT

Ion mobility in solid solutions of the fluorite structure 50PbF$_2$–30BiF$_3$–20KF (I) and 50PbF$_2$–30BiF$_3$–20NaF (II) was studied by NMR method. Analysis of ^{19}F, ^{23}Na NMR spectra made it possible to reveal the character of ion motions in the fluoride and sodium sublattices with temperature variation, to determine the types and temperature ranges in which they took place. It was found that the dominant form of ionic mobility in the samples I and II above 380 K was the diffusion of fluoride and sodium ions. According to preliminary results of electro-physical studies, the conductivity reached values of ~ 2×10^{-2} – 10^{-3} S/cm above 500 K. The solid solutions I and II can be recommended as a basis for use in the development of new functional materials..

Keywords: Solid Solutions 50PbF$_2$–30BiF$_3$–20K(Na)F; Ion Mobility; Ionic Conductivity; ^{19}F, ^{23}Na NMR Spectra; Functional Materials

1. Introduction

The fluorite-related solid solutions are known to exhibit fluorine ionic conductivity and may be used as solid electrolytes [1-4]. Solid electrolytes based on PbF$_2$ [5] and BiF$_3$, such as MBiF$_4$ (M = K, Rb, Tl) [6,7] and Pb$_{1-x}$Bi$_x$F$_{2+x}$ [1,6,8-10], are of special interest due to the high ionic conductivity of about 10^{-2} S/cm at 500 K. There are a few papers [1,3,7,11] on the conductivity of fluorite solid solutions formed in the KF□BiF$_3$ system. Contrary to earlier data [7], authors of [3] observed phase transitions in the solid solutions *x*KF–(1–*x*)BiF$_3$ (0.35 ≤ *x* ≤ 0.50) attributed to transformation of the meta-stable fluorite-structured phase [12] into the stable form of a structure being similar to NaNdF$_4$ compound. Under solid-phase interaction in the BiF$_3$–KF system, it was found a formation of KBi$_2$F$_7$, KBiF$_4$, and KBi$_3$F$_{10}$ compounds, as well as of a phase of variable composition in the range of 48-70 mol.% BiF$_3$ [13]. X-ray analysis of the BiF$_3$–NaF system showed a presence of the NaBiF$_4$ compound and a phase of variable composition of the fluorite structure in the range of 65-73 mol.% BiF$_3$ [14]. The diffusion of fluoride and sodium ions in the solid solutions Na$_{1-x}$Bi$_x$F$_{1+2x}$ of the fluorite structure and NaBiF$_4$ were studied by ^{19}F, ^{23}Na NMR [15,16]. It was noted in [15] that there was no motion of sodium ions in the NaBiF$_4$ compound, whereas in the solid solutions, the diffusion of Na$^+$ ions was observed. Ionic mobility in the fluorine sublattice of NaBiF$_4$ compound was attributed to reorientation of fluorine-containing groups, and the number of high-mobile fluoride ions increased in the solid solutions with temperature increase. Thus, in PbF$_2$□BiF$_3$, KF□BiF$_3$, and NaF–BiF$_3$ systems, the fluorine solid solutions of high ionic conductivity are formed, but there are no published data on ion mobility and transport properties in solid solutions in the ternary PbF$_2$□BiF$_3$□NaF system. As concerns the study of solid solutions in the PbF$_2$□BiF$_3$□KF system, some data were presented in our recent paper [17].

The purpose of this work was to consider ion mobility in the solid solution 50PbF$_2$□30BiF$_3$□20NaF and to compare obtained data with our earlier similar results for the solid solution 50PbF$_2$□30BiF$_3$□20KF [17].

2. Experimental

Original materials for solid-phase synthesis of solid solutions of the fluorite structure were the preliminarily vacuum dried bismuth trifluoride, lead difluoride, potassium and sodium fluoride (grade "chemically pure"). The mixtures of powdered fluorides were melted in a closed glassy carbon crucible in a dry box filled by argon at temperature of 700-800°C for 15 minutes. The sample single-phase and characterization as compounds of the fluorite structure were confirmed by X-ray diffraction analysis performed on a Bruker D8 ADVANCE diffractometer with CuK$_\alpha$ radiation.

^{19}F, ^{23}Na NMR spectra were recorded on a multinuclear digital spectrometer Bruker AV-300 at Larmor frequencies of 282.404 and 79.4 MHz, respectively, in the temperature range of 150-450 K. The temperature accuracy was ± 2 K. Calculations of a rms width of NMR spectra (or the second moment S$_2$, in G^2) were performed using an original code by formulas given in [18]. The error in S$_2$ value did not exceed 10%. The width ΔH of lines (at half height, in kHz), chemical shift (CS, δ in ppm) and integral intensity of ^{19}F NMR spectrum components were measured with the accuracy of 3%. The CS values of ^{19}F NMR signals were determined relative to the reference C$_6$F$_6$ (CS of C$_6$F$_6$ is -589 ppm relative to gaseous F$_2$, for which δ(F$_2$) = 0 ppm), and of ^{23}Na NMR signals – relative to the aqueous solution NaCl.

3. Results and Discussion

Parameters of ^{19}F NMR spectra and temperature ranges, in which some particular type of ion motions took place in the fluoride sublattice of fluorite solid solutions in the ternary PbF_2–BiF_3–K(Na)F systems, were determined by nature of the alkali cation and its concentration. The shape of BiF_3 line and the almost constant second moment (S_2(F) = 55 G^2) under temperature variations within 290-420 K were the evidences that BiF_3 was characterized by the absence of F^- ion motion with frequencies $\omega_c > \gamma\Delta H$ ($\nleqslant 10^4$ Hz) in this temperature range. Contrary to BiF_3, in the lead difluoride β-phase there was diffusion of F^- ions at temperatures above 370 K [19]. Introduction of potassium (sodium) fluoride into the PbF_2–BiF_3 system caused a sharp decrease of the activation energy of a local (diffusion) motion in the fluoride sublattice relatively to β-PbF_2, as evidenced by nature of $\Delta H_{1/2}$(F) temperature dependences (**Figure 1**).

^{19}F NMR spectrum of the solid solution $50PbF_2$–$30BiF_3$–$20KF$ (I) at 150 K was a single, slightly asymmetric, line with ΔH = 42.7 kHz and CS = 126 ppm (**Figure 2**). For solid solutions of fluorite structure, the CS anisotropy should be practically absent, and, hence, the observed spectrum asymmetry could be attributed to a presence of different fluoride ions in the lattice. Indeed, the experimental spectrum of this sample at 150 K could be decomposed into two Gaussian components with CS of 157 and 92 ppm indicated a presence of at least two different types of fluoride ions in the lattice. The same deconvolution procedure, done for ^{19}F NMR spectra of fluorite solid solutions $Na_{1-x}Bi_xF_{1+2x}$ at 175 K, allowed to authors of [16] to attribute two revealed components to two different fluoride sublattices, formed by the cubic and cubic-octahedral clusters. Considering the absence of a plateau in the dependence $\Delta H_{1/2}$ = f(T) in the range of 200-150 K (**Figure 1**), it may be concluded that the rigid lattice for fluoride subsystem was observed below 150 K. The temperature increase to 200 K caused a NMR spectrum transformation and registration of a new "narrow" component with CS = 118 ppm.

The observed changes in NMR spectra were due to an appearance of high-mobile fluoride ions (E_a < 23 kJ/mol) increased with temperature. As it follows from a ratio of the components integral intensities in the NMR spectrum, at 300 K, the number of high-mobile fluoride ions was about 95%. At
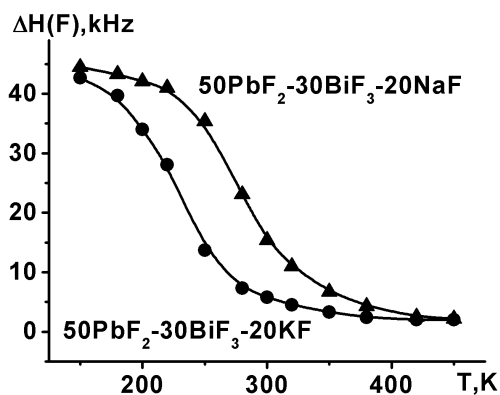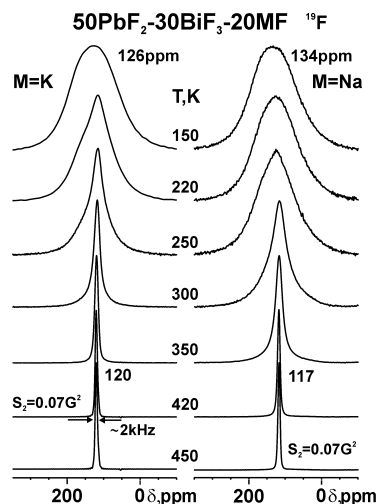

Figure 2. Transformation of the ^{19}F NMR spectra of solid solutions $50PbF_2$–$30BiF_3$–$20MF$ (M = Na, K) with temperature variation.

420 K, the NMR spectrum was a single line (ΔH = 2 kHz, S_2 = 0.05 G^2), its shape with accuracy up to 3% may be described by a weakly resolved pent tent (with a small share of the Lorentzian function) being characteristic for nuclei with an axially symmetric tensor of magnetic shielding. As a result of the NMR spectrum simulations at 450 K, the parameters of this tensor components were determined: δ_{11} = δ_{22} = 121.1, δ_{33} = 114.75, and δ_{iso} = ⅓(δ_{11} + δ_{22} + δ_{33}) = 119 ppm. The observed ΔH and S_2(F) values indicated a dominant role of diffusion in the fluoride sublattice of solid solution $50PbF_2$–$30BiF_3$–$20KF$ at temperatures above 400 K.

^{19}F NMR spectra of the solid solution $50PbF_2$–$30BiF_3$–$20NaF$ (II) of fluorite structure in the temperature range of 150-230 K consisted of a single, slightly asymmetric, line with ΔH = 41.5-38 kHz (**Figure 2**). Nature of temperature dependence of the NMR spectrum second moment (**Figure 1**) evidenced that, in this temperature range, the fluoride sublattice of sample II may be considered as rigid. Taking into account the above mentioned for ^{19}F NMR spectra of the solid solution I, at 150 K, the sample II NMR spectrum may be represented as two components with CS of 151 and 106 ppm indicated an existence of at least two different positions of fluorine ions in the lattice. With the temperature increase from 230 to 300 K, the NMR spectrum transformation was observed, associated with a narrowing of the spectrum to 22.5 kHz and an appearance of a new "narrow" component with CS = 122 ppm above 245 K, indicated on a development of the ion local motion in the fluorine sublattice. The number of high-mobile fluoride ions increased with temperature, and, at 350 K, the ratio of integral intensities of the narrow and broad components (the number of mobile and immobile fluoride ions) was 87.5:12.5. At 380 K, the NMR spectrum consisted of a nearly Lorentzian line with ΔH = 5.3 kHz and CS = 121 ppm. Heating of the sample to 450 K caused a narrowing of the resonance line to 2.5 kHz and a decrease of the second moment to 0.15 G^2. In this case, the spectral shape may be described by superposition of a weakly resolved pent tent, being characteristic for an axially symmetric tensor with parameters δ_{11} = 123.8, δ_{22} = δ_{33} = 118, and δ_{iso} = 119.9 ppm, and a Lorentzian function. It should be noted that since the ^{19}F

Figure 1. Temperature dependences of ^{19}F NMR spectrum width of solid solutions $50PbF_2$–$30BiF_3$–$20MF$ (M = Na, K).

NMR spectrum shape of samples I and II at 450 K was described by various pent tents (the tents were "flipped" relative to each other), so the tensor parameters were different. For example, a similar situation occured for a axially symmetric tensors described the ^{19}F NMR spectra of polycrystalline M_2AF_6 samples with undistorted octahedrons AF_6 [20]: at maximal shielding along the A-F bond there was a tent with $\sigma_{11} = \sigma_{22}$, at minimal shielding – a "flipped" tent with $\sigma_{22} = \sigma_{33}$. The observed ΔH and $S_2(F)$ values indicated a presence of diffusion in fluorine sublattice of the solid solution $50PbF_2–30BiF_3–20NaF$ at temperature above 400 K.

^{23}Na NMR spectra (nuclear spin $I = 3/2$) of the solid solution $50PbF_2–30BiF_3–20NaF$ at temperature below 250 K consisted of a single symmetric line with CS = –17.5 ppm (the absence of satellites was due to averaging of the tensor of an electric field gradient at resonating ^{23}Na nuclei), the resonance line width was determined by internuclear interactions of $Na^+ – Na^+$, $Na^+ – F^-$, and $Na^+ – M^{n+}$. With the temperature increase from 150 to 420 K, the resonance line narrowing was observed (from 6.5 to 1.5 kHz), caused by a partial averaging of dipole-dipole interactions between sodium and fluorine nuclei due to an appearance of ion mobility in the fluoride subsystem, as well as, perhaps, by a transition of sodium ions to local motion (diffusion).

4. Conclusions

The nature of ion mobility was studied in the solid solutions $50PbF_2–30BiF_3–20K(Na)F$ with temperature variation. The introduction of potassium or sodium cations into the fluorite lattice $PbF_2–BiF_3$ system caused an improvement of ionic mobility. The observed transformations of ^{19}F NMR spectra were associated with a gradual change in ionic dynamics in the fluoride sublattice with temperature, from the rigid lattice through local ionic motion to a translational diffusion of fluoride ions.

The presence of diffusion in the fluoride and sodium sublattices of the studied solid solutions indicated the existence of high ionic conductivity. According to the preliminary data of electro-physical research, conductivity in the solid solutions I and II reached values of $\sim 2\times 10^{-2} – 10^{-3}$ S/cm at temperature above 500 K, that allowed to recommend these systems as a basis for the development of new functional materials.

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