New anion-conducting solid solutions $Bi_{1-x}Te_x(O,F)_{2+\delta}$ ($x > 0.5$) and glass–ceramic material on their base[☆]

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ABSTRACT

The anion-excess fluorite-like solid solutions with general composition $Bi_{1-x}Te_x(O,F)_{2+\delta}$ ($x > 0.5$) have been synthesized by a solid state reaction of TeO_2, BiF_3 and Bi_2O_3 at 873 K with following quenching. The homogeneity areas and polymorphism of the I ↔ IV $Bi_{1-x}Te_x(O,F)_{2+\delta}$ phases were investigated. The crystal structure of the low temperature IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ phase has been solved using electron diffraction and X-ray powder diffraction ($a = 11.53051(9)$ Å, S.G. Ia-3, $R_I = 0.046$, $R_P = 0.041$). Glass formation area in the Bi_2O_3–BiF_3–TeO_2 (10% TiO_2) system was investigated. IV$Bi_{1-x}Te_x(O,F)_{2+\delta}$ phase starts to crystallize at short-time (0.5–3 h) annealing of oxyfluoride glasses at temperatures above T_g (600–615 K). The ionic conductivity of the crystalline $Bi_{1-x}Te_x(O,F)_{2+\delta}$ phase and corresponding glass-ceramics was investigated. Activation energy of conductivity $E_a = 0.41(2)$ eV for the IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ crystalline samples and $E_a = 0.73$ eV for the glass-ceramic samples were obtained. Investigation of the oxyfluoride samples with a constant cation ratio demonstrates essential influence of excess fluorine anions on the ionic conductivity.

1. Introduction

Ionic conductivity of $MX_{2\pm\delta}$ fluorite-like phases usually exceeds the conductivity of MX_2 fluorite-stoichiometric phases by several orders of magnitude due to a formation of defects. The most common way of doping is heterovalent substitution, e.g., introduction of $M'F_3$ into MF_2: $M_{1-x}Ln_xF_{2+x}$ [1] or M'_2O_3 into ZrO_2: $Zr_{1-x}Y_xO_{2-x}$ [2].

The defects in fluorite-like structure, e.g., in BiOF can be created by heterovalent substitution either in cation sublattice (e.g., by partial substitution of Bi(III) by Te(IV), as in the fluorite-like phases $Bi_{1-x}Te_x(F,O)_2$ [3,4]) or in anion sublattice $F^- \leftrightarrow O^{2-}$ (as in the fluorite-like phases $Bi(F,O)_{2+\delta}$, e.g., $Bi(F,O)_{2.45}$ [5]). One can expect that promising fluorite-like phases will be obtained by simultaneously modifying cation and anion sublattices allowing flexible control of the properties of solid solutions. Generally, the M/M′ cation ratio, the X/Y anion ratio and the anion nonstoichiometry (δ) in $M_{1-x}M'_x(X,Y)_{2\pm\delta}$ solid solutions contribute to the properties of these phases. The chosen reference system to investigate the composition-properties relationships will be a solid solution in

which the anion sublattice is formed of F^- and O^{2-} and the cation sublattice is formed of metals with constant oxidation state. In this case two factors out of three (quantity of anion excess (δ), cation composition (x) and anion composition (y)) are independent. The composition of the solid solution can be chosen to fix one of the factors (including δ = const) and investigate the contribution of the other factor to ionic conductivity. Such an approach can contribute to understanding the problem of transport properties handling regardless of the way of obtaining defects in the fluorite lattice.

The aim of the present work is the crystallographic and structural characterization and the investigation of the influence of chemical composition on ionic conductivity of anion-excess fluorite-like solid solutions with general composition $Bi_{1-x}Te_x(O,F)_{2+\delta}$ ($x > 0.5$) in both crystalline and glass–ceramic forms.

2. Material and methods

The starting materials were high-purity bismuth oxide Bi_2O_3, bismuth fluoride BiF_3, bismuth oxyfluoride BiOF and tellurium oxide TeO_2. Tellurium oxide was prepared by oxidation of tellurium with a mixture of nitric and hydrochloric acids followed by precipitation of compound with ammonia solution with pH ≈2–3. Precipitate was filtrated, flushed with water and dried
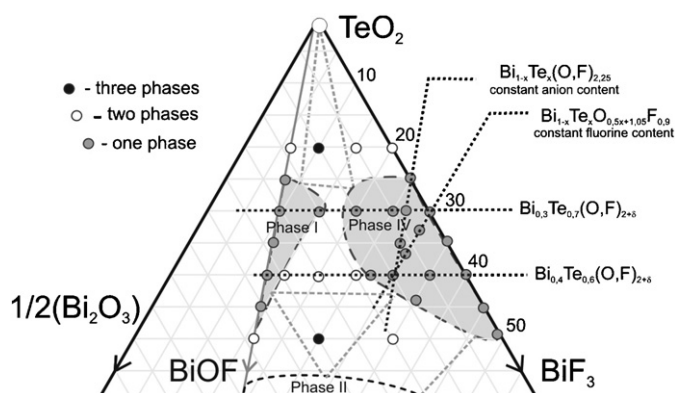
Fig. 1. Scheme of solid solutions regions within BiF_3–Bi_2O_3–TeO_2 concentration triangle at 873 K.

at 120 °C [6]. Bismuth oxyfluoride was obtained by solid state annealing (873 K, 12 h, Cu–ampoules, Ar) from stoichiometric mixture of Bi_2O_3 and BiF_3 [7]. Since the starting materials can be subjected to pyrohydrolysis, the Bi_2O_3 and TeO_2 oxides were preliminary annealed to exclude traces of water and other impurities. All starting materials were kept in a dessicator with P_2O_5 and controlled by X-ray powder diffraction analysis.

Crystalline $Bi_{1-x}Te_x(O,F)_{2+\delta}$ samples were obtained through solid state synthesis. The compositions of the samples were chosen on sections with constant cation content $Bi_{1-x}Te_x(O,F)_{2+\delta}$ ($x = 0.2$, 0.3, 0.4 and 0.5), constant overall anion content $Bi_{1-x}Te_x(O,F)_{2.25}$, constant fluorine content $Bi_{1-x}Te_xO_{0.5x+1.05}F_{0.9}$, $BiOF$–TeO_2, BiF_3–TeO_2 and are presented in Fig. 1. Homogenized mixtures of starting fluorides and oxides in the form of powder or pellets, 8 mm in diameter, were introduced into platinum or gold tubes placed into quartz ampoules. After the degassing in dynamic vacuum at 423 K for 2 h quartz ampoules were sealed. The samples were annealed at 873 K for 3 h and finally quenched by placing the sealed ampoules into icy water.

Glasses were obtained by melting Bi_2O_3 + BiF_3 + TeO_2 starting mixtures (10% TiO_2 was added for better glass formation) at 1173 K for 10 min in air in platinum crucibles with following quenching by pouring the melt onto a copper plate. The transparent glasses obtained this way did not contain any crystalline phase. Glass–ceramic samples were obtained by annealing the synthesized oxyfluoride glass. Glass compositions and conditions of their annealing are given below.

Investigation of phase composition was performed using X-ray powder diffraction analysis with a Guinier camera FR-552 with effective diameter of 228 mm ($CuK_{\alpha1}$ radiation) and with PANalytical X'Pert (CuK_{α}) diffractometer.

X-ray powder diffraction (XRPD) data for the Rietveld refinement were obtained with a STOE STADI-P ($CuK_{\alpha1}$, Ge- monochromator, linear position-sensitive detector) diffractometer. The Rietveld refinement was performed by means of JANA2000 program package [8].

Conductivity measurements were carried out by two-point technique with a Solartron SI 1287 frequency response analyzer in the frequency range of 1–10^6 Hz over the thermal interval 293–673 K in dry argon atmosphere on the ceramic pellets with a diameter of 8 mm and thickness of 1–2 mm (pellet density was 80–85% with respect to the theoretical value) with silver electrodes. The electrodes were deposited using fast dry silver paste "Agar Scientific Ltd". The Ag//sample//Ag pellets were placed into a quartz cell, which was degassed in the dynamic vacuum at 423 K for 2 h and filled with dry argon. The obtained impedance hodographs were processed using the "Zview2.1" program[1].

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[1] 1998 Scribner Associates, Inc., written by Derek Johnson.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) experiments were carried out on Perkin-Elmer TG7 and DSC-ATD Netzsch 404 Eos thermal analyzers in dry argon in platinum crucibles with heating/cooling rate of 10° per minute.

Samples for electron microscopy were crushed in ethanol and the fragments were deposited on a holey carbon grid. Electron diffraction experiments were performed on Philips CM20 electron microscope (with accelerating voltage of 200 kV). EDX analysis was carried out on Philips CM20 transmission electron microscope equipped with a LINK-2000 attachment. $Te(L_{\alpha})$ and $Bi(L_{\alpha})$ lines were used for analysis. The determined cation compositions were in good agreement with the bulk composition of the samples.

The potentiometric measurements by fluoride-selective electrode (crystal based on LaF_3) and reference electrode (saturated calomel electrode) were performed in order to determinate content of fluorine. Samples were dissolved in 5% HNO_3 and then put into 50 ml plastic can. TISAB III reagent was used as a buffer. Standard solution of BiF_3 in nitric acid was used for calibration. Losses of fluoride-ions were relatively large (9–16%) for the glass samples and much smaller (~2%) for the crystalline samples.

3. Results and discussion

3.1. Solid solutions $Bi_{1-x}Te_x(O,F)_{2+\delta}$ ($x \geq 0.5$) in the BiF_3–Bi_2O_3–TeO_2 system at 873 K

The homogeneity ranges of the solid solutions in the BiF_3–Bi_2O_3–TeO_2 system at 873 K are presented on the concentration triangle (Fig. 1) [3,9,10]. In this system fluorite-like anion-excess solid solutions I, II and IV with the common formula $Bi_{1-x}Te_x(O,F)_{2+\delta}$ have been investigated [9,10]. Left border lines of the concentration ranges of the solid solutions I and II are located on the $BiOF$–TeO_2 line. A presence of fluorite-like phases along this line was reported in [3]. However, the concentration range and crystallographic characteristics of these phases are different from those established by us earlier [9]. No information was reported in [3] about investigations of the compositions outside of the $BiOF$–TeO_2 line. In this work the solid solutions I and IV with $x > 0.5$ quenched from 873 K are investigated in detail.

The homogeneity range of the IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ solid solution is adjacent to the BiF_3–TeO_2 side of the compositional triangle spreading between 50 and 75 mol% TeO_2. Unit cell parameters (a_0) of the face-centered cubic fluorite sublattice of this solid solution consistently decrease with the increasing TeO_2 content (Table 1), due to smaller ionic radius of Te(IV) cation in comparison with Bi(III) and decreasing anion content.

XRPD patterns of the IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ samples (Table 1) demonstrated superstructure reflections, which can be indexed with a body-centered cubic unit cell with a parameter $a = 2a_0$. The same superstructure was observed for other samples of the IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ solid solutions inside their homogeneity range. The dependence of the lattice parameters of IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ solid solution on the Te content (x) along the lines of fixed amount of fluoride ions ($Bi_{1-x}Te_xO_{0.5x+1.05}F_{0.9}$ section) and fixed anion excess ($\delta = 0.25$) ($Bi_{1-x}Te_x(O,F)_{2.25}$ section), and the dependence of the lattice parameters on anion excess (δ) along the lines of fixed

Table 1
Lattice parameters of the IV-$Bi_{1-x}Te_x(O,F)_{2+\delta}$ solid solutions along the BiF_3–TeO_2 line.

Composition, mol% TeO_2	50	60	70	75
a_0 (sublattice) (Å)	5.765(1)	5.7321(6)	5.7056(9)	5.6934(7)
a (lattice) (Å)	11.5377(1)	11.465(2)	11.412(1)	11.387(3)