

## ORIGINAL PAPER

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## Oxygen ionic transport in Bi<sub>2</sub>O<sub>3</sub>-based oxides: The solid solutions Bi<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub>

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**Abstract** The minimum concentration of niobium to stabilize the fluorite-type f.c.c. phase in the Bi<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> oxide system at temperatures below 996 K was ascertained to be about 10 mol%. Thermal expansion, electrical conductivity and crystal lattice parameters of the Bi(Nb)O<sub>1.5+δ</sub> solid solutions decrease with increasing niobium content. Thermal expansion coefficients were calculated from the dilatometric data to be  $(10.3\text{--}14.5) \times 10^{-6} \text{ K}^{-1}$  at temperatures in the range 300–700 K and  $(17.5\text{--}26.0) \times 10^{-6} \text{ K}^{-1}$  at 700–1100 K. The conductivity of the Bi<sub>1-x</sub>Nb<sub>x</sub>O<sub>1.5+δ</sub> ceramics is predominantly ionic. The p-type electronic transference numbers of the Bi(Nb)O<sub>1.5+δ</sub> solid solutions in air were determined to be less than 0.1. Annealing at temperatures below 900 K results in a sharp decrease in conductivity of the Bi<sub>1-x</sub>Nb<sub>x</sub>O<sub>1.5+δ</sub> ceramics.

**Key words** Bismuth-niobium oxide · Oxygen ionic conductivity · Transference numbers · Thermal expansion

### Introduction

Oxygen ionic conductors on the basis of stabilized δ-Bi<sub>2</sub>O<sub>3</sub> are of interest as materials for high-temperature oxygen pumps and sensors [1–4]. For these applications, the promise of Bi<sub>2</sub>O<sub>3</sub>-based fluorite-like solid solutions is based on their very high ionic conductivity as compared with that of well-known solid electrolytes such as Zr(Y)O<sub>2</sub>, Ce(Gd)O<sub>2</sub> and La(Sr)Ga(Mg)O<sub>3</sub> [5, 6]. For

instance, the oxygen ionic conductivity of Bi<sub>0.8</sub>Er<sub>0.2</sub>O<sub>1.5</sub> and Bi<sub>0.85</sub>Nb<sub>0.15</sub>O<sub>1.65</sub> 970 K has been reported to be  $3.7 \times 10^{-1} \text{ S cm}^{-1}$  and  $1.9 \times 10^{-1} \text{ S cm}^{-1}$  respectively [3, 4]. At lower temperatures, however, a transformation of the δ-Bi<sub>2</sub>O<sub>3</sub> phase into a rhombohedral phase and the formation of superstructures may lead to a sharp decrease in conductivity [7–10]. Additions of ZrO<sub>2</sub> and CeO<sub>2</sub> have been reported to suppress this decay [10, 11].

One of the most promising applications of the Bi<sub>2</sub>O<sub>3</sub>-based ionic conductors is dual-phase oxygen membranes, which can be visualized as being a dispersion of an electronic conductor phase in an oxygen-ion-conducting matrix [12]. Both metals and oxide compounds have been studied as the electronic conductor in the dual-phase membranes [12]. Shen et al. [13] have investigated mixed conductors consisting of the stabilized fluorite Bi(Y)O<sub>1.5</sub> ionic-conductive matrix phase and Bi<sub>2</sub>CuO<sub>4-δ</sub> electronic-conductive second phase. It has been found that the oxygen ionic transference number of Bi<sub>0.75</sub>Y<sub>0.25</sub>O<sub>1.5</sub>–Bi<sub>2</sub>CuO<sub>4-δ</sub> ceramics is comparable with their electronic transference number at 920 K at a content of about 30 vol% electronic conductor [13].

Our previous work [14, 15] showed that structure and transport properties of Bi<sub>2</sub>O<sub>3</sub>-containing ceramics in ternary oxide systems depend on the order in which the components are added in the course of preparation. Introduction of a less soluble component and synthesis of binary solid solutions with subsequent adding of a more soluble component is a promising method to prepare Bi<sub>2</sub>O<sub>3</sub>-based electrolytes with two dopants [14, 15].

The present work was aimed at the study of Bi<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> solid solutions, which are considered as a basis for further modifications.

### Experimental

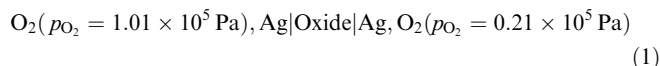
A standard ceramic synthesis technique using high-purity Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O and Nb<sub>2</sub>O<sub>5</sub> as starting materials was performed for the preparation of Bi<sub>1-x</sub>Nb<sub>x</sub>O<sub>1.5+δ</sub> ( $x = 0.05, 0.08, 0.10$  and 0.16) powders. The solid-state reactions were conducted in air at

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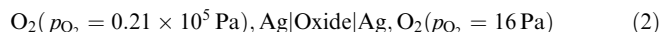
temperatures of 1120–1170 K for 20–30 h with multiple repeated intermediate grindings. Ceramics specimens were pressed (200–600 MPa) in the shape of bars ( $4 \times 4 \times 30 \text{ mm}^3$ ) and disks of various thicknesses (diameter 12 or 15 mm). The ceramics were sintered in air at 1200–1250 K for 20–40 h.

The techniques of X-ray diffraction (XRD) investigation, X-ray fluorescence analysis (XRF), atomic emission spectroscopy (AES) and differential thermal analysis (DTA) were described in detail in our earlier publications [15–18]. XRF and AES were used to verify cation compositions of the powders and ceramics. The procedures of electrical conductivity measurement and thermal expansion investigation have also been described elsewhere [16–18].

The experimental technique to determine oxygen ion transference numbers was described in [16]. The transference numbers of the ceramics were measured by a modified EMF method [19] using the concentration cell:



To estimate the transference parameters at lower oxygen partial pressures, we also studied the cell



In order to maintain steady oxygen chemical potentials at the electrodes, corresponding gases (oxygen, air or nitrogen) were supplied into the electrode volume continuously. The oxygen concentration in the nitrogen flux was measured using a Zirkon-M gas-analyzer. During the investigations, a modification of the EMF method proposed by Gorelov [16, 19] was used to eliminate an effect of the electrode polarization resistance on the ion transference number value measured.

## Results and discussion

According to the results of XRD studies, the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics were single phase at  $x \geq 0.08$ . The crystal lattice of the solid solutions is face-centered cubic (f.c.c.) isostructural to that of  $\delta\text{-Bi}_2\text{O}_3$ . The ceramics of  $\text{Bi}_{0.95}\text{Nb}_{0.05}\text{O}_{1.5+\delta}$  consists of two phases:  $\alpha$ - and  $\delta$ - $\text{Bi}_2\text{O}_3$ . This is in excellent agreement with the phase diagram of the  $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$  oxide system [20]. The parameters of the solid solution unit cells are presented in Table 1. The unit cell volume decreases regularly with increasing niobium concentration.

**Table 1** Properties of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics.  $\rho_{\text{exp}}$ , density of ceramics;  $\rho_{\text{theor}}$ , theoretical value of the density calculated from the XRD data;  $\bar{\alpha}$ , thermal expansion coefficient calculated from dilatometric data and averaged in the given temperature range

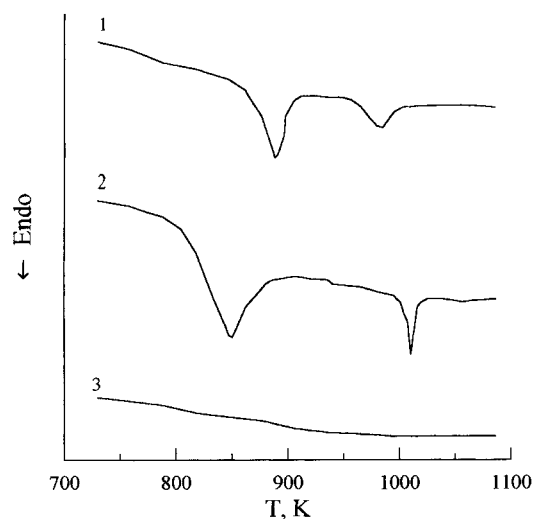
$x$	$\rho_{\text{exp}}$ , $\text{kg/m}^3$	$\frac{\rho_{\text{exp}}}{\rho_{\text{theor}}}$ , %	Parameter of the unit cell $a$ , nm ( $\pm 0.0001 \text{ nm}$ )	Mean values of thermal expansion coefficient	
				$T$ , K	$\bar{\alpha} \times 10^6$ , $\text{K}^{-1}$
0.05	8030		0.5489	300–700	$14.5 \pm 0.7$
0.08	7860	90	0.5531	300–700	$12.6 \pm 0.5$
				700–1020	$26 \pm 1$
0.10	7990	90	0.5514	300–680	$10.7 \pm 0.6$
				680–1040	$20.6 \pm 0.2$
0.16	7840	91	0.5499	300–700	$10.3 \pm 0.6$
				700–1040	$17.5 \pm 0.5$

Thermal effects observed in the DTA curves of  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  are consistent with the phase diagram [20]. The following endothermic effects determined by DTA in a heating regime should be noted particularly. Firstly, an endothermic effect was observed for  $\text{Bi}_{0.92}\text{Nb}_{0.08}\text{O}_{1.5+\delta}$  at  $996 \pm 1 \text{ K}$ , whereas the  $\text{Bi}_{0.90}\text{-Nb}_{0.10}\text{O}_{1.5+\delta}$  powder demonstrates no effects in the subsolidus temperature range (Fig. 1). As 996 K is close to the  $\alpha \rightarrow \delta$  phase transition temperature [20], this suggests that the  $\delta$ -phase of  $\text{Bi}_{0.92}\text{Nb}_{0.08}\text{O}_{1.5+\delta}$  is not completely stabilized. Secondly, endothermic effects were found at 858 K for  $\text{Bi}_{0.95}\text{Nb}_{0.05}\text{O}_{1.5+\delta}$  and at 804 K for  $\text{Bi}_{0.92}\text{Nb}_{0.08}\text{O}_{1.5+\delta}$ . These DTA peaks may be ascribed to the phase transition associated with the disordering oxygen sublattice [7, 10]. Thus, the minimum concentration of niobium oxide which is necessary to stabilize the  $\delta$ -phase of  $\text{Bi}_2\text{O}_3$  in the high-temperature range corresponds to 10 mol%.

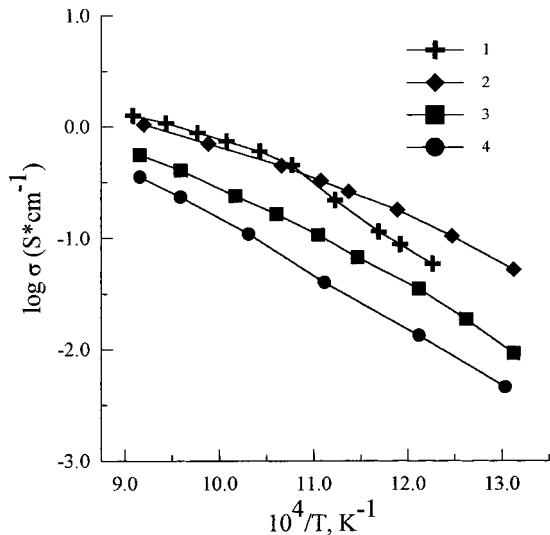
Electrical conductivity of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics (Fig. 2) correlates well with the XRD data. The  $\alpha \rightarrow \delta$  phase transition with increasing temperature leads to a sharp increase in the conductivity of  $\text{Bi}_{0.95}\text{Nb}_{0.05}\text{O}_{1.5+\delta}$ . A maximum in the electrical conductivity at temperatures below 900 K was found for the  $\text{Bi}_{0.92}\text{Nb}_{0.08}\text{O}_{1.5+\delta}$  ceramics. Further increase in the niobium concentration results in decreasing conductivity. In order to calculate the activation energy for electrical conductivity, we used the standard model [21]:

$$\sigma = \frac{A_0}{T} \cdot \exp\left[-\frac{E_a}{RT}\right] \quad (3)$$

where  $\sigma$  is the specific electrical conductivity,  $A_0$  is the pre-exponential factor, and  $E_a$  is the activation energy. Regression parameters obtained by fitting of the experimental data are presented in Table 2. The activation energy for electrical conductivity of  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  at  $x \geq 0.08$  increases with increasing niobium content.



**Fig. 1** DTA curves of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  powders in air:  $x = 0.05$  (1), 0.08 (2), 0.10 (3)



**Fig. 2** Temperature dependence of the electrical conductivity of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics in air:  $x = 0.05$  (1),  $0.08$  (2),  $0.10$  (3),  $0.16$  (4)

Such behavior conforms well with both the hypothesis that conductivity of solid solutions with f.c.c. structure is proportional to the crystal lattice parameter (i.e. is determined by the size of the oxygen ion transfer channels) and the notion that ionic transport in the  $\delta\text{-Bi}_2\text{O}_3$ -based oxides decreases with increase in the stabilizing dopant concentration owing to the stronger bond of the dopant cations with oxygen anions [2, 22].

The studies of the oxygen ion transference numbers ( $t_0$ ) suggest that the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  solid solutions prepared are predominantly ionic conductors (Table 3). At high oxygen partial pressures, the electronic transference numbers of the ceramics at  $x \geq 0.08$  are less than 0.1. Notice that the values of  $t_0$  determined using the cell (Eq. 2) represent only a qualitative estimation, as the oxygen partial pressure gradient is excessively large in this case [21]. The results of the oxygen ion transference number measurements are in agreement with the oxygen pressure dependence of the conductivity presented in Fig. 3. The conductivity of  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  decreases with decreasing oxygen concentration in the gas phase. This may indicate a presence of a p-type electronic component of the conductivity in air [21]. For the

**Table 2** Regression parameters of temperature dependence of electrical conductivity for the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics in air.  $E_a$ , activation energy for electrical conductivity;  $\rho$ , correlation coefficient

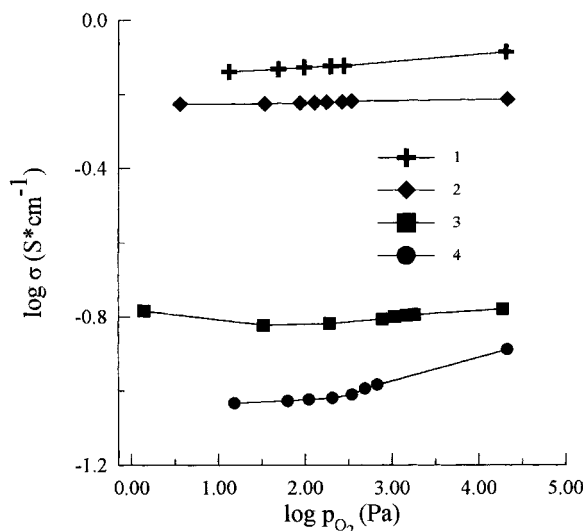
$x$	$T$ , K	$E_a$ , kJ/mol	$\ln(A_0)$ (S/m)	$\rho$
0.05	810–930	$121 \pm 9$	$26 \pm 1$	0.998
	930–1100	$58 \pm 4$	$18.3 \pm 0.6$	0.997
0.08	760–840	$90 \pm 2$	$22 \pm 3$	0.9992
	840–1100	$62 \pm 3$	$18.6 \pm 0.4$	0.9991
0.10	760–1100	$93 \pm 4$	$21.3 \pm 0.7$	0.997
0.16	760–1100	$101 \pm 2$	$21.8 \pm 0.3$	0.9998

**Table 3** Oxygen ion transference numbers of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics. The cells (1 and 2) refer to the oxygen concentration cells described by Eqs. 1 and 2, respectively. The table contains the ion transference number values and their errors calculated according to [20]

$x$	$T$ , K	Cell	$t_0$
0.08	950	1	$0.95 \pm 0.01$
	950	2	$0.79 \pm 0.02$
0.10	950	1	$0.97 \pm 0.03$
	950	2	$0.94 \pm 0.03$
	923	1	$0.98 \pm 0.04$
	860	1	$0.96 \pm 0.02$
0.16	950	1	$0.96 \pm 0.01$
	950	2	$0.92 \pm 0.04$

$\text{Bi}_{0.92}\text{Nb}_{0.08}\text{O}_{1.5+\delta}$  and  $\text{Bi}_{0.90}\text{Nb}_{0.10}\text{O}_{1.5+\delta}$  ceramics, the ratio of the conductivity decrease to the total conductivity value in air is close to the electronic transference numbers determined by the e.m.f. method. For  $\text{Bi}_{0.84}\text{Nb}_{0.16}\text{O}_{1.5+\delta}$ , however, the decrease in conductivity with decreasing oxygen partial pressure is much larger, which can be ascribed to the ordering of the oxygen sublattice [7, 8].

The temperature dependencies of the relative elongation of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics (Fig. 4) are characteristic of most  $\delta\text{-Bi}_2\text{O}_3$ -based solid solutions [15] and can be adequately approximated by two linear segments in the ranges 300–700 K and 700–1100 K. A sharp increase in the thermal expansion coefficients (TECs) at temperatures above 700 K is probably connected with increasing oxygen ion mobility [23]. This is confirmed by the correlation between the conductivity and the TEC. Mean TECs calculated from the dilatometric data are in the range  $(10.3\text{--}14.5) \times 10^{-6} \text{ K}^{-1}$



**Fig. 3** Dependence of electrical conductivity of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics with  $x = 0.05$  (1),  $0.08$  (2),  $0.10$  (3),  $0.16$  (4) on the oxygen partial pressure at  $947 \pm 2 \text{ K}$

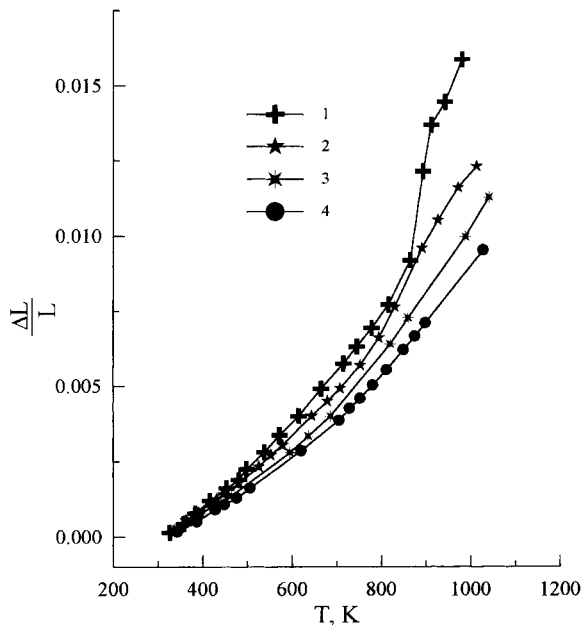


Fig. 4 Temperature dependence of relative elongation of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics in air:  $x = 0.05$  (1),  $0.08$  (2),  $0.10$  (3),  $0.16$  (4)

at 300–700 K and  $(17.5\text{--}26.0) \times 10^{-6} \text{ K}^{-1}$  at 700–1100 K (Table 1).

Figure 5 presents the isothermal dependence of the conductivity of  $\text{Bi}_{0.90}\text{Nb}_{0.10}\text{O}_{1.5+\delta}$  on time at 883 K. For comparison, we also show the data on the  $\text{Bi}(\text{Zr}, \text{Y})\text{O}_{1.5+\delta}$  solid solutions, the properties of which have been reported earlier [14]. The decrease in conductivity with time at temperatures below 900 K is typical of ionic conductors based on bismuth oxide and is caused by the phase changes of the materials [8, 9, 11]. Thus, further modification of the  $\text{Bi}(\text{Nb})\text{O}_{1.5+\delta}$  solid solutions is required in order to enhance their stability at moderate temperatures.

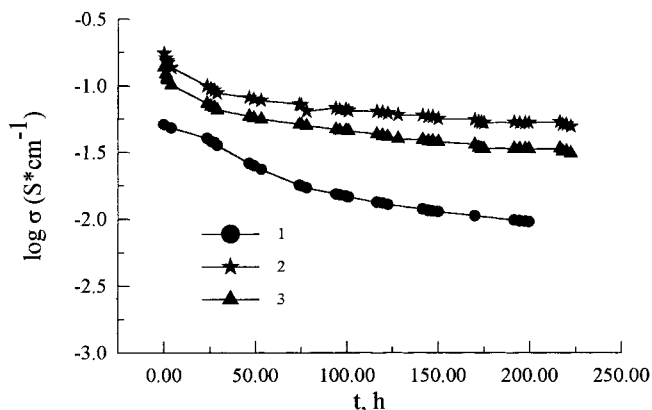


Fig. 5 Time dependence of conductivity at  $873 \pm 1 \text{ K}$ :

- 1  $\text{Bi}_{0.90}\text{Nb}_{0.10}\text{O}_{1.5+\delta}$
- 2  $(\text{Bi}_{0.95}\text{Zr}_{0.05})_{0.85}\text{Y}_{0.15}\text{O}_{1.5+\delta}$
- 3  $(\text{Bi}_{0.93}\text{Zr}_{0.07})_{0.85}\text{Y}_{0.15}\text{O}_{1.5+\delta}$

## Conclusions

The minimum concentration of niobium to stabilize the fluorite-type f.c.c. phase in the  $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$  oxide system at temperatures below 996 K was found to be about 10 mol%. Electrical conductivity as well as thermal expansion of the  $\text{Bi}(\text{Nb})\text{O}_{1.5+\delta}$  solid solutions decrease with increasing niobium content. The ceramics of  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  are predominantly ionic conductors, but the presence of p-type electronic conductivity is characteristic of these materials in air. It was established that the electron transference number values of the  $\text{Bi}(\text{Nb})\text{O}_{1.5+\delta}$  solid solutions in air are less than 0.1. Thermal expansion coefficients were calculated from the dilatometric data to be  $(10.3\text{--}14.5) \times 10^{-6} \text{ K}^{-1}$  at 300–700 K and  $(17.5\text{--}26.0) \times 10^{-6} \text{ K}^{-1}$  at 700–1100 K. Annealing at temperatures below 900 K results in a sharp decrease in conductivity of the  $\text{Bi}_{1-x}\text{Nb}_x\text{O}_{1.5+\delta}$  ceramics; further doping is necessary in order to improve stability of the  $\delta\text{-Bi}_2\text{O}_3$ -like phase.

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