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Synthesis, Structure and Functional Characteristics of Solid Electrolytes Based on Lanthanum Niobates

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***Abstract*—**The solid solutions of lanthanum niobates substituted by yttrium, bismuth and tungsten were synthesized. The structure of the solid solutions is either $LaNbO_4$-based monoclinic or $BiNbO_4$-based triclinic. The series where niobium is substituted by tungsten on B site reveals phase-modulated structure. The values of cell parameters decrease with increasing the dopant concentration for all samples except the tungsten series although the latter show higher total conductivity.

***Keywords*—**Impedance spectroscopy, $LaNbO_4$, lanthanum ortho-niobates.

I. Introduction

RARE earth ortho-niobates with the general formula $LnNbO_4$ (Ln = lanthanide) have been widely studied due to their potential use as ferroelectric, phosphors or laser materials [1]-[8]. These materials have also been proposed as potential ionic conductors concerning two phases especially: a high temperature tetragonal scheelite phase and a low temperature monoclinic fergusonite phase which can be considered as a distorted version of the scheelite structure.

The electro-transport properties can be modified by doping of complex oxides such as $LnMO_{4\pm\delta}$ by various cations. Such substitution can be done in two ways: by substitution in the A sublattice (rare earth element Ln); or by substitution in the B sublattice (pentavalent cation). Recently, combinations of A- and B-site co-doping were studied as a further route towards enhancing the electrical conductivity [1]. Various double-substituted compositions have been studied such as those involving 1% Ca, Ga, Ba, Sr for A-site doping and 1% Ga, Ge, Ti, Al for B-site doping [1]-[3].

It has been shown [2] that for a number of dopants the limit of solid solutions formation is very low – such series as $LaNb_{1-x}M_xO_{4-\delta}$, where M = Ga, Ge, Si, Al, B, P, Zr, Ti, are single-phase only at $x\leq0.03$. On the contrary the iso-valence substituton results in formation of solid solutions up to $x=0.3$ [3]. The compounds are crystallized in either fergusonite (Sp.Gr. $I2/c$), or sheelite (Sp.Gr. $I41/a$) structure.

As it has been described in [4], [5], $LnMO_{4\pm\delta}$ solid solutions in a humid atmosphere are good protonic conductors, and increasing the concentration of oxygen vacancies should not only contribute to the oxygen-ionic, but also to protonic transport. The introduction of electron-acceptor ion will lead to an increase in the concentration of oxygen vacancies and an increase in both types of conductivity. The introduction of the electron-donor ion also improves the ionic transport by oxygen ions in interstitial positions, reducing the electronic contribution to electrical conductivity and the total change in the electronic structure of the conductor [6], [7].

Reference [7] studied the compositions $LnNbO_4$ and $LnNb_{0.92}W_{0.08}O_{4.04}$, where Ln = La, Pr, Nd. For the tungsten-substituted sample $LaNb_{0.92}W_{0.08}O_{4.04}$ the super-structure reflections characteristic for a modulated structure were revealed by X-ray analysis. Besides, the presence of the modulated structure was confirmed by the electron diffraction method. The sample $LaNb_{0.92}W_{0.08}O_{4.04}$ showed the highest electrical conductivity among the studied compositions. According to [8], the $LaNb_{0.84}W_{0.16}O_{4.08}$ also reveals the super-structure ordering and is a promising composition for use in fuel cells. Its total conductivity value is 0.1 $S\times cm^{-1}$ at 1273 K which is comparable with the conductivity value of yttrium-stabilized zirconia. Insignificant electronic component of the electrical conductivity is detected only at low oxygen partial pressure ($P_{O2}<10^{-22}$ atm). In general, the tungsten-substituted samples reveal conductivity 2-4 orders of magnitude higher than that of the parent compound.

II. Experimental

The solid solutions $La_{1-x}M_xNbO_4$ (M=Y, Bi; $0.1\leq x\leq1.0$; $\Delta x=0.1$), $LaNb_{1-y}W_yO_{4\pm\delta}$ ($0.02\leq y\leq0.10$; $\Delta y=0.02$) were synthesized using conventional solid state technique at 873-1673 K. Phase composition and phase formation processes were controlled by means of X-Ray method (CuK_α-radiation, monochromator of pyrolytic carbon on reflected beam). High-temperature X-Ray measurements were carried out with D8 ADVANCE diffractometer. The TOPAS program package [9] was used for calculation of the cell parameters and for crystal structure refinement. Particle sizes were determined using a laser dispersion analyzer Shimadzu SALD-7101. The conductivity of the samples was investigated by impedance spectroscopy (impedancemeter Elins Z-3000) in the temperature range 1123-723 K.

III. Results and Discussion

According to the X-Ray data the solid solutions are formed

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within all chosen concentration ranges. The structure of the final product of the samples $La_{1-x}Y_xNbO_4$ ($0.0<x<0.7$), $LaNb_{1-y}W_yO_{4\pm\delta}$ (y=0.02-0.10) is monoclinic (Sp.Gr. *I*2/*b*) The samples of the $La_{1-x}Bi_xNbO_4$ series form two different solid solutions: monoclinic modification of $LaNbO_4$ (Sp.Gr. *I*2/*b*), forming solid solutions with x = 0.0-0.3, and triclinic modification of $BiNbO_4$ (Sp.Gr. *P*-1), forming solid solutions with x = 0.8-1.0.

In contrary to the $La_{1-x}Y_xNbO_4$ and $La_{1-x}Bi_xNbO_4$ solid solutions series, the $LaNb_{1-y}W_yO_{4\pm\delta}$ revealed disproportionated modulated structure, previously noted by [10]. The sample $LaNb_{0.92}W_{0.08}O_{4.04}$ shows splitting of the structure into two after a prolonged annealing (32 hours): lines of both modulated and non-modulated structures are present in the X-ray patterns. The smaller the annealing time, the larger is the concentration of the phase-modulated structure. The modulated structure can be distinguished as a single separate phase only for the composition corresponding to the formula $LaNb_{0.90}W_{0.10}O_{4.05}$. Fig. 1 shows comparison of X-ray patterns of different structure modifications and compositions.

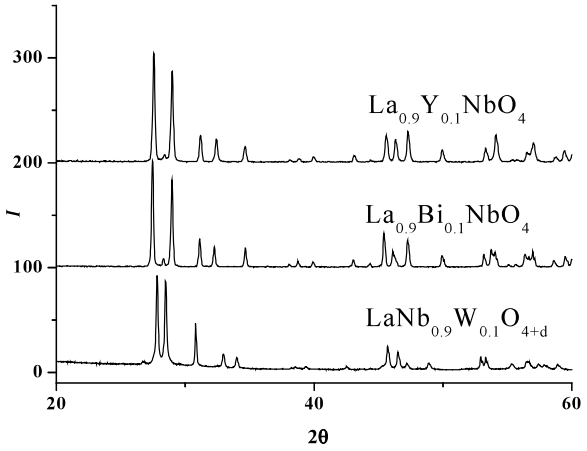

Fig. 1 X-ray patterns of $La_{0.9}Me_{0.1}NbO_{4+d}$, Me = Y, Bi and $LaNb_{0.9}M_{0.1}O_{4+d}$ M = W

For all series of solid solutions studied the unit cell parameters were calculated. The values of all cell parameters decrease with increasing the dopant concentration for all solid solution series except for the $LaNb_{1-y}W_yO_{4\pm\delta}$ one where the modulated structure appears (Fig. 2). This can be due to dimensional factor of the ions. The yttrium ion is smaller than lanthanum or bismuth, the latter two are comparable. It provides significant decrease of the cell parameters for the Y-doped lanthanum niobate. In the case of substitution of niobium by tungsten within the range of one structural modification the unit cell enlargers only along the *c* parameter. Obviously the sharp kink of the cell parameters of $LaNb_{1-y}W_yO_{4\pm\delta}$ is observed for the sample with pure modulated structure.

The phase stability of $LaNb_{0.90}W_{0.10}O_{4.05}$ was studied by means of high-temperature X-ray analysis in the range 303-1173 K. Heating of the $LaNb_{0.90}W_{0.10}O_{4.05}$ sample to the temperature higher than *ca.* 773 K results in a phase transition of the monoclinic modification to the tetragonal one. The similar phase transition at temperature *ca.* 814 K is characteristic for the parent compound $LaNbO_4$ [11], however in that case the authors revealed a small temperature range of coexistence of both structural modifications of the compound.

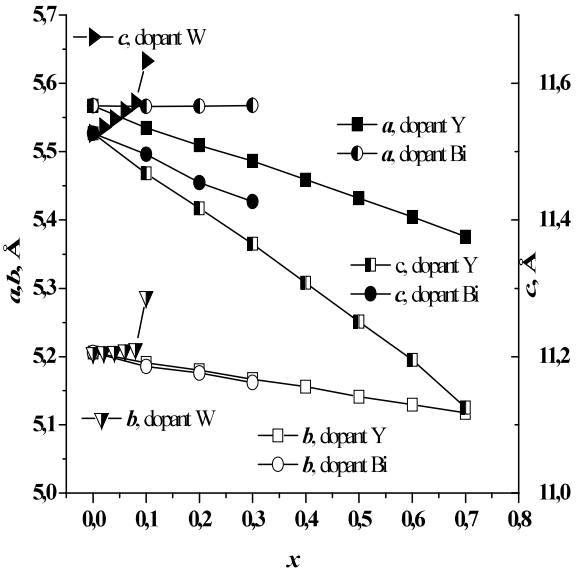

Fig. 2 Unit cell parameters of $La_{0.9}Me_{0.1}NbO_{4+d}$, Me = Y, Bi and $LaNb_{0.9}M_{0.1}O_{4+d}$ M = W *vs.* dopant concentration

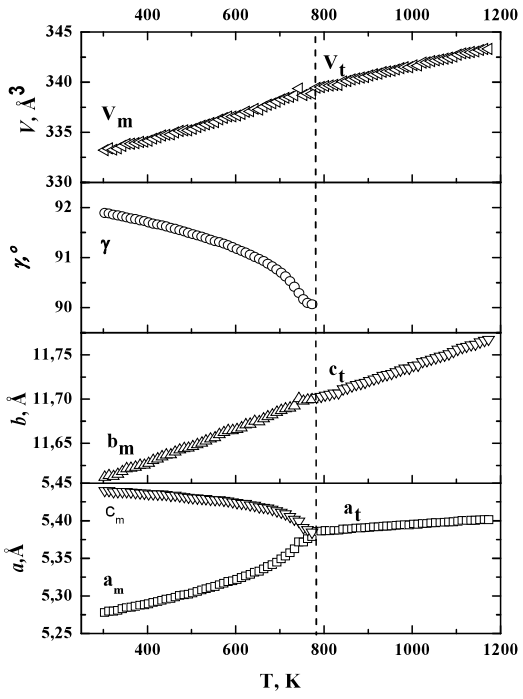

Fig. 3 Temperature dependencies of the unit cell parameters of the substituted lanthanum niobate $LaNb_{0.90}W_{0.10}O_{4.05}$ (*m* – monoclinic modification, *t* – tetragonal modification)

Fig. 3 shows change of the unit cell parameters of $LaNb_{0.90}W_{0.10}O_{4.05}$ while heating. The phase transition from monoclinic to tetragonal modification starts already at *ca.* 593 K. It is characterized by changing of *a* and *c* parameters to become equal, as well as approaching of the γ-angle to 90°. Besides, the phase transition temperature lowers with increasing of the dopant concentration in the solid solutions.

The grain sizes of the powder samples were estimated by means of laser diffraction, optic and electronic microscope methods. The average grain sizes were determined to be in the range 0.5-14 μm. The maximum of the distribution is around 5 μm for all solid solutions studied.

The SEM image of the cross-section of the ceramic sample is shown in Fig. 4. It is clearly observed that the ceramic pellet exhibits a fairly dense microstructure with an average grain size in the range of 5-10 μm.

To study the electrical conductivity of the solid solutions, the powders were pressed into pellets and sintered at 1520 – 1670 K. Typical impedance plots at different temperatures are show in Fig. 5 for the $La_{0.9}Y_{0.1}NbO_4$ sample as an example. It is well seen that the shape of the plots changes with temperature. Normally in the temperature range studied the impedance plot reveals one or two resolved semi-circles which are characteristic of the sample resistance and electrode processes. The can be described by the equivalent electrical circuit consisting of R1 and R2 resistances together with the CPE elements. It describes total resistance of the sample, i.e. the sum of bulk and grain boundary components. The electrode processes were not analyzed in the present work. The shape of the equivalent electrical circuits is generally in accordance with other studies [12].

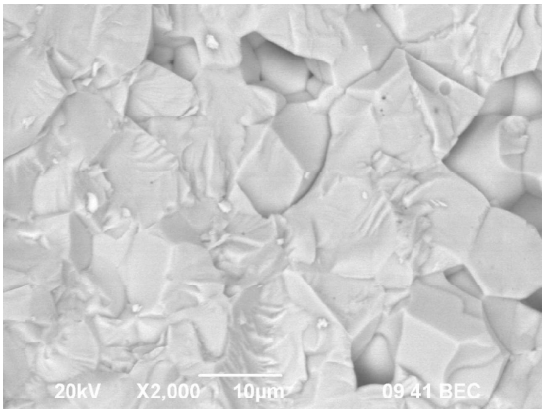

Fig. 4 SEM micrograph of the cross-section of ceramics $LaNb_{0.9}W_{0.1}O_{4.05}$ sintered at 1673 K

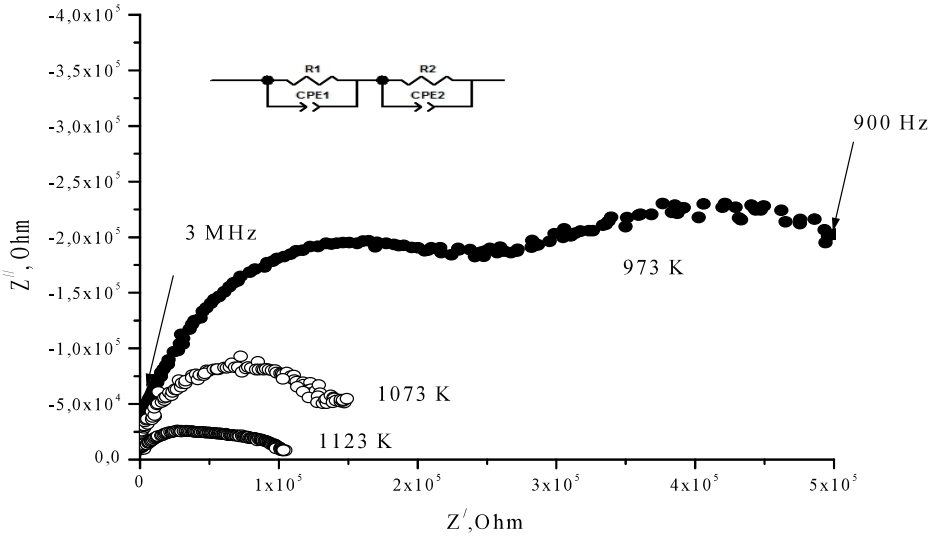

Fig. 5 Impedance plots of the $La_{1-x}Bi_xNbO_4$ (x=0.3) compositions

According to the results of impedance measurements the temperature dependencies of the total conductivity in the coordinates -lg(σ) - 1000/T were plotted (Fig. 6). General view of the temperature dependence of total electrical conductivity of the solid solutions studied is linear and typical for ionic conductors.

The value of the total electrical conductivity and the general shape of the plots are quite sensitive to the dopant nature and their concentration in the samples. Thus the $LaNb_{1-y}W_yO_4$ solid solutions show higher electrical conductivity among the three studied solid solutions series (Fig. 6). Moreover, increasing dopant concentration results in increase of the conductivity of the sample.

The most significant increase of the conductivity values is observed for the solid solutions doped with tungsten. It the case of yttrium or bismuth- substituted samples the plots reveal a parabolic-like shape (Fig. 7).

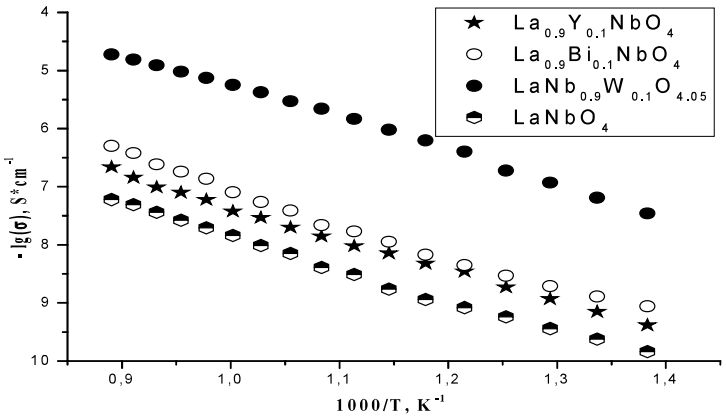

Fig. 6 The temperature dependence of the electrical conductivity of different compositions

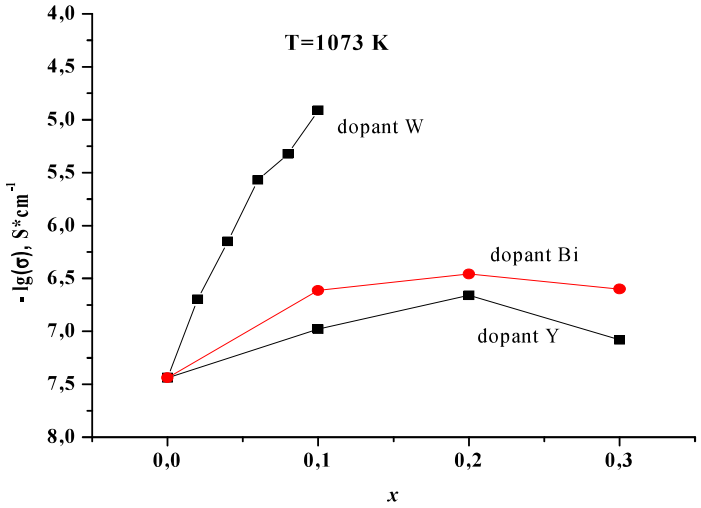

Fig. 7 Electrical conductivity values *vs.* dopant concentration of different compositions

The observed activation energy change with the temperature change is associated with the phase transition of substituted lanthanum niobate from monoclinic to tetragonal structure. Increasing of tungsten content results in decreasing of activation energy and also decreasing of the phase transition temperature. It is in a good agreement with structure characterization studies (Table I).

TABLE I
ACTIVATION ENERGY VALUES AND PHASE TRANSITION TEMPERATURES OF $LaNb_{1-x}W_xO_{4+D}$

Composition, *x* value	E_{act}±0.05 ($T>T_{transition}$, eV)	E_{act}±0.05 ($T<T_{transition}$, eV)	$T_{transition}$, K
0	1.16	1.39	950
0.02	1.24	1.40	950
0.04	1.18	1.29	920
0.06	1.15	1.26	930
0.08	1.13	1.25	910
0.10	0.99	1.23	910

IV. CONCLUSION

The solid solutions series $La_{1-x}M_xNbO_4$ (M=Y, Bi; $0.1\leq x\leq 1.0$), $LaNb_{1-y}W_yO_{4\pm\delta}$ ($0.02\leq y\leq 0.10$). The structure of the samples $La_{1-x}Y_xNbO_4$ and $LaNb_{1-y}W_yO_{4\pm\delta}$ within the whole concentration range is monoclinic (Sp.Gr. *I*2/*b*). The solid solutions $La_{1-x}Bi_xNbO_4$ are based on monoclinic modification of $LaNbO_4$ (Sp.Gr. *I*2/*b*, x = 0.0-0.3), or on triclinic modification of $BiNbO_4$ (Sp.Gr. *P*-1, x = 0.8-1.0). The composition $LaNb_{0.90}W_{0.10}O_{4.05}$ corresponds to the concentration threshold of stabilization of the modulated monoclinic modification of $LaNb_{1-x}W_xO_{4\pm d}$. The $LaNb_{1-x}W_xO_{4\pm d}$ monoclinic samples undergo phase transition at 910-950 K, increasing o dopant concentration is accompanied by decrease of the phase transition temperature. The value of the total electrical conductivity and the general shape of the plots are sensitive to the dopant concentration in the samples. Increasing dopant concentration results in increase of the conductivity of the sample.

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