Mixed conductivity in $\text{La}(\text{Ga},\text{Mg},\text{Nb})\text{O}_{3-\delta}$ Perovskites

V.V.KHARTON¹, *, A.P.VISKUP¹, G.C.MATHER², A.A.YAREMCHENKO¹, E.N.NAUMOVICH¹, F.M.B.MARQUES²

¹Institute of Physicochemical Problems, Belarus State University, 14 Leningradsкая Str., Minsk 220080, Republic of Belarus

²UIMC, Departamento de Eng.Cerâmica e do Vidro, Universidade de Aveiro, 3810 Aveiro, Portugal

Solid-solution formation has been found in the perovskite-type system $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ ($x = 0 - 0.20$). Increasing dopant concentration leads to lower oxygen ionic conductivity and, at temperatures above 1000 K, higher p-type electronic conductivity. Oxygen-ion transference numbers in air were determined to vary in the range 0.78 to 0.96, decreasing with increasing x and temperature. Thermal expansion coefficients of ceramic samples of $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ were calculated in a temperature range of 300 to 1100 K to be essentially independent of composition, varying in the range $(10.0 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$. Values of the activation energy for the total electrical conductivity in air are 104-106 kJ/mol in the temperature range 670 – 1000 K and 67 – 76 kJ/mol in the temperature range 1000 – 1200 K. The method of synthesis was found to affect both the symmetry of the perovskite unit cell and phase composition. The presence of second phases led to a dramatic decrease in conductivity.

Key words: lanthanum gallate, perovskite, ceramic synthesis, mixed conductor, transference number

Conductividad mixta en perovskitas de $\text{La}(\text{Ga},\text{Mg},\text{Nb})\text{O}_{3-\delta}$

Se ha encontrado la formación de una solución sólida en el sistema $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ ($x = 0 - 0.20$). Un aumento de la concentración de dopante lleva a una menor conductividad iónica de oxígeno y a temperaturas superiores a 1000 K, una mayor conductividad electrónica de tipo p. El número de transferencia del ión oxígeno en aire fue determinado y varía en el rango 0.78 a 0.96 disminuyendo con el aumento de x y de la temperatura. El coeficiente de expansión térmico de las muestras cerámicas de $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ fue calculado en el rango de temperatura de 300 a 1100 K siendo independiente de la composición, y variando en el rango $(10.0 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$. Los valores de la energía de activación para la conductividad eléctrica total en aire son 104-106 KJ/mol en el rango de temperatura 670-1000 K y 67-76 kJ/mol en el rango de temperaturas 1000-1200 K. Se encontró que el método de síntesis afecta tanto a la simetría de la celda unidad de la red perovskita como a la composición de fases. La presencia de fases secundarias lleva a la disminución dramática de la conductividad.

Palabras clave: Galato de Lantano, perovskita, síntesis cerámica, conductores mixtos, número de transferencia

1. INTRODUCTION

Perovskite-like solid solutions derived from lanthanum gallate, LaGaO_3 , are of significant interest for electrochemical applications such as solid oxide fuel cells (SOFCs), oxygen sensors, and ceramic membranes for oxygen separation and partial oxidation of hydrocarbons (1-7). Among the advantages of LaGaO_3 – based solid electrolytes and mixed ionic-electronic conductors are their stability under a wide range of oxygen partial pressures, a high oxygen-ion mobility, and relatively low thermal expansion coefficients (TECs) comparable to that of stabilized zirconia. Significant levels of oxygen ionic conductivity can be achieved in lanthanum gallate by substituting lanthanum with alkaline-earth elements (Sr, Ca, Ba) and/or incorporating bivalent metal cations (e.g. Mg) into the gallium sublattice in order to increase the oxygen-vacancy concentration. Introduction of cations with variable valence, such as cobalt or nickel, into the B sites of the ABO_3 perovskite lattice in $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ may also result in greater ionic conductivity (2,3,6). Electronic conduction in LaGaO_3 – based oxides also increases with a greater concentration of transition-metal cations (2-7); such doping can, therefore, be considered as a promising strategy for obtaining mixed-conductive materials

for oxygen-separation membranes (5-7). In addition, B-site doping is expected to reduce volatilisation of gallium oxide during sintering, which is characteristic of the gallate ceramics (1). Substitution of gallium with magnesium may also be preferable to incorporation of alkaline-earth cations into the A sublattice, given the reactivity of the strontium-containing perovskites with gaseous species such as water vapour and CO_2 (6-8). In an attempt to both reduce the Ga content in lanthanum gallate and determine the effect of simultaneous doping with Nb and Mg on the electrical properties, we have synthesised compositions in the system $\text{LgGa}(\text{Mg},\text{Nb})\text{O}_{3-\delta}$. Here, we report on the transport properties in this series, and the effect of preparation conditions on symmetry, phase composition and electrical properties.

2. EXPERIMENTAL PROCEDURE

Solid-state synthesis of $\text{LaGa}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ (LGMN0), $\text{LaGa}_{0.75}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_{0.10}\text{O}_{3-\delta}$ (LGMN1) and $\text{LaGa}_{0.65}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_{0.20}\text{O}_{3-\delta}$ (LGMN2) was performed

employing two different preparation routes. The first method, referred to hereafter as Method I, involved mixing stoichiometric amounts of high-purity lanthanum nitrate, magnesium acetate, and niobium and gallium oxides, with subsequent thermal decomposition of the metal salts. The oxide mixtures were then annealed in air in a temperature range of 1520–1670 K for 35–40 h with 7 intermediate regrindings and pressed (350–500 MPa) into disks of various thickness (diameter of 12 and 15 mm) and bars (4 × 4 × 30 mm); final firing was performed in air at 1800–1850 K for 6–10 hours. In the second preparation method, Method II, stoichiometric mixtures of the binary-metal oxides were firstly pre-reacted at 1370 K then pressed into disks and sintered at 1870 K for 6–20 hours. Method II was used to prepare samples of LGMN0 and LGMN2. Physicochemical and structural characterisation of the reaction products was carried out by XRD, X-ray fluorescence analysis (XFA), scanning electron microscopy (SEM), emission spectroscopic analysis, infrared (IR) absorption spectroscopy, thermal gravimetric analysis (TGA) and dilatometry. Details of experimental procedures and equipment have been reported elsewhere (4,6–10); included in these references is a description of the determination of oxygen-ion transference numbers by the e.m.f. method and Faradaic efficiency studies.

In the case of samples prepared by Method II, the crystal structures of phases LGMN0 and LGMN2 were refined from X-ray powder diffraction data by the Rietveld method using the program FULLPROF [11]. Diffraction data were collected on a Rigaku Geigerflex diffractometer (CuK_α radiation) over the range $10^\circ \leq 2\theta \leq 110^\circ$ using a stepwidth of 0.02° ; collection time was approximately 10h. The total electrical conductivity was measured in air by ac impedance spectroscopy using an HP 4284A analyser with a frequency range of 20 Hz to 1 MHz in a temperature range of 370–1270 K; constant-frequency measurements were also conducted with this apparatus (4,8,9). The partial electronic and ionic conductivities were calculated from the data on total electrical conductivity and ion transference numbers, measured by the e.m.f. and Faradaic efficiency methods.

3. RESULTS AND DISCUSSION

3.1. Phase composition and crystal structure

The XRD powder patterns of $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})\text{O}_{3-\delta}$ prepared by Method I showed the formation of perovskite-type phase within the studied composition range ($x = 0 - 0.20$). The crystal structure of these oxides was identified as rhombohedrally distorted; lattice parameters (a and a) are listed in Table 1. The unit cell volume increases with increasing x as a result of the larger ionic radii of Mg^{2+} and Nb^{5+} cations compared to Ga^{3+} . The powder patterns of all materials synthesised by Method I exhibited traces of impurity phase: La_2O_3 for LGMN0, and La_2O_3 and MgO for both LGMN1 and LGMN2. In addition, one unidentified reflection was observed at $2\theta = 38.05 - 38.25$ (CuK_α -radiation) in the XRD patterns of all compositions. The intensity of these additional peaks did not exceed 1–2 % of the intensity of the strongest reflection of the perovskite phase. These impurity phases are, most probably, the result of incomplete solid-state reaction (12), and are assumed not to affect the transport properties to any significant extent.

The second phases identified in the XRD powder patterns of compositions synthesised by Method II were different to those

TABLE 1. PROPERTIES OF $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})\text{O}_{3-\delta}$ CERAMICS PREPARED BY METHOD I.

x	Unit cell parameters		Activation energy for electrical conductivity		Average TECs $\bar{\alpha} \times 10^6, \text{K}^{-1}$ (300–1100 K)
	a, Å	$\alpha, ^\circ$	T, K	$E_a, \text{kJ/mol}$	
0	5.526	60.17	670–950 950–1180	104 ± 2 67 ± 4	10.1 ± 0.1
0.10	5.541	60.08	760–950 950–1170	106 ± 3 76 ± 4	9.9 ± 0.1
0.20	5.546	60.12	760–1030 1030–1190	105 ± 4 74 ± 5	9.9 ± 0.1

found for Method I. This time, the impurities were identified as MgO for LGMN0 and MgGa_2O_4 for LGMN2; their amounts were also higher than that found for the phases prepared by Method II, particularly in the case of LGMN0 (the most intense MgO peak was 6.5% of the intensity of I_{max}). These results are consistent with reports in the literature which have indicated that there is a significant dependence of the phase composition of LaGaO_3 -based ceramics on the synthesis and processing conditions employed. Djurado et.al. (12), for example, have shown that to obtain single-phase perovskite from the binary oxides using 2–3 sintering-regrinding cycles is problematic.

Further inspection of the powder patterns of the Method II compositions indicated that, in both LGMN0 and LGMN2, the main perovskite phase was similar to undoped LaGaO_3 with the orthorhombic GdFeO_3 -type structure. The structural parameters of LaGaO_3 (S.G.: Pnma) were, thus, used as starting parameters for the Rietveld refinements of LGMN0 and

TABLE II A. STRUCTURE REFINEMENT DATA FOR LGMN0 PREPARED BY METHOD II.

Atom	Position	x/a	y/b	c/z	B ($\text{\AA}^2$)	Site
La	4c	0.0054(5)	0.25	-0.0017(6)	0.84(2)	1.0(-)
Ga/Mg	4b	0	0	0.5	0.53(3)	0.85/0.15(-)
O(1)	4c	-0.027(4)	0.25	0.433(3)	0.4(2)	0.975(-)
O(2)	8d	0.256(7)	0.460(2)	-0.267(3)	0.4(2)	1.95(-)

S.G: Pnma; $a = 5.5180(3)$, $b = 7.8394(5)$, $c = 5.5494(3)$ Å; $R_p = 6.81\%$, $R_{wp} = 10.3$, $R_{exp} = 9.62$, $\chi^2 = 1.16$.

TABLE II B.

Selected bond lengths (in Å)		Selected angles	
La-O(2)	$3.08(2) \times 2$	O(1)—Ga/Mg—O(1)	180
La-O(2)	$2.93(2) \times 2$	O(1)—Ga/Mg—O(2)	$93.7(7) \times 2$
La-O(2)	$2.61(2) \times 2$	O(1)—Ga/Mg—O(2)	$91.1(7) \times 2$
La-O(2)	$2.50(3) \times 2$	O(1)—Ga/Mg—O(2)	$88.9(7) \times 2$
La-O(1)	$2.96(2) \times 2$	O(1)—Ga/Mg—O(2)	$86.3(7) \times 2$
La-O(1)	$2.42(2)$	O(2)—Ga/Mg—O(2)	180×2
La-O(1)	$2.61(1)$	O(2)—Ga/Mg—O(2)	$91.6(1) \times 2$
		O(2)—Ga/Mg—O(2)	$88.4(1) \times 2$
Ga-O(2)	$2.03(2) \times 2$		
Ga-O(2)	$1.94(3) \times 2$		
Ga-O(1)	$2.000(4) \times 2$		

LGMN2. The profile was described by a Pseudo-Voigt profile-shape function and four asymmetry parameters to describe peaks below $2\theta = 40^\circ$; the background was interpolated linearly from a suitable number of points. For LGMN0, the main MgO reflections were excluded from refinement. In neither case were there reflections at low angles which may have indicated supercell formation as a result of B-cation order. The Ga, Mg and Nb cations were, thus, disordered over the B-cation site and given a common isothermal temperature factor (ITF). For both phases, the oxygen-vacancy concentration was averaged over the O(1) and O(2) sites and remained invariant since correlation of the oxygen content and thermal vibration factors led to unreasonable values. In the case of LGMN2, refinement of the ITF's of both the B cations and oxygens resulted in very low or negative values. As MgGa_2O_4 is present as an impurity phase in this composition, it is likely that the true B-cation content is richer in Nb than that of the nominal composition. The ITF's of both the B-cations and oxygens were, therefore, fixed at sensible values. It is probable that these further restrictions and compositional inaccuracies in the refinement of LGMN2 are the reason for the higher final R-factors in this case: $R_p = 6.81$ and $R_p = 12.1$ for LGMN0 and LGMN2, respectively. The final refined structural data and bond distances and angles are given in Tables 2 (LGMN0) and 3 (LGMN2); the observed and difference diffraction patterns of LGMN0 are shown in Fig. 1.

The BO_6 octahedra in LGMN0 are relatively regular (ave. B-O bond distance = $1.99\text{\AA}$); the A cations sit in distorted 12-coordinate sites (bond length ranges from 2.42 to $3.08\text{\AA}$) as a result of the partial collapse of the structure associated with tilting and rotating of the BO_6 octahedra. The unit cell of LGMN2 is larger than that of LGMN0, as was found for the compositions prepared by Method I. The expansion of the orthorhombic unit cell takes place along *a*; *b* and *c* are practically equivalent in both compositions. The BO_6 octahedra in LGMN2 are distorted much more than in LGMN0, with B-O bond lengths ranging from 1.61 to $2.39\text{\AA}$; the average B-O bond length ($2.01\text{\AA}$) is, however, typical for BO_6 octahedra. The distortion in the cubooctahedral A-site is also much greater in LGMN2: La-O bond lengths in LGMN2 range from 2.33 to $3.21\text{\AA}$.

Fig.1. Observed and difference diffraction profiles of LGMN0 prepared by Method II.

3.2. Effect of solid-state synthesis procedure on electrical properties

The temperature dependence of the total electrical conductivity in the oxide system $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66-x})\text{O}_{3-\delta}$ is shown in Fig.2; data for samples synthesised by both methods are presented. It can be seen that the conductivity of the materials prepared by Method II is significantly lower than that of the Method-I materials. For LGMN2, the difference in conductivity values between samples synthesised by the two methods is as high as an order of magnitude; samples prepared by Method II also have a lower activation energy for the electrical conductivity. In view of the presence of MgO second phase observed in the latter composition by XRD, it is probable that there is a lower concentration of dissolved magnesium than the Method-I analogue as a result of a lower number of grinding-annealing cycles and shorter sintering time. As a rule, the free energy of formation of perovskite-type LnBO_3 - based solid solutions (Ln is rare-earth element; B = Co, Mn, Cr) decreases on doping with bivalent elements such as Sr, Ca or Mg (13). Perovskite with a lower dopant concentration is, therefore, likely to form in the early stages of solid-state reaction. Hence, when an insufficient number of grinding-annealing cycles is employed, the amount of impurity phase is higher, the oxygen-vacancy concentration of the main phase is lower and ionic conductivity is substantially reduced in comparison to materials with the nominal stoichiometry. It has also been reported that the activation energy of electrical conductivity in the $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ system increases with increasing magnesium content (14,15). Since a lower activation energy was obtained for the materials prepared by Method II (Fig.2), this is further evidence that these compositions contain a lower amount of magnesium than those synthesised by Method I. Analogously, the low conductivity of LGMN2 prepared by Method II results, most probably, from the segrega-

Fig.2. Temperature dependence of the total electrical conductivity of $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66-x})\text{O}_{3-\delta}$ ceramics in air: (1) and (2), LGMN0; (3), LGMN1; (4) and (5), LGMN2. Curves (1), (3) and (4) correspond to samples prepared by Method I; curves (2) and (5) correspond to samples prepared by Method II.

tion of MgGa_2O_4 phase and a subsequently lower oxygen-vacancy concentration in the main perovskite phase. The oxygen-vacancy content is expected to be even lower in this case than in LGMN0 (prepared by Method II) since the ratio of pentavalent niobium cations will be higher than in the formula composition as a result of the MgGa_2O_4 impurity.

Impedance spectroscopy gave further information about the quality of samples prepared by Method II; Cole-Cole plots of LGMN0 are shown in Figs. 3 (a) (598K) and (b) (548K). (It should be noted that, at temperatures above 770 K, the high-frequency part of the spectra appeared below the real axis due to inductive effects inherent to the experimental set-up). The impedance spectra revealed the presence of a significant low-frequency arc (usually identified as grain-boundary response) which contributed substantially to the total resistivity of samples prepared by Method II. Similar impedance spectra have been reported for $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_3$ electrolyte prepared by an analogous technique (16). In this case, poor transport properties in the grain boundaries were attributed to the segregation of a second Sr-rich phase (15).

Further inspection of the spectra presented in Figure 3 indicated that the low-frequency arc is the convolution product of at least two different contributions: a classical grain-boundary response and an additional element related to the presence of an insulating second phase, most probably MgO , in accordance with the XRD data. Figure 3a shows the spectrum obtained at 598 K which has been deconvoluted into different elements using a well-known regression technique developed by Boukamp (17). The open symbols describe the sum of the contributions of two high- and low-frequency RQ circuits (where

R is the resistance and Q is a pseudocapacitance) representing the bulk and grain-boundary which was, initially, assumed to describe the entire spectrum. The individual contributions of these RQ circuits are shown as a solid line. Comparison of the fit result with typical spectra obtained from ceramic bodies suggests that the high-frequency contribution is underestimated and that the low-frequency contribution is overestimated. In particular, the parameter n , which describes the deviation of the Q element from pure capacitive behaviour ($n=1$ in the case of a pure capacitance; $n < 1$ for depressed arcs), is reasonable for the high-frequency (bulk) contribution (0.94) but a value of only 0.75 for the low-frequency (grain-boundary) arc is excessively low. Consequently, the fit estimate of very similar conductivities for both bulk and grain boundary is not realistic. A more likely explanation for the impedance response is the presence of a third contribution at intermediate frequencies, related to the blocking effect of an insulating second phase (MgO). The effect of such second phases on the appearance of impedance spectra has been described in detail in previous studies on zirconia-based electrolytes, and is known to be effective in a range of frequencies between those commonly attributed to the bulk and grain-boundary responses (18). However, deconvolution of the entire spectrum into three RQ elements, again by linear regression, led to a model where the intermediate-frequency contribution was unreasonably large with respect to the high-frequency contribution. This solution is, again, somewhat unrealistic since the percentage of MgO in these samples is relatively small. As a consequence, it was considered fruitless to undertake a systematic analysis of all spectra in this manner. There is, nevertheless, substantial evidence for the presence of a third (insulating) contribution to the impedance spectra. Analogously, the apparent grain-boundary resistance observed for $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ prepared by Method II is very high, and is likely to be affected by the presence of insulating MgO or MgGa_2O_4 .

Since the formation of Mg-rich second phases may result in much poorer electrical properties, it is essential to optimise the preparation conditions in order to attain complete solid-state reaction and a homogenous reaction product. It should be borne in mind, however, that increasing the time or temperature of processing introduces problems associated with the possible volatilisation of gallium oxide (1). As a consequence of the presence of impurities affecting the conductivity of the materials prepared by method II, a more detailed study of their transport properties was not undertaken.

3.3. Ionic conduction

Total conductivity in the $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ system was found to decrease with increasing dopant concentration (Fig.2). Increasing the temperature to 950 – 1000 K results in a deviation from linearity in the Arrhenius conductivity plots due to a previously reported "order-disorder" transition (15). The activation energy values for electrical conductivity (E_a), listed in Table 1, were calculated by the standard Arrhenius model:

$$\sigma = \frac{A_0}{T} \cdot \exp\left(-\frac{E_a}{RT}\right) \quad [1]$$

where A_0 is the pre-exponential factor. The E_a values for $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ in the low-temperature range (670 – 1000 K) are close to each other, varying from 104

Fig.3. Typical impedance spectra of LGMN0 samples prepared by Method II: (A), at 598 K, and (B), at 548 K (filled symbols). The high- and low-frequency contributions obtained from fitting the experimental data to a simple arrangement of two parallel RQ elements in series (solid lines) are also shown in Fig.3A. The sum of these contributions is represented by open symbols.

TABLE III A.

Atom	Position	x/a	y/b	c/z	B ($\text{\AA}^3$)	Site
La	4c	0.0240(1)	0.25	-0.0084(3)	0.28(3)	1.0(-)
Ga/Mg/Nb	4b	0	0	0.5	0.5(-)	0.65/0.282/0.066(-)
O(1)	4c	-0.013(2)	0.25	0.410(5)	0.8(-)	0.948(-)
O(2)	8d	0.348(5)	0.494(2)	-0.247(4)	0.8(-)	1.896(-)

S.G: Pnma; a = 5.5426(4), b = 7.8386(5), c = 5.5485(4) $\text{\AA}$; $R_p = 12.1\%$, $R_{wp} = 15.7$, $R_{exp} = 13.6$, $\chi^2 = 1.34$.

TABLE III B.

Selected bond lengths (in $\text{\AA}$)		Selected angles	
La-O(2)	$3.21(2) \times 2$	O(1)—Ga/Mg/Nb—O(1)	180
La-O(2)	$2.94(2) \times 2$	O(1)—Ga/Mg/Nb—O(2)	$98.9(6) \times 2$
La-O(2)	$2.58(2) \times 2$	O(1)—Ga/Mg/Nb—O(2)	$99.4(9) \times 2$
La-O(2)	$2.54(2) \times 2$	O(1)—Ga/Mg/Nb—O(2)	$81.1(6) \times 2$
La-O(1)	$3.03(1) \times 2$	O(1)—Ga/Mg/Nb—O(2)	$80.6(9) \times 2$
La-O(1)	2.62(1)	O(2)—Ga/Mg/Nb—O(2)	180×2
La-O(1)	2.33(3)	O(2)—Ga/Mg/Nb—O(2)	$94.5(1) \times 2$
		O(2)—Ga/Mg/Nb—O(2)	$85.5(1) \times 2$
Ga-O(2)	$1.61(2) \times 2$		
Ga-O(2)	$2.39(3) \times 2$		
Ga-O(1)	$2.024(7) \times 2$		

to 106 kJ/mol. Since the conductivity at temperatures below 1000 K is mainly ionic (Table 3), the similar activation-energy values for all three compositions indicate that the ionic transport mechanism is the same throughout the $\text{LaGa}(\text{Mg}, \text{Nb})\text{O}_{3-\delta}$ solid-solution series. At higher temperatures (1000 – 1200 K), the activation energy for the total electrical conductivity varies in the range 67 – 76 kJ/mol and increases slightly with increasing x. In this high-temperature regime, the E_a values are less accurate since there is a greater electronic contribution to the total conductivity when temperature increases (Table 4).

Fig.4. Temperature dependence of the p-type electronic conductivity in air of the $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ system prepared by Method I: (1) and (4), LGMN0; (2) and (5), LGMN1; (3) and (6), LGMN2. The electronic conductivity values were calculated from the total electrical conductivity data and transference numbers determined by the e.m.f. method (curves 1 – 3) and Faradaic efficiency measurements (curves 4 – 6).

TABLE IV.

Oxide	T, K	t_o
LGMN0	1173	0.922 ± 0.003
	1073	0.920 ± 0.002
	973	0.944 ± 0.006
	873	0.959 ± 0.002
LGMN1	1173	0.798 ± 0.006
	1073	0.825 ± 0.006
	973	0.878 ± 0.006
	873	0.903 ± 0.004
LGMN2	1173	0.790 ± 0.006
	1073	0.815 ± 0.007
	973	0.881 ± 0.004
	873	0.925 ± 0.004

The total-conductivity and oxygen-ion transference-number data indicate that ionic conductivity in $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ also decreases with increasing Nb content. The activation-energy values are essentially independent of composition, and indicate that only the ionic charge-carrier concentration, and not the carrier mobility, decreases with increasing dopant content. It can be assumed, therefore, that the lower ionic conductivity in LGMN2 is due to a partial trapping of the oxygen sites by pentavalent niobium cations since the oxygen-vacancy concentration is constant throughout the series. Oxygen sites near Nb^{5+} then become unavailable for hopping oxygen vacancies.

3.4. Thermal expansion and stability in different atmospheres

Dilatometric studies of the materials prepared by Method I indicated that thermal expansion values are essentially independent of composition and are close to linear in a temperature range of 300 – 1100 K. Table 1 lists the thermal expansion coefficients (TECs), calculated by fitting the dilatometric data and averaged over this temperature range (TEC values for all compositions are $(10.0 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$). Such low thermal expansion coefficients for the title phases are similar to the values required to provide good compatibility with stabilized zirconia ceramics in high-temperature electrochemical cells.

Thermal gravimetric analysis of $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ powders indicated good stability in gas mixtures that contain up to 17 % carbon dioxide and 25 % water vapour. Samples annealed in dry CO_2 -free air and then exposed to these atmospheres in a temperature range of 900 – 1100 K showed negligible weight change, within the limits of experimental error. Stability of the materials in these gases is a necessary requirement for use in high-temperature electrochemical cells due to the presence of both atmospheric air and hydrocarbon oxidation products.

3.5. Electronic transport

Measurement of the conductivity of $\text{LaGa}(\text{Mg},\text{Nb})\text{O}_{3-\delta}$ as a function of oxygen partial pressure revealed that the total conductivity decreased with decreasing oxygen partial pressure, indicating that electronic conduction in air is p-type. This result is in agreement with transference-number results obtained by the e.m.f. method (Table 4). Although the presence of p-type electronic conductivity in $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ solid solutions has previously been reported in the literature (for instance, (15)), the mechanism of electron-hole transport in these materials is still unclear.

Fig.4 presents the temperature dependence of the partial electronic conductivity (σ_e) of $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ solid solutions in air, calculated from the results on the total conductivity (Fig.2) and ion transference numbers (t_o)

$$\sigma_e = (1 - t_o) \cdot \sigma \quad [2]$$

The transference numbers were determined by the e.m.f. method (Table 4) and calculated from Faradaic efficiency data. The results of both these techniques are in close agreement (Fig.4). Oxygen-ion transference numbers for the title phases, averaged over an oxygen partial pressure range of 2.1×10^4 to 1.01×10^5 Pa, vary from 0.78 to 0.96. A smaller dopant concentration and lower temperature leads to a lower electronic contribution to the conductivity.

The activation energy for p-type electronic transport, estimated using both the transference-number and electrical conductivity data, increases with increasing x, from 94 kJ/mol (LGMN0) to 119 kJ/mol (LGMN2) in a temperature range of 870 – 1070 K. At temperatures above 1000 K, doping with niobium results in increasing partial electron-hole conductivity (Fig.4). Most probably, the p-type conduction in the high-temperature range occurs via hopping electron holes between Nb cations and, therefore, increases with niobium concentration. Below 1000K, however, the electronic conductivity values of LGMN0 and LGMN1 are similar but LGMN2 has lower electronic conduction, indicating that the role of niobium ions in electronic transport decreases with decreasing temperature.

In summary, simultaneous substitution of gallium with magnesium and niobium in lanthanum gallate resulted in lower ionic conduction and higher electronic transport. This doping strategy is not, therefore, suitable for obtaining improved oxygen-ion-conducting solid electrolytes. However, the transport and physicochemical properties of $\text{LaGa}(\text{Mg},\text{Nb})\text{O}_{3-\delta}$ including high ionic and electronic conductivity, relatively low TEC and stability in different atmospheres, may prove advantageous for application in thin-film oxygen-separation membranes in combination with porous zirconia-based substrates.

4. CONCLUSIONS

The solid-solution series $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ ($x = 0 - 0.20$) with a perovskite-type structure was prepared by two synthesis techniques. Phase composition, crystal structure and electrical properties of the materials depend to a considerable extent on the conditions of their synthesis. The segregation of second phase as a result of incomplete solid state reaction led to a dramatic decrease in the electrical conductivity. Thermal expansion coefficients of $\text{LaGa}(\text{Mg},\text{Nb})\text{O}_{3-\delta}$ ceramics were calculated from dilatometric data to be independent of composition and to vary in the range $(10.0 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$.

Oxygen-ion conduction in the $\text{LaGa}_{0.85-x}\text{Mg}_{0.15}(\text{Nb}_{0.33}\text{Mg}_{0.66})_x\text{O}_{3-\delta}$ system decreases with increasing x, whilst p-type electronic conduction at temperatures above 1000 K increases. Oxygen-ion transference numbers in air varied from 0.78 to 0.96, decreasing with increasing x and temperature. The values of the activation energy for the total electrical conductivity are 104-106 kJ/mol in the temperature range 670 – 1000 K and 67 – 76 kJ/mol in the temperature range 1000 – 1200 K

ACKNOWLEDGEMENTS

This research was partially supported by the Belarus Foundation for Basic Research, FCT (Praxis, Portugal), the Belarus Ministry of Education and Science and the company Northern Realm. The authors are sincerely grateful to Anneta A. Tonoyan for some XRD measurements and useful consultations.

REFERENCES

1. J.W.Stevenson, T.R.Armstrong, L.R.Pederson, J.Li, C.A.Lewinsohn and S.Baskaran, "Effect of A-site cation nonstoichiometry on the properties of doped lanthanum gallate", *Solid State Ionics*, **113-115**, 571-583 (1998).
2. T.Ishihara, T.Akabay, H.Furutani and Y.Takita, "Improved oxide ion conductivity of Co doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite type oxide". *Solid State Ionics*, **113-115**, 585-591 (1998).
3. N.Trofimenko and H.Ullmann, "Transition metal doped lanthanum gallates", *Solid State Ionics*, **118**, 215-227 (1999).
4. R.T.Baker, B.Gharbage, and F.M.B.Marques, "Ionic and electronic conduction in Fe and Cr doped $(\text{La},\text{Sr})\text{GaO}_{3-\delta}$ ", *J.Electrochem.Soc.*, **144**, 3130-3135 (1997).
5. M.Schwartz, J.H.White, and A.F.Sammells, "Solid state oxygen anion and electron mediating membrane and catalytic membrane reactors containing them, International Patent Application PCT WO 97/41060 (1997).
6. A.A.Yaremchenko, V.V.Kharton, A.P.Viskup, E.N.Naumovich, N.M.Lapchuk and V.N.Tikhonovich, "Oxygen Ionic and Electronic Transport in $\text{LaGa}(\text{Ni})\text{O}_{3-\delta}$ Perovskites", *J. Solid State Chem.*, **142**, 225-235 (1999).
7. A.A.Yaremchenko, V.V.Kharton, A.P.Viskup, E.N.Naumovich, V.N.Tikhonovich and N.M.Lapchuk, Mixed Electronic and Ionic Conductivity of $\text{LaCo}(\text{M})\text{O}_3$ (M= Ga, Cr, Fe or Ni). V. Oxygen Permeability of Mg-Doped $\text{La}(\text{Ga},\text{Co})\text{O}_{3-\delta}$ Perovskites, *Solid State Ionics*, accepted for publication (1998).
8. B.Gharbage, R.T.Baker and F.M.B.Marques, "Role of water vapour pressure on the electrical conductivity of $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_3$ ", *J.Mater.Sci.Lett.*, **17**, 75-77 (1998).
9. E.N.Naumovich, S.A.Skilkov, V.V.Kharton, A.A.Tonoyan and A.A.Vecher, "Solid oxide electrolytes in the system $\text{Bi}_2\text{O}_3\text{-PbO- Y}_2\text{O}_3$ ", *Russian J. Electrochem.*, **30**, 642-645 (1994).
10. V.V.Kharton, V.N.Tikhonovich, Li Shuangbao, E.N.Naumovich, A.V.Kovalevsky, A.P.Viskup, I.A.Bashmakov and A.A.Yaremchenko, "Ceramic microstructure and oxygen permeability of $\text{SrCo}(\text{Fe},\text{M})\text{O}_3$ (M= Cu or Cr) perovskite membranes", *J. Electrochem. Soc.*, **145**, 1363-1374 (1998).
11. J.Rodriguez-Carvajal, FULLPROF: a program for Rietveld refinement and pattern matching analysis, In: Satellite Meeting on Powder Diffraction, Abstracts of the XVth Conference of the International Union of Crystallography (Toulouse, 1990), 127.
12. E.Djurado and M.Labeau, "Second phases in doped lanthanum gallate perovskites", *J.European Ceram.Soc.*, **18**, 1397-1404 (1998).
13. S.F.Palguev, V.K.Gilderman and V.I.Zemtsov, "High-temperature oxide electronic conductors for electrochemical devices" (Nauka, Moscow, 1990) [in Russian].
14. P.Huang and A.Petric, "Superior oxygen ion conductivity of lanthanum gallate doped with strontium and magnesium", *J.Electrochem.Soc.*, **143**, 1644-1648 (1996).
15. K.Huang, R.S.Tichy and J.B.Goodenough, "Superior perovskite oxide-ion conductor; strontium- and magnesium-doped LaGaO_3 : I, Phase relationships and electrical properties", *J.Am.Ceram.Soc.*, **81**, 10, 2565-2575 (1998).
16. R.T.Baker, B.Gharbage and F.M.B.Marques, "Processing and electrical conductivity of pure, Fe- and Cr-substituted $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_3$ ", *J.European Ceramic Soc.*, **18**, 105-112 (1998).
17. B.A. Boukamp, "A nonlinear least square fit procedure for analysis of impedance data electrochemical systems", *Solid State Ionics*, **20**, 31-38 (1986).
18. M.C. Steil, "Contribution of Impedance Spectroscopy to the Study of the Electrical Properties of Cubic Zirconia Based Heterogeneous Materials", Ph.D. Thesis, Ecole des Mines de Saint-Etienne, France (1996) (in French).