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Ceramics International 39 (2013) 4239–4244

CERAMICS INTERNATIONAL

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High temperature monoclinic-to-tetragonal phase transition in magnesium doped lanthanum ortho-niobate

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Received 3 September 2012; accepted 28 September 2012
Available online 10 November 2012

Abstract

Magnesium doped lanthanum ortho-niobate ($La_{0.98}Mg_{0.02}NbO_4$) was prepared by the molten salt synthesis method. X-ray diffraction and dilatometry methods were used to study high temperature behavior of the ceramic material. Special attention was paid to the phase transition between the monoclinic and tetragonal phases. The values of spontaneous strain on the basis of unit cell parameter, obtained by Rietveld refinement, have been calculated as well as Landau order parameter. The thermal expansion coefficient (TEC) of $La_{0.98}Mg_{0.02}NbO_4$ was determined to be 12×10^{-6} 1/K and 8×10^{-6} 1/K below and above 500 °C, respectively.

Keywords: Molten salt synthesis; Lanthanum ortho-niobate; TEC; X-ray diffraction

1. Introduction

Lanthanum niobates constitute a wide group of cation conducting materials. Acceptor doped lanthanum niobates have been studied for the last ten years because of their relatively high ionic conductivity and stability under carbon dioxide containing atmospheres. They have been investigated since Haugsrud's and Norby's work published in 2001 in which calcium doping was presented [1]. Since then other dopants have been examined e.g. strontium [2] or magnesium [3,4]. Enhancing proton conductivity by doping made lanthanum niobate a candidate for the electrolyte in various devices like fuel cells, hydrogen sensors, humidity sensors etc. Therefore, it is very important to understand phenomena occurring in doped $LaNbO_4$. In this work magnesium doped lanthanum niobate, $La_{0.98}Mg_{0.02}NbO_4$, ceramics have been synthesized and characterized. Special attention has been paid to the phase transition between the monoclinic and tetragonal phases. The phase transition of rare earth niobates has been widely investigated but in the case of doped lanthanum niobates only a few papers have been published previously [5–7]. Also for the first time, thermal expansion coefficient of $La_{0.98}Mg_{0.02}NbO_4$ is reported, as well as spontaneous strain value and Landau order parameter. the phenomena related to the phase transition are very important because they occur in the temperature range in which such devices like fuel cells or gas sensors work. Moreover, the phase transition influences the thermal expansion coefficient and as a result may cause a misfit between the electrolyte and other parts of a device.

2. Experimental

2.1. Sample synthesis

Magnesium doped lanthanum niobate, $La_{0.98}Mg_{0.02}NbO_4$, was synthesized by the molten salt synthesis method (MSS). Nb_2O_5, MgO and La_20_3 oxides, all of 99.99% purity (Sigma Aldrich) were used as substrates. First, lanthanum oxide was heated at 900 °C for 3 h. Then, stoichiometric amounts of the oxides were mixed with KCl in 1:2 weight ratios of the oxides to the salt. The mixture was heated in an open alumina crucible at 1000 °C for 3 h. Owing to the salt melting, synthesis took place in the liquid state. After cooling to room temperature, with cooling rate of 3 K/min, the salt was removed from the products by repeated washing with deionized water. The resulting powder was dried for 24 h at 75 °C. The powders were

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http://dx.doi.org/10.1016/j.ceramint.2012.09.102

uniaxially pressed at 100 MPa into cylindrical pellets of 10 mm in diameter. The pellets were sintered at 1400 °C for 12 h.

2.2. Structural characterization

The structural characterization of the samples were performed by X-ray diffraction (XRD) using the Philips X′pert Pro MPD system with the CuKα radiation. The high temperature X-ray diffraction (HT-XRD) data were collected up to 700 °C. The sintered samples were ground to obtain powder and then measured by HT-XRD. The patterns were analyzed by Rietveld refinement method using a version of the program LHPM1 [8]. As an initial point of the analysis, unit cell parameters of the fergusonite (space group no. 15, I2/c) [9] and scheelite (space group no. 88, I 4/a) [10] crystal structures of $LaNbO_4$ were utilized. Measurements of the thermal expansion coefficient (TEC) of the ceramic samples were carried out with a dilatometer (DIL 402C, Netzsch Gmbh) in air from room temperature to 1000 °C and back down with the ramp rate of 2 °C/min. The initial sample length was 23.770 mm. The thermal expansion coefficient was calculated from Eq. (1) where L_1 is the initial length of the sample, L_2 length of the sample after testing and T_1 and T_2 is the initial and test temperature of measurement, respectively.

$$\alpha = \frac{L_2 - L_1}{L_1(T_2 - T_1)} \tag{1}$$

3. Structural phase transition

3.1. Spontaneous strain

It is known that a structural phase transition involves a crystal lattice rearrangement. In the case of the phase transition from the high-temperature scheelite to the low-temperature fergusonite structure small displacements of cations and a considerable change of anion positions take place [11]. As a result of such atomic displacements two polymorphs differ in the structure type and arrangement of cation-oxygen polyhedra. Lowering of the point-group symmetry from 4/m (scheelite) to 2/m (fergusonite) results in two orientation states in the monoclinic phase. The orientation states are crystallographically and energetically equivalent. The distortion of each orientation state (S_1 and S_2) in relation to the initial tetragonal structure results in forming a spontaneous strain. According to Aizu [12] for each of the S_1 and S_2 states it is possible to write the second-rank strain tensor of monoclinic symmetry. Eq. (2) shows the strain tensor for a single orientation state $e_{ij}(S_1)$, while Eq. (3) presents the relation between the $e_{ij}(S_1)$ and $e_{ij}(S_2)$ tensors

$$e_{ij}(S_1) = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{21} & 0 \\ \varepsilon_{12} & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix} \tag{2}$$

$$e_{ij}(S_2) = \mathrm{Re}_{ij}(S_1)R^T \tag{3}$$

where ε_{ij} are strain components while the R and R^{T} are respectively the 90° rotation matrix around the b axis of the monoclinic unit cell and its transpose. Schlenker et al. suggested that particular components of the strain tensor can be calculated from the lattice parameters of the crystal before and after the transition on the basis of equations given as [13]

$$\varepsilon_{11} = \frac{c_M \sin\beta}{a_T} - 1 \tag{4}$$

$$\varepsilon_{22} = \frac{a_M}{a_T} - 1 \tag{5}$$

$$\varepsilon_{33} = \frac{b_M}{c_T} - 1 \tag{6}$$

$$\varepsilon_{12} = \varepsilon_{21} = \frac{1}{2}\frac{c_M \sin\beta}{a_T} \tag{7}$$

where a_M, b_M, c_M, β *and* a_T, c_T are the monoclinic and tetragonal unit cell parameters, respectively. It should be also noted that in the case of $LaNbO_4$ the relations between crystallographic axes are as follows: the ***c*** axis of tetragonal unit cell corresponds to the ***b*** axis of monoclinic unit cell. While $u = 0.5(\varepsilon_{22} - \varepsilon_{11})$, $v = \varepsilon_{12} = \varepsilon_{21}$ are the longitudinal and the shear spontaneous strain respectively, on the basis of calculated constituents, the strain tensor following Aizu [12] can be represented as

$$e^s_{ij}(S_1) = \begin{pmatrix} -u & v & 0 \\ v & u & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{8}$$

$$e^s_{ij}(S_2) = \begin{pmatrix} u & -v & 0 \\ -v & -u & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{9}$$

The scalar value of the spontaneous strain can be calculated on the basis of

$$\varepsilon_s^2 = \sum_{i=1}^{3}\sum_{j=1}^{3} \varepsilon_{ij}^2 \tag{10}$$

3.2. Landau order parameter

The Landau order parameter, η, specifies a new physical property occurring in a system as a result of a phase transition from the initial phase, in which this property was absent. In the case of the scheelite-fergusonite transition this parameter can be considered as a measure of the distortion of the atomic lattice configuration. The spontaneous strain as a physical parameter serving to characterize the change of the crystallographic unit cell in a phase transition may be treated as the property correlated to the order parameter. The relation between the order parameter and the spontaneous strain may be either linear or not. Since the scheelite-fergusonite transition in magnesium doped lanthanum niobate discussed in this work is expected

to be a second-order transition, temperature dependence of the order parameter may be described by [12,13]

$$\eta \propto \sqrt{\frac{T_0 - T}{T_0}} \tag{11}$$

where T_0 is the transition temperature.

4. Results and discussion

4.1. High temperature X-ray diffraction

High temperature X-ray diffraction patterns obtained at selected temperatures are presented in Fig. 1. The results of the Rietveld refinement are collected in Table 1 while an example of the fitted profile of the pattern recorded at 470 °C as well as the difference plot are shown in Fig. 2. The quality of the Rietveld profiles (R_p value) was between 15 and 23%, with the lower R_p values corresponding to the temperature far from the phase transition, that is below 350 °C and above 490 °C. At room temperature all the reflexes can be indexed in the monoclinic fergusonite-type structure (I2/a), whereas above 490 °C the patterns correspond to the tetragonal body-centered scheelite-type structure ($I4_1/a$). The Rietveld refinement showed that already at 470 °C more than 95% of the sample is tetragonal while at 500 °C the sample has pure tetragonal scheelite-type structure. The temperature of the phase transition in lanthanum niobates has been recently determined. For non-doped $LaNbO_4$ it is about 500 °C [6,14], while in the case of doped samples the transition temperature is lower, for example in the $La_{0.98}Ca_{0.02}NbO_4$ it is above 440 °C [5].

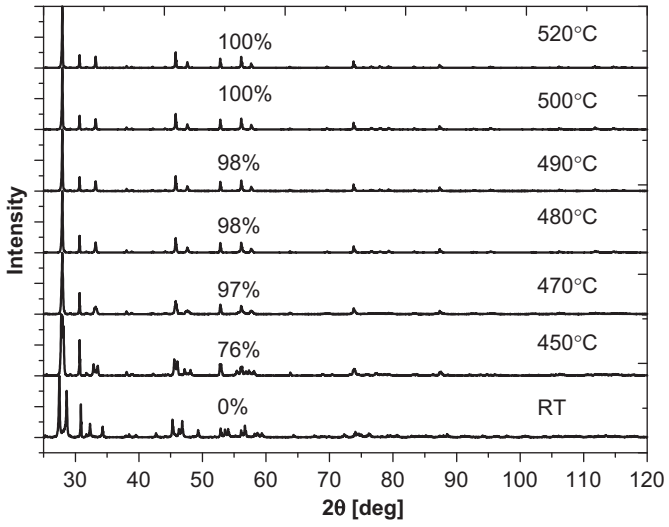

Fig. 1. X-ray spectra collected at selected temperatures. In the figure percentage of tetragonal phase, calculated by Rietveld refinement, is also shown.

Table 1
Unit cell parameters and volume of the scheelite ($I41/a$) and fergusonite (in a non-standard setting $I12/a1$) polymorphs, respectively determined at selected temperatures.

Temperature (C)	a (Å)	b (Å)	c (Å)	β (°)	V(Å^3)
25	5.5564(1)	11.5291(3)	5.2037(2)	93.908(2)	332.573
60	5.5601(1)	11.5279(3)	5.2072(1)	93.949(1)	332.969
130	5.5407(1)	11.5629(3)	5.2308(1)	93.384(2)	334.533
200	5.5431(2)	11.5722(3)	5.2373(1)	93.308(2)	335.394
250	5.5341(2)	11.5883(3)	5.2510(2)	93.028(2)	336.279
300	5.5197(2)	11.6061(3)	5.2664(2)	91.748(2)	337.222
340	5.5104(2)	11.6202(3)	5.2807(2)	92.417(2)	337.831
350	5.5079(4)	11.6240(5)	5.2848(2)	92.336(2)	338.069
360	5.5042(3)	11.6274(5)	5.2893(2)	92.267(2)	338.250
400	5.4887(2)	11.6414(4)	5.3074(2)	90.900(2)	339.07
460	5.4478(4)	11.6672(0)	5.3575(2)	90.8442(8)	340.491
490	5.3999(4)	-	11.6689(7)	90	340.255
500	5.4006(1)	-	11.6708(2)	90	340.389
510	5.4015(1)	-	11.6737(3)	90	340.600
520	5.4016(2)	-	11.6761(4)	90	340.676
550	5.4041(1)	-	11.6796(2)	90	341.090
600	5.4048(1)	-	11.6835(3)	90	341.295
650	5.4079(1)	-	11.6979(3)	90	342.112
660	5.4081(1)	-	11.7007(3)	90	342.215
675	5.4082(1)	-	11.7028(3)	90	342.289

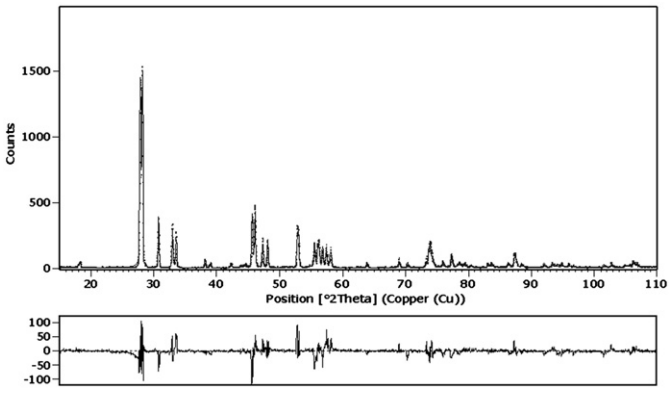

Fig. 2. Observed (dotted line) and calculated (solid line) diffraction patterns of $La_{0.98}Mg_{0.02}NbO_4$ recorded at 470 °C. The lower curve shows the difference between observed and calculated patterns.

4.2. Unit cell parameters, spontaneous strain and Landau order parameter

The evolution of the unit cell parameters as a function of temperature is depicted in Fig. 3. It can be observed that while the **a** axis parameter for the monoclinic phase decreases the c parameter for the same phase increases with temperature and their values tend to the value of **a** axis parameter for the tetragonal polymorph of $LaNbO_4$. This is consistent with the fact that both structures of $LaNbO_4$ are related in such a way that the ***a***, ***b*** and ***c*** axes of the monoclinic cell correspond to the ***b***, ***c*** and ***a*** axes of the tetragonal unit cell (with ***a*** and ***b*** axis parameters of tetragonal structure equal one to another), respectively.

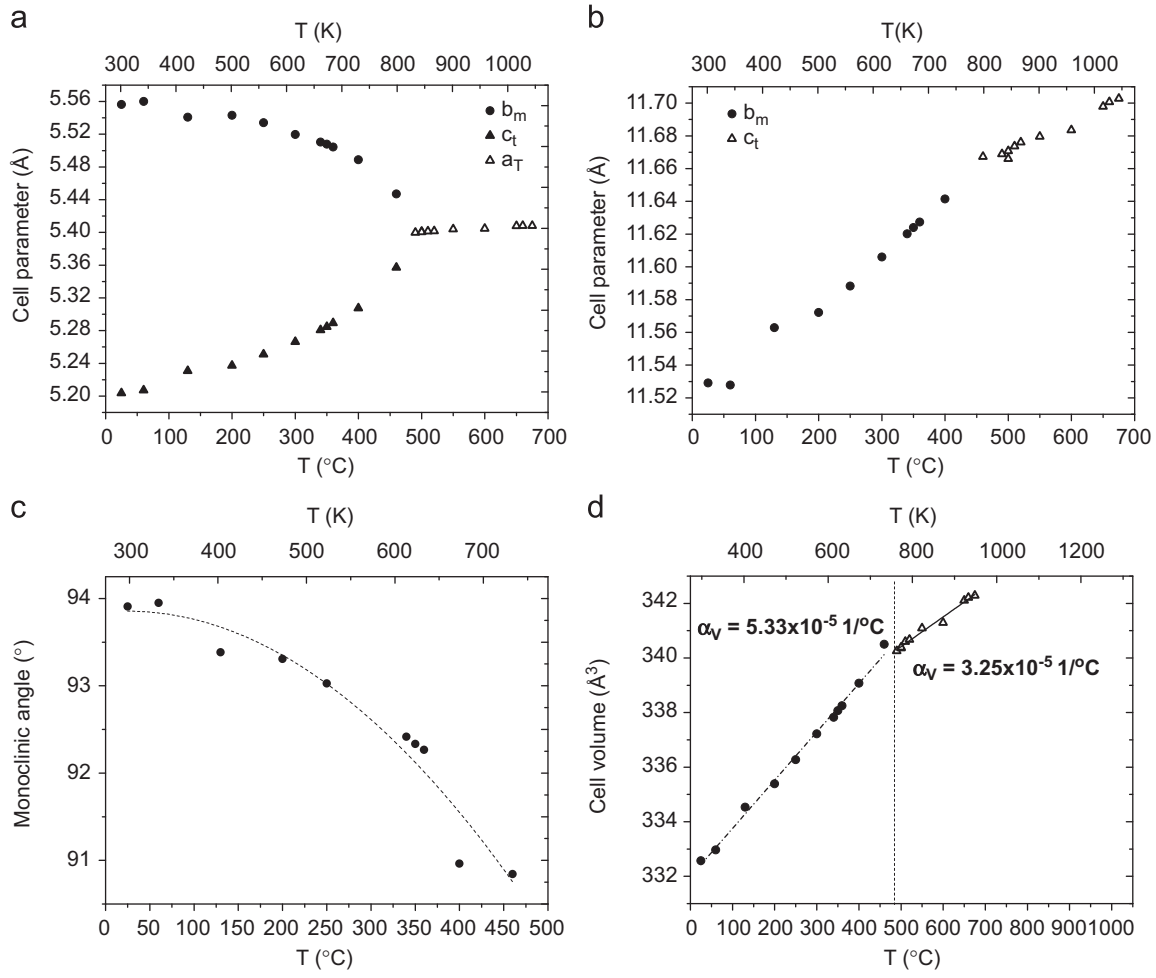

Fig. 3. Evolution of the cell parameters (a, b and c) and unit cell volume (*d*) with temperature. Open and full symbols denote cell parameters of for the scheelite ($I41/a$) and fergusonite (in a non-standard setting $I12/a1$) polymorphs, respectively. The line is provided to guide the eye.

Monoclinic angle, β, increases with the temperature decrease and at room temperature is 93.9°. All the plots shown in Fig. 3 at temperature about 490 °C demonstrate either a change in slope or other features characteristic for the phase transition.

In order to discuss the tetragonal-to-monoclinic phase transition in the $La_{0.98}Mg_{0.02}NbO_4$ material, for each of investigated temperatures components of the strain tensor as well as longitudinal and shear spontaneous strain were calculated on the basis of Eqs. (4)–(9). The scalar spontaneous strain was determined from Eq. (10). The values of longitudinal and shear components and the scalar spontaneous strain are presented in Table 2. All types of strain increase with the decrease of temperature. It is consistent with the increasing monoclinic distortion of the cell. It can also be observed that the longitudinal spontaneous strain is slightly higher than the absolute value of shear spontaneous strain in all investigated temperatures. The relative difference between them is larger as temperature tends to the transition temperature. In the non-doped $LaNbO_4$ material similar relation between the strain components was observed but the relative difference between them was larger. For example, at room temperature it was approximately 19% and 3%, while at temperature $T/T_c \approx 0.72$ it was 21% and 5% in $LaNbO_4$ and $La_{0.98}Mg_{0.02}NbO_4$, respectively [16]. The values of scalar spontaneous strain are similar to these obtained by Jian et al. for non-doped $LaNbO_4$ [16]. This indicates that

Table 2
Longitudinal and shear components and scalar spontaneous strain in the monoclinic fergusonite phase of $La_{0.98}Mg_{0.02}NbO_4$.

Temperature (C)	u	v	ε_s
25	0.0339	−0.0330	0.0669
60	0.0339	−0.0333	0.0673
130	0.0296	−0.0287	0.0583
200	0.0292	−0.0280	0.0572
250	0.0269	−0.0257	0.0527
300	0.0237	−0.0149	0.0396
340	0.0217	−0.0206	0.0424
350	0.0211	−0.0200	0.0411
360	0.0203	−0.0194	0.0397
400	0.0169	−0.0083	0.0266
490	0	0	0

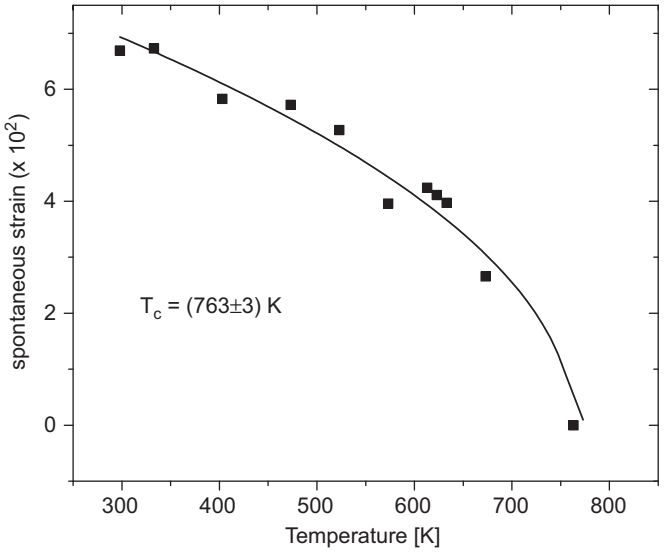

Fig. 4. Relation between the magnitude of the spontaneous strain and temperature. Solid line shows the result of the least-square fitting the experimental data points by temperature dependence described by Eq. (11).

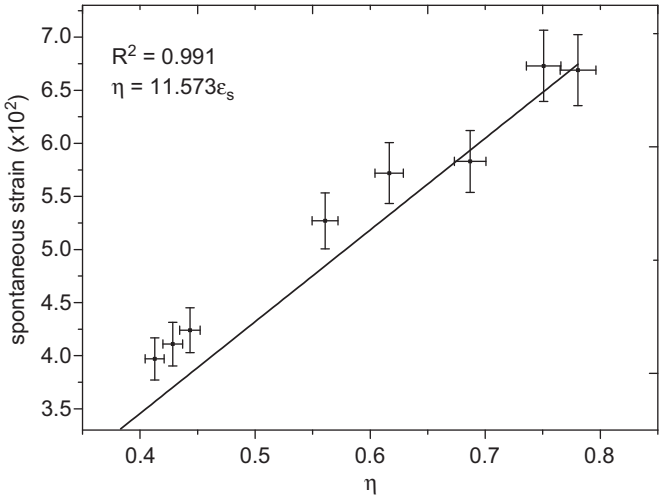

Fig. 5. Correlation between the scalar spontaneous strain and Landau order parameter.

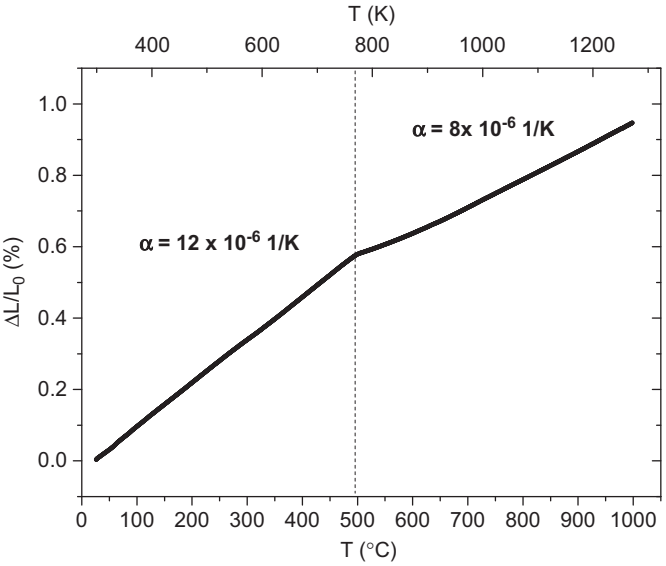

Fig. 6. Relative length change of the magnesium doped lanthanum orthoniobate as a function of temperature.

doping by magnesium decreases the difference between the shear and longitudinal strain components but do not cause significant change in the ε_s magnitude.

The phase transition in magnesium doped lanthanum niobate is expected to be a second-order transition. Therefore temperature dependence of the order parameter should be described by Eq. (11). In the case of the scheelite-fergusonite transition the physical property usually taken into consideration as correlated with the order parameter is a scalar spontaneous strain [e.g. [15], [16]]. It may be also expected that the relation between the order parameter and the spontaneous strain is linear. The scalar spontaneous strain plotted as a function of temperature and order parameter is shown in Figs. 4 and 5, respectively, The temperature evolution of the scalar spontaneous strain (Fig. 4) shows that the value of ε_s tends to zero at the temperature of transition. Moreover, the experimental data follow the temperature dependence described by Eq. (11). The transition temperature determined on the basis of the least-square fit of the experimental data points with the expected temperature dependence was $T_c = (490 \pm 3)$ °C. Fig. 5 shows that the relation between Landau order parameter and the scalar spontaneous strain, within the uncertainty of the results, is linear and may be described by the relation

$$\eta = k\varepsilon_S \tag{12}$$

where k is a constant factor. The value of k found by a fitting procedure is 11.191 ± 0.002 (with R-square correlation coefficient of 0.994). These results confirm that, as it was expected, the scheelite-to-fergusonite transformation in $La_{0.98}Mg_{0.02}NbO_4$ is a second-order transition. The value of k factor for magnesium doped $LaNbO_4$ is higher than that for non-doped $LaNbO_4$ determined by Jian et al. in their research ($k = 10.52$) [16].

4.3. Dilatometry results

Fig. 6 shows the dilatometry results of the $La_{0.98}Mg_{0.02}NbO_4$ sample. The thermal expansion coefficient (TEC) values are also displayed in the figure. The average value of TEC was 12×10^{-6} 1/K between room temperature and 490 °C while it was 8×10^{-6} 1/K above 500 °C. These values are in a good agreement with the results obtained by other groups. For instance, TEC of non-doped lanthanum niobate was found to be 15.3×10^{-6} 1/K and 8.8×10^{-6} 1/K [6], while that of strontium, calcium and barium doped

lanthanum niobate was between 12×10^{-6} 1/K and 18×10^{-6} 1/K and between 8.1×10^{-6} 1/K and 9.1×10^{-6} 1/K in the monoclinic and tetragonal structure, respectively [17]. In the case of isotropic solids volumetric and linear TECs are proportional one to another with the proportionality factor approximately equal to 3 ($\alpha_v \approx 3\alpha_l$). Hence, the values of volumetric thermal expansion coefficients estimated from the dilatometry results are approximately 3.6×10^{-5} 1/K below 500 °C and 2.4×10^{-5} 1/K above 500 °C whereas these obtained from the XRD measurements are 5.3×10^{-5} 1/K and 3.2×10^{-5} 1/K, respectively. It can be seen that there is a qualitative agreement between the values. The difference is caused by the anisotropy of niobate crystals and porosity of the ceramics. The temperature of the change in TEC (490 °C) corresponds to the temperature of the transition from the monoclinic to tetragonal phase. The high temperature change in physical properties of the samples, like TEC change, can be considered as a drawback because of possible misfit between the electrolyte and other elements of the device (e.g. electrodes). The decrease of TEC of 33% at 500 °C can be considered as high, however it is lower than in the case of either non-doped (42% [6]) and comparable to the other doped lanthanum niobate materials (31–40% [17]).

5. Conclusions

The scheelite-fergusonite phase transition in magnesium doped lanthanum niobate, $La_{0.98}Mg_{0.02}NbO_4$, was studied and discussed on the basis of high temperature X-ray diffraction method. Unit cell parameters, the strain tensor components, longitudinal and shear spontaneous strain and scalar spontaneous strain were determined. Temperature dependence of scalar spontaneous strain, which was considered as a phenomenological order parameter, confirmed that the structural transformation in $La_{0.98}Mg_{0.02}NbO_4$ is a second-order phase transition. The thermal expansion coefficient has been measured and its value (12×10^{-6} 1/K—below 500 °C and 8×10^{-6} 1/K above 500 °C) was similar to other materials of the lanthanum niobate group.Both experimental methods allowed us to determine the phase transition temperature of $La_{0.98}Mg_{0.02}NbO_4$. It was found to be 490 °C.

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