Thermal expansion of doped lanthanum gallates

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Abstract. Thermal expansion of several compositions of Sr and Mg-doped LaGaO$_3$ including an A-site deficient composition $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$ were measured in the temperature range from 298 to 1273 K. The effect of doping on thermal expansion was studied by varying the composition at one site of the perovskite structure (either A or B), while keeping the composition at the other site invariant. Thermal expansion varied nonlinearly with temperature and exhibited an inflexion between 550 and 620 K, probably related to the change in crystal structure from orthorhombic to rhombohedral. The dependence of average thermal expansion coefficient (α_{av}) on the dopant concentration on either A or B site of the perovskite structure was found to be linear, when the composition at the other site was kept constant. Mg doping on the B-site had a greater effect on the average thermal expansion coefficient than Sr doping on the A-site. Cation deficiency at the A-site decreases thermal expansion when compositions at both sites are held constant.

Keywords. Coefficient of thermal expansion; perovskite; doped lanthanum gallate; solid oxide fuel cells.

1. Introduction

Perovskite compositions of the ABO$_3$ type with various A and B site substitutions have been able to meet many of the material requirements imposed on components of solid oxide fuel cell (SOFC) stack. SOFCs operate at elevated temperatures ranging from 1073 to 1273 K and the components of the cell are subjected to temperature differentials during fabrication, start-up and operation. Since the components are in intimate mechanical contact, any stress generated due to their thermal expansion mismatch during thermal cycling could lead to catastrophic failure of the cell. The functional materials must have similar thermal expansions to avoid mechanical stresses. Hence it is useful to study the thermal expansion of SOFC materials and tailor them to ensure the absence of significant stress build-up.

Yttria-stabilized zirconia is the electrolyte currently used in SOFC and its thermal expansion behaviour is well established. There has been a surge of interest in novel solid electrolyte materials for SOFC application at lower temperatures. The foremost among them is LaGaO$_3$-based oxides with perovskite structure, which show far superior ionic conductivity compared to yttria-stabilized zirconia (Ishihara *et al* 1995). Sr- and Mg-doped LaGaO$_3$ oxides have the highest electrical conductivity among them, with ionic transference number close to one over a wide range of oxygen pressures, and are used as interconnect and electrolyte materials in SOFC (Hayashi *et al* 1999). Data

on the thermal expansion of doped LaGaO$_3$ has been reported by Feng and Goodenough (1994), Stevenson *et al* (1997), Ishihara *et al* (1998), Hayashi *et al* (1999, 2000) and Aleksandrovskii *et al* (2001).

Stevenson *et al* (1997) measured linear thermal expansion (TEC) coefficient of two Sr- and Mg-doped LaGO$_3$ samples from 293 to 1473 K. The TEC was found to increase with increasing temperature. The average thermal expansion coefficients of the doped samples were higher than that of YSZ and increased with doping on both A and B-sites (Stevenson *et al* 1997). Ishihara *et al* (1998) measured the thermal expansions of $La_{1-x}Sr_xGa_{0.8}Mg_{0.2}O_{2.9-x/2}$ at $x = 0.1$ and $x = 0.2$ and reported that the average thermal expansion coefficient of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ between 298 and 1273 K was similar to that of YSZ. Although their data show gradual increase in the slopes of thermal expansion with temperature, the authors conclude that the temperature dependence of expansion is insignificant and the phase transition found in LaGaO$_3$ around 420 K disappeared in the thermal expansion curve of doped-LaGaO$_3$ (Ishihara *et al* 1998). Hayashi *et al* (2000) measured TEC of $La_{0.9}Sr_{0.1}Ga_{1-y}Mg_yO_{3-\delta}$ ($y = 0.1$ to 0.3) and $La_{0.8}Sr_{0.2}Ga_{1-y}Mg_yO_{2.85}$ ($y = 0.1$, 0.2) in the temperature range from 100 to 873 K and showed that doping increases thermal expansion. Pure LaGaO$_3$ exhibited a shrinkage related to orthorhombic to rhombohedral structure transition at 421 K (Hayashi *et al* 2000). The dimensional change became smaller and broader with doping. The transition temperature increased with Mg content and decreased with Sr concentration (Hayashi *et al* 2000). They examined TEC of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ at 200 K as a function of oxygen vacancy and concluded that TEC

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increases linearly with oxygen vacancy concentration regardless of the relative distribution of dopants on the two sites (Hayashi *et al* 2000). This suggests that Sr on La-site and Mg on Ga-site have equal effect on thermal expansion. Aleksandrovskii *et al* (2001) have shown that the unit cell volume of LaGaO$_3$ increases almost linearly with Sr + Mg content.

To remove the discrepancies in the literature on thermal expansion, new measurements were conducted on the system La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-0.5(x+y)}$ $(0.1 \leq x \leq 0.2;\ 0.1 \leq y \leq 0.2)$ in the temperature range from 298 to 1273 K using a horizontal quartz dilatometer. The effect of cation deficiency on the *A*-site on thermal expansion of doped LaGaO$_3$ was explored as this has not been fully elucidated in the literature. The results have been interpreted in relation to ionic radii and oxidation state of the cations, oxygen nonstoichiometry and crystal structure.

2. Experimental

2.1 *Sample preparation and characterization*

Polycrystalline samples of superionic conductor, La$_{1-x}$Sr$_x$ Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ $(\delta = 0.5(x + y))$ (LSGM), were prepared by conventional ceramic processing. Samples were prepared using powders of La$_2$O$_3$, SrCO$_3$, MgO and Ga$_2$O$_3$ of purity > 99.9%. Before weighing, La$_2$O$_3$ and MgO were calcined at 1273 K in dry argon for 12 ks to remove moisture. The powders were mixed and ground in an agate ball mill and precalcined at 1473 K in air for 120 ks. The calcined powders were ground in an agate ball mill, sieved (160 μm mesh) and cold isostatically compacted at 500 MPa. The samples were sintered at 1723 K in air for 30 ks with intermediate regrinding, sieving and compacting. The final sintering was done at 1773 K for 240 ks. The prolonged heat treatment was necessary to dissolve metastable phases that form during synthesis and obtain equilibrium phase composition. The presence of impurity phases influences thermal expansion. There is no change in thermal expansion for sintering time > 180 ks. To prevent Ga depletion from the surface and grain boundaries by volatilization, the compacted samples were buried in loose powder of the same composition. The dimensions of the sintered bars were ~3.5 × 3.5 × 55 mm. The faces of the sintered compact were cut and polished. Each composition was examined by X-ray diffraction and all the samples were confirmed to be essentially single phase with perovskite structure. Traces of secondary phase, LaSrGa$_3$O$_7$ were observed in (La$_{0.8}$Sr$_{0.2}$)(Ga$_{0.9}$Mg$_{0.1}$)O$_{2.85}$. The intensity of impurity reflection in XRD pattern was < 3% of the strongest perovskite peak. The overall composition was verified by inductively-coupled plasma (ICP) spectroscopic analysis.

The bulk density of the sintered bars was determined by Archimedes' liquid displacement technique using dis-

tilled water as the medium. The densities of the samples were 92 to 94% of the theoretical values.

2.2 *Measurement of thermal expansion*

Linear thermal expansion measurements were conducted on sintered rods (3 × 3 × 50 mm) during heating at 0.067 K/s from 298 K to 1273 K in air using a horizontal quartz dilatometer which was calibrated with a sapphire single crystal.

3. Results and discussion

The thermal expansion curves for the series (La$_{0.8}$Sr$_{0.2}$) (Ga$_{1-y}$Mg$_y$)O$_{2.9-0.5y}$ for *y* = 0.1, 0.15, and 0.2 are shown in figure 1. It is evident from the figure that the change in length and therefore, the linear thermal expansion coefficient is a nonlinear function of temperature. There are inflexions in the thermal expansion curves in the temperature range from 570 to 610 K. The thermal expansion of LaGaO$_3$ increases slightly with magnesium concentration on the Ga-site when *A*-site composition is kept invariant. LaGaO$_3$ has an orthorhombic structure at room temperature and transforms to rhombohedral symmetry around 420 K (Marti *et al* 1994). It has been reported that the substitution of magnesium for gallium on the *B*-site increases the transition temperature (Hayashi *et al* 2000). This phase transition manifests itself as an inflexion or
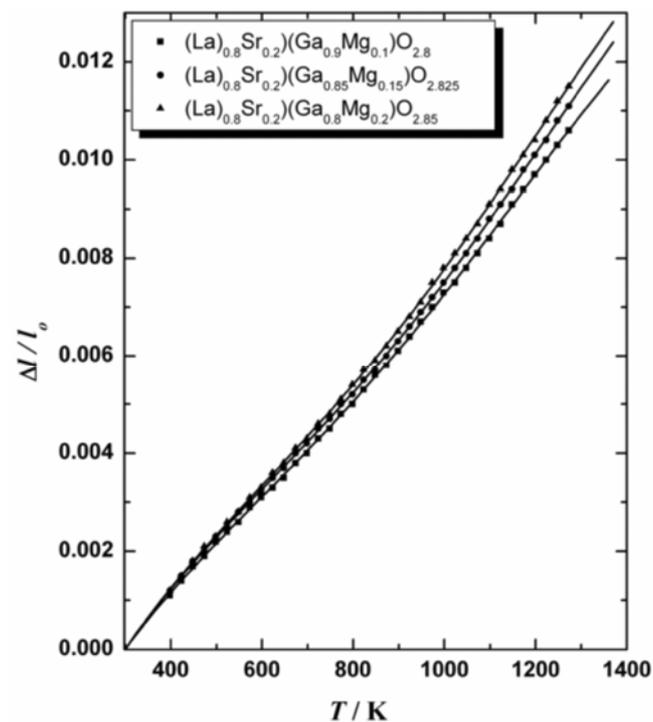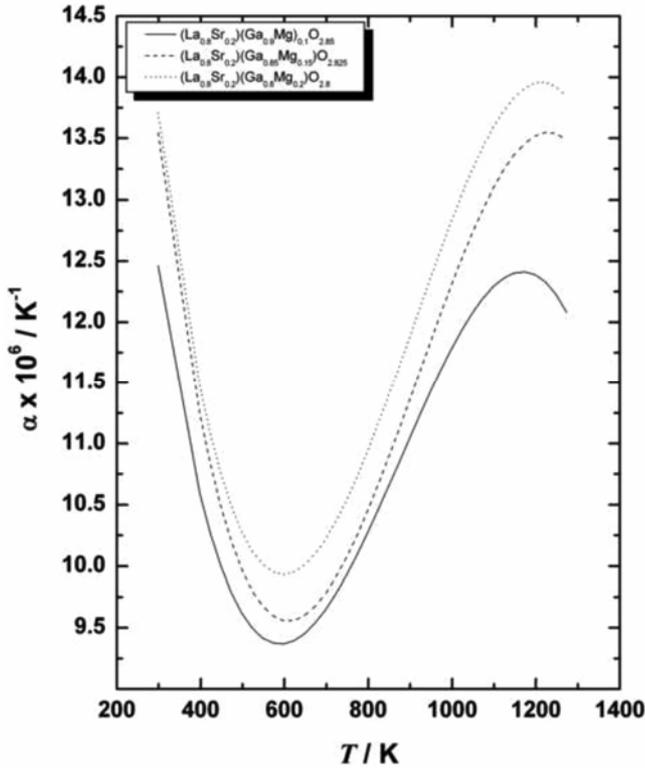

Figure 1. Thermal expansion of (La$_{0.8}$Sr$_{0.2}$)(Ga$_{1-y}$Mg$_y$)O$_{2.9-0.5y}$ for *y* = 0.1, 0.15 and 0.2 from 298 to 1273 K.

Table 1. Coefficients of the polynomial expression for thermal expansion as a function of temperature.

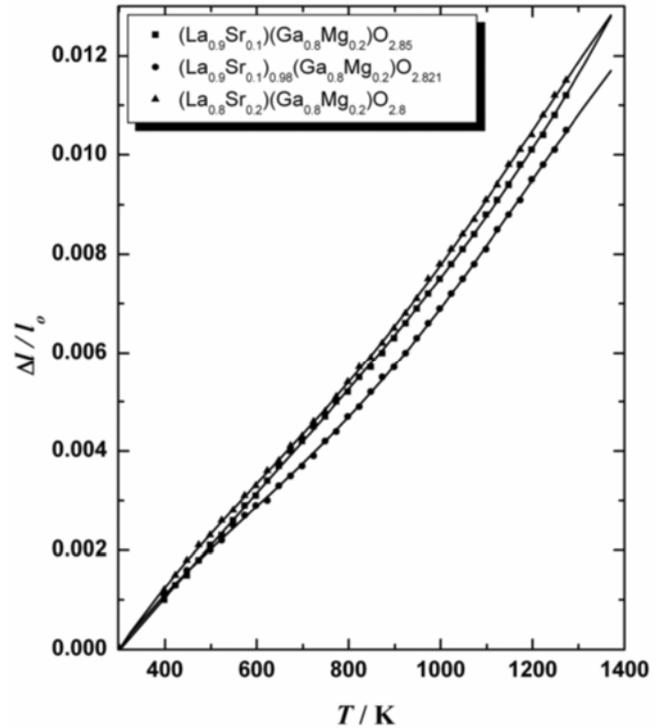| Sample	Coefficients				
	$B_0 \times 10^3$	$B_1 \times 10^5$	$B_2 \times 10^8$	$B_3 \times 10^{11}$	$B_4 \times 10^{15}$
$(La_{0.8}Sr_{0.2})(Ga_{0.9}Mg_{0.1})O_{2.85}$	-5.32	2.5282	-3.2454	2.7609	-7.8529
$(La_{0.8}Sr_{0.2})(Ga_{0.85}Mg_{0.15})O_{2.825}$	-5.94	2.8587	-3.7475	3.0704	-8.3566
$(La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.2})O_{2.8}$	-5.98	2.8628	-3.7434	3.1166	-8.6035
$(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_{2.85}$	-3.34	1.1314	-0.0495	-0.14894	1.5281
$(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$	-5.69	2.8681	-4.1972	3.6087	-10.1985

Figure 2. Variation of thermal expansion coefficient of $(La_{0.8}Sr_{0.2})(Ga_{1-y}Mg_y)O_{2.9-0.5y}$ for $y = 0.1$, 0.15 and 0.2 from 298 to 1273 K.

Figure 3. Thermal expansion of $(La_{1-x}Sr_x)(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ for $x = 0.1$ and 0.2 and $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$ in the temperature range from 298 to 1273 K.

anomalous thermal expansion. Since the thermal expansion curves cannot be represented adequately by one or two straight lines, a fourth degree polynomial was used for curve fitting. The polynomial was of the form

$$\frac{\Delta l}{l} = Y = B_0 + B_1 T + B_2 T^2 + B_3 T^3 + B_4 T^4, \quad (1)$$

where T is the absolute temperature and B_0, B_1, B_2, B_3 and B_4 are constants, specific to each composition. The thermal expansion coefficient denoted by α is given by the slope of the curve and hence for any temperature T, it can be expressed as the derivative of (1)

$$\alpha = \left| \frac{dY}{dT} \right|_T = B_1 + 2B_2 T + 3B_3 T^2 + 4B_4 T^3. \quad (2)$$

The values of B_0, B_1, B_2, B_3 and B_4 for various compositions are listed in table 1. The fitted curves are shown in figure 1. The variation of α with temperature is displayed in figure 2. The error in α is estimated to be $\pm 0.1 \times 10^{-6} \, K^{-1}$. Thermal expansion coefficient for $(La_{0.8}Sr_{0.2})(Ga_{1-y}Mg_y)O_{2.9-0.5y}$ for $y = 0.1$, 0.15 and 0.2 shows minima between 570 and 610 K. The minimum shifts slightly towards higher temperature with the increase in magnesium doping.

Thermal expansion curves for $(La_{1-x}Sr_x)_{1-z}(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ are shown in figure 3. There is an increase in the thermal expansion of $LaGaO_3$ with increase in the strontium concentration on the La-site. When the compositions on both sites are kept constant, net cation deficiency on the A-site causes a small decrease in thermal expansion. The variation of thermal expansion coefficient with tem-

perature for $(La_{1-x}Sr_x)_{1-z}(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ is shown in figure 4. TEC for $(La_{1-x}Sr_x)_{1-z}(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ shows a minimum between 575 and 600 K. The minimum shifts towards lower temperature with the introduction of cation deficiency on the A-site.

The average thermal expansion coefficient (α_{av}) (calculated by considering the total thermal expansion over the temperature range and deducing the change in thermal expansion per unit change in temperature) between 298 and 1273 K is displayed in figure 5 as a function of magnesium concentration, with constant composition at the A-site. Since thermal expansion is nonlinear, the average value (α_{av}) depends on the temperature range. The variation of α_{av} for the series $(La_{0.8}Sr_{0.2})(Ga_{1-y}Mg_y)O_{2.9-0.5y}$ can be represented by the relation

$$\alpha_{av}(298\text{--}1273 \text{ K}) = (9.95 + 9.4y) \times 10^{-6}. \tag{3}$$

Similarly for the series, $(La_{1-x}Sr_x)_{1-z}(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$, the variation of the average thermal expansion coefficient with strontium concentration can be represented by

$$\alpha_{av}(298\text{--}1273 \text{ K}) = (11.06 + 3.8x) \times 10^{-6}. \tag{4}$$

This is graphically represented in figure 6. These linear relations are useful for estimating the average thermal expansion coefficient for compositions that have not been

studied experimentally: α_{av} (298–1273 K) = (11.06 + 3.8x + 9.4y) $\times 10^{-6}$. It is apparent that Mg substitution on the Ga-site has greater effect in increasing α_{av} than Sr doping on the La-site. This is contrary to Hayashi *et al* (2000) who suggested that thermal expansion coefficient at 200 K is linearly proportional to the concentration of oxygen vacancies formed as a result of doping regardless of the nature and site of the dopants. The results obtained in this study show that the thermal expansion coefficient varies linearly with oxygen vacancy concentration only when composition on one site is held constant. Reduction in the unit cell volume should result in an increase in the coefficient of thermal expansion as per Grüneisen's relation (Eastabrook 1957). Since this does not happen, it is likely that the increase in the unit cell volume is off-set by the vacancy effect. The ionic size difference between La^{3+} and Sr^{2+} as well as between Ga^{3+} and Mg^{2+} could possibly provide an explanation for the varying effects of strontium and magnesium doping on α_{av}.

The average thermal expansion coefficient also depends on the temperature range in which the SOFC electrolyte is operated. A comparison of the α_{av} obtained in this study with the data available in the literature for few compositions of doped lanthanum gallates in different temperature ranges, is provided in figure 7. The small difference between the results from various studies may be in part the result from microstructural effects.
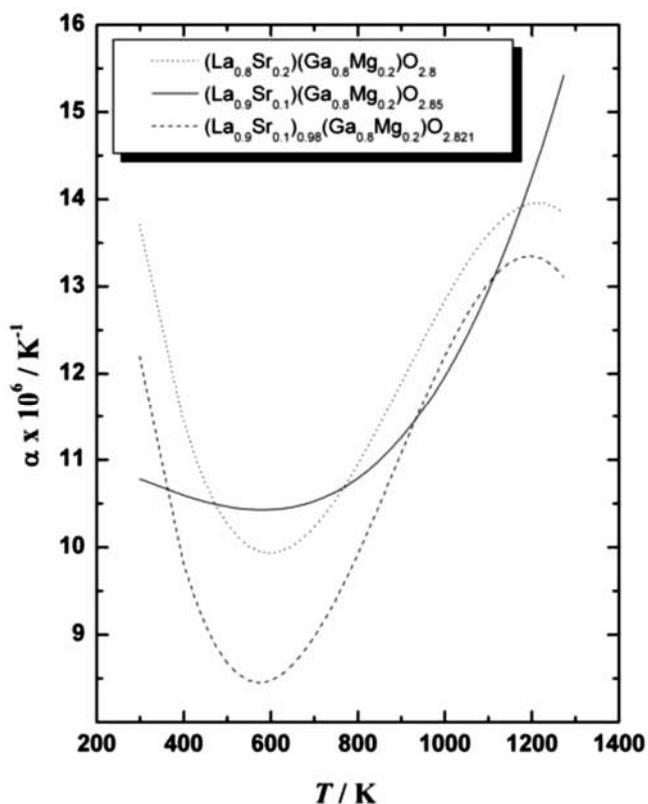
Figure 4. Variation of thermal expansion coefficient of $(La_{1-x}Sr_x)(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ for $x = 0.1$ and 0.2 and $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$ in the temperature range from 298 to 1273 K.
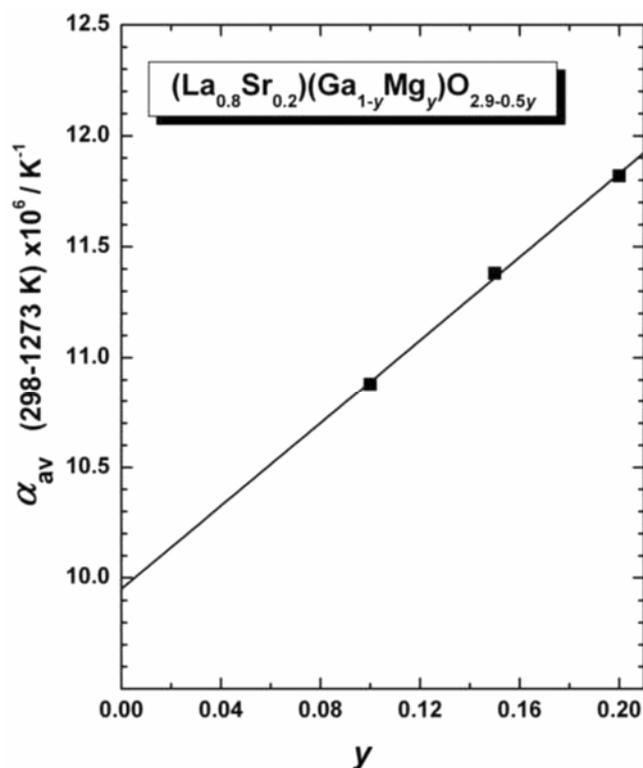
Figure 5. Average thermal expansion coefficient as a function of Mg concentration for the series $(La_{0.8}Sr_{0.2})(Ga_{1-y}Mg_y)O_{2.9-0.5y}$ in the temperature range from 298 to 1273 K.
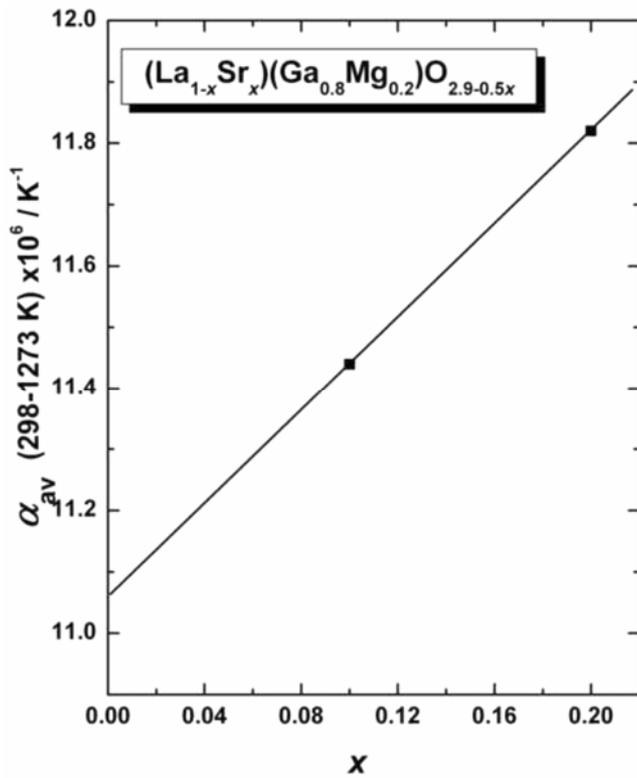
Figure 6. Average thermal expansion coefficient as a function of Sr concentration for the series $(La_{1-x}Sr_x)(Ga_{0.8}Mg_{0.2})O_{2.9-0.5x}$ in the temperature range from 298 to 1273 K.

Figure 7. Comparison of the average thermal expansion coefficient obtained in the study with data available in the literature for LSGM electrolytes.

4. Conclusions

Thermal expansion behaviour of LSGM, including an A-site cation deficient composition $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$ was investigated in the temperature range from 298 to 1273 K. Thermal expansion varied nonlinearly with temperature and became larger with the increase of dopant concentration. The A-site cation deficient $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{2.821}$ showed a decrease in the thermal expansion in the temperature range from 298 to 1273 K when compared with $(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_{2.85}$ and $(La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.2})O_{2.8}$. The study clarified the dependence of TEC on oxygen vacancy concentration and revealed that the TEC varies linearly with oxygen vacancy concentration only when composition on one site of the perovskite is kept constant. Based on this result, empirical relation is proposed to predict the α_{av} of unknown LSGM composition.

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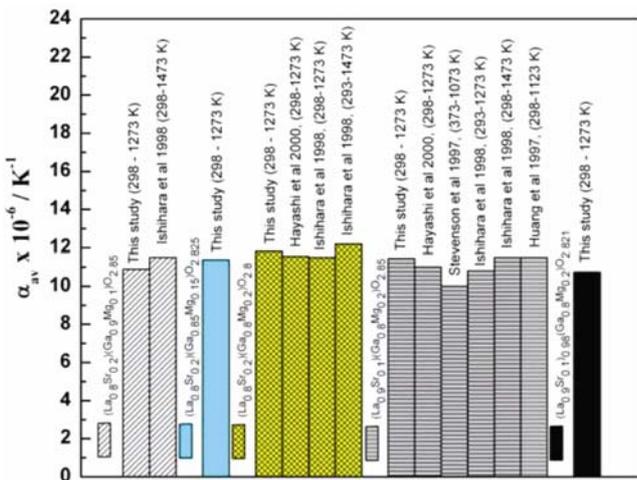Stevenson J W, Armstrong T R, McCready D E, Pederson L R and Weber W J 1997 *J. Electrochem. Soc.* **144** 3613