Solid super-ionic conductors are important materials for technical applications, e.g. in fuel cells. Recently, a new type of oxygen ionic conductor was reported, based on perovskite-type LaGaO$_3$, allowing operating temperatures at 800 °C [1]. Oxygen vacancies in the anion lattice, necessary to enhance the ionic conduction, can be introduced by doping LaGaO$_3$ with aliovalent oxides like SrO and MgO. In order to understand the conduction mechanism in La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-0.5(x+y)}$ samples, it is essential to determine the phase relationships as a function of temperature and composition. As shown in our earlier work, this is not feasible with simple XRD measurements using a laboratory diffractometer [2]. Only the combination of scattering experiments using synchrotron radiation and neutrons allows a complete structural description as a function of temperature. In a final step this study aims at a correlation of structural features with anomalies found in the conductivity data as a function of temperature and composition.

Pure lanthanum gallate (LaGaO$_3$) has a distorted perovskite structure (orthorhombic, space group $Pnma$) at ambient temperature [e.g. 2]. At high temperatures there is a structural phase transition to a rhombohedrally distorted perovskite-type ($R-3c$) at about 150 °C. Both distortions are due to rotations of the O$_6$-octahedra and can be described within the Glazer nomenclature [3] by an in-phase tilting around the $b$-axis plus an anti-phase tilting around [101] (symbol b'a'b') and an anti-phase tilting around [111] (a' a a'), respectively. We have previously reported on neutron powder diffraction measurements (at D2B/ILL) of sol-gel synthesized La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ [2]. At high temperatures (above 800 °C), the average structure is cubic $Pm\bar{3}m$ with a statistical distribution of the vacancies, whereas at room temperature we found the space group $Imma$, which formally corresponds to an anti-phase tilting around [101] only (tilt-system symbol b'a'0b'), i.e. the room temperature distortion of pure LaGaO$_3$ can be derived by the onset of the additional in-phase rotation around [010]. However, a recent analysis of another sample with the same overall composition prepared by a solid state synthesis, using instrument E9/HMI [4], revealed that the structures could be better refined in space group $I\bar{2}/a$ for temperatures up to 900 °C, as was also proposed by Slater et al. [5]. Furthermore, it was found that structural parameters (e.g. lattice parameters and monoclinic angle) displayed an intriguing deviation from a “normal” linear trend with increasing temperature [4]. This might reflect the anomalies found in the electrical conductivity data [1]. In this contribution we report on detailed structural investigations of different La$_{1-x}$Sr$_x$Ga$_{1-x}$Mg$_x$O$_{3-0.5(x+y)}$ samples (LSGM) with various (Mg, Sr)-dopant concentrations (with x = 0.1, 0.2 and y = 0.1, 0.15, 0.2) leading to different concentrations of oxygen vacancies.

The samples were prepared by a novel solution combustion synthesis technique using appropriate solutions of the respective nitrate solutions and employing urea as a complexing agent [6]. The resulting gel was calcined in an open muffle furnace at 823 K followed by sintering of the fine powder at 1673 K for 24 h. The synchrotron data were collected at the instrument B2 using a wavelength of 0.907 Å. The diffractometer was equipped with a STOE capillary furnace. The high resolution mode was used with an analyzer in front of the detector. The 2θ-range was 18.5° to 59.6° with a step width of 0.004°. Only short regions around specific Bragg reflections were recorded in the temperature range between room temperature and 900 °C to save measuring time. The data were analyzed with the Rietveld program FullProf [8].
RT \((\text{Imma}, a = 7.8011(3) \text{ Å}, b = 5.5052(2) \text{ Å}, c = 5.5365(2) \text{ Å})\). At \(~ 450 \, ^\circ\text{C}\) a phase transition to a rhombohedrally distorted perovskite-type structure \((R\bar{3}c)\) is observed which is not transforming into the cubic structure up to the highest temperature reached (i.e. \(950 \, {^\circ}\text{C}\)).

![Graph](image)

Figure 1: Temperature dependence of the (pseudo-)cubic lattice parameters of (a) \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) and \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}\) and (b) \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}\).

Apparently, for samples with a higher dopant concentration \((x+y \geq 0.35)\) the cubic structure is already favoured at room temperature. However, additional measurements using synchrotron radiation indicate the existence of a different rhombohedral structure \((R\bar{3}m)\) at temperatures above \(700 \, ^\circ\text{C}\) in the case of \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) \(\text{[4]}\). The alternative space group \(R\bar{3}c\) with a doubled \(c\) lattice constant could be discarded because of the absence of superstructure reflections in concomitant neutron scattering experiments. This result constitutes the first example of space group \(R\bar{3}m\) within the subgroup family of the ideal parent \(Pm\bar{3}m\) perovskite.

It has been shown that the high resolution synchrotron diffraction data with a Ge(111) analysing crystal between sample and detector allows to detect the tilting of the \(O_6\) octahedra in perovskite-type structures and, hence, to study the phase transition from the orthorhombic to the rhombohedral lattice. However, additional measurements using the image plate detector system failed to resolve the splitting of the orthorhombic reflections. The described measurements underline the importance of combining scattering experiments using synchrotron radiation and neutrons for the determination of slight distortions from the cubic aristotype. Therefore, future work will involve neutron scattering experiments in which the scattering contrast for oxygen is enhanced. Those measurements yield information about the mobility and diffusion pathways of the mobile oxygen ion from the pdf maps obtained by refinements using anharmonic Debye-Waller factors.

**Acknowledgment**

The financial support of the DFG (No. LE781/7-1) is gratefully acknowledged.

**References**