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# Crystal structure and electron density in the apatite-type ionic conductor $La_{9.71}(Si_{5.81}Mg_{0.18})O_{26.37}$

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ABSTRACT

Crystal structure and electron density in the apatite-type ionic conductor $La_{9.71}(Si_{5.81}Mg_{0.18})O_{26.37}$ have been investigated at 302, 674 and 1010 K by Rietveld refinement and a whole-pattern fitting approach based on the maximum-entropy method (MEM) using synchrotron X-ray powder diffraction data. Second harmonic generation measurements indicated that the space group of this material is centrosymmetric. Among the possible hexagonal groups $P6_3/m$, $P6_3$ and $P\overline{3}$ the former is correct for $La_{9.71}(Si_{5.81}Mg_{0.18})O_{26.37}$. Rietveld refinements suggested an oxygen interstitial site (0.03,0.15,0.85) near the hexagonal axis. MEM analyses revealed that the $Si_{0.97}Mg_{0.03}$ atom has covalent bonds with four adjacent oxygen atoms to form a tetrahedron. The oxygen O4 atom located at the 2*a* site (0.0,0.0,1/4) exhibited large atomic displacement parameters along the *c* axis and electron density mapping also indicated the wide distribution consistent with migration of oxygen ions in this direction.

## 1. Introduction

Solid oxides that exhibit high ionic conductivity have attracted widespread interest in recent years owing to their technological importance in a number of applications, such as oxygen sensors, separation membranes and solid oxide fuel cells. It is well known that among many structural families, fluorite- and perovskite-type structures show higher oxide-ion conductivities and interesting structural properties [1–5]. The other family is of the apatite-type which has recently appeared as a new class of oxide ion conductors following the pioneering work of Nakayama et al. [6–8]. These materials take the general formula $A_{10-x}M_6O_{26+y}$ (where $A =$ rare earths, alkaline earths; $M =$ Si, Ge, P, V, etc). Among them, rare earth silicates and germanates are of particular interest because of their higher oxide ion conductivity.

The conductivity of the apatite-type lanthanum silicates can be increases with Mg substitution for Si [9–11]. It has also been reported [5,12–14] that the conductivity of the apatite-type systems is enhanced largely by the incorporation of excess oxygen where the number of oxygen atoms per formula unit is larger ($O_{26+y}$) than that of the oxygen stoichiometric composition $O_{26}$. The crystal structures of Mg-doped lanthanum silicates with stoichiometric $O_{26}$ oxygen atoms, $La_{9.5}Si_{5.75}Mg_{0.25}O_{26}$ and $La_{9.67}Si_{5.5}Mg_{0.5}O_{26}$, have been studied by Kendrick et al. [9]. They reported the space group to be hexagonal $P6_3$ and suggested the presence of a small level of interstitial oxygen at the periphery of hexagonal channel close to the silicon groups through the difference Fourier maps, but they did not succeed in the refinement of the positional parameters of the oxygen atoms in their Rietveld analysis. Yoshioka [10,11] studied the ionic conductivity of Mg-doped lanthanum silicates with excess oxygen atoms $La_{9.6}Si_{5.8}Mg_{0.2}O_{26.1}$ and $La_{10}Si_{6-x}Mg_xO_{27-x}$ and reported that the composition at $x = 0.3$ has the highest conductivity at 1073 K, but, the structural details are not satisfactorily understood. Based on the analogous composition reported in the literature the excess interstitial was assumed to reside in $P6_3/m$ without crystal structure refinement. Therefore, the space group and position of the interstitial site must be clear. Furthermore, no study on electron density distribution of these apatite-type ionic conductors has yet been published.

The purpose of the present study is to determine the crystal structure with correct space group and to investigate the electron density distribution of $La_{9.71}(Si_{5.81}Mg_{0.18})O_{26.37}$ using second-harmonic-generation (SHG) measurements, Rietveld refinement [15,16] and the maximum-entropy method (MEM) [17–19]. This is followed by MEM-based pattern fitting (MPF) [19,20] of synchrotron X-ray powder diffraction data measured at 302, 674 and 1010 K. MEM-based pattern fitting (MPF) can be very effective for

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determining precise electron density distributions that visualizes covalent bonding as we reported [21–27] for many compounds with different types of structure.

## 2. Experimental procedure

A $La_{9.71}Si_{5.81}Mg_{0.18}O_{26.37}$ sample was prepared by solid-state reaction from high-purity powders of $La_2O_3$, $SiO_2$ and MgO previously dried at 1273 K for 4 h. The powders were mixed in appropriate ratios, ground with ethanol and calcined at 1573 K for 16 h. The calcined powders were further ground, pressed into disks and sintered at 1873 K for 4 h in air. The first sintering gave porous disks because of high reactivity of the calcined powders with the atmospheric $H_2O$ and $CO_2$. They were thus reground, pressed into disks and sintered again at 1823 K for 8 h on MgO-stabilized $ZrO_2$ setters placed inside a $MoSi_2$ furnace, resulting in dense ceramic disks with a diameter of ~13 mm and a thickness of ~1 mm. One of the sintered disks was crushed and ground into a powder for use in laboratory-based and synchrotron X-ray powder diffraction measurements. Inductively coupled plasma optical emission spectroscopy chemical analyses indicated that the chemical formula of the final product was $La_{9.71(1)}(Si_{5.81(1)}Mg_{0.18(1)})O_{26.37(2)}$ where the number in parenthesis is the error in the last digit. The value for oxygen 26.37 was calculated to achieve charge neutrality. The SHG measurement was done by the powder method with a Nd:YAG laser operating at a wavelength of 1064 nm, which was used as the radiation source with an irradiation time of 8 s. The laser power was 300 μJ. The sample was ground to a grain size of 1–2 μm in order to avoid the possible influence of domain structure and phase-matching conditions.

Synchrotron X-ray powder diffraction data were collected on a powder diffractometer installed at beam line 19B2 of SPring-8, Japan, with the Debye–Scherrer geometry. The wavelength of the monochromatized X-rays was determined to be 0.49952 Å using the NIST SRM silicon powders. The $La_{9.71}Si_{5.81}Mg_{0.18}O_{26.37}$ sample was loaded into a quartz-glass capillary tube with an inner diameter 0.3 mm and the tube rotated at 60 rpm during the measurements to minimize preferred-orientation and large-grain effects. The diffraction data were measured at 302, 674 and 1010 K over a $2\theta$ range from 0.01° to 78.13° with a step interval of 0.01°. The sample temperature was calibrated with a thin thermocouple.

**Table 1**

Refined structural parameters of the $La_{9.71}(Si_{5.8}Mg_{0.2})O_{26.37}$, SG $P6_3/m$ (No.176).

| Temperature | | 302 (K) | 674 (K) | 1010 (K) |
|---|---|---|---|---|
| Atom, Site, Occupancy | Structural parameters | | | |
| La1 | *x* | 1/3 | 1/3 | 1/3 |
| 4*f* | *y* | 2/3 | 2/3 | 2/3 |
| g(La1) = 0.927 | *z* | −0.0006(2) | −0.0006(2) | −0.0004(2) |
| | $U$ (Å$^2$) | 0.0131(2) | 0.0199(2) | 0.0273(2) |
| La2 | *x* | 0.01128(10) | 0.01110(10) | 0.01136(10) |
| 6*h* | *y* | 0.23998(7) | 0.23894(7) | 0.23932(7) |
| g(La2) = 1.0 | *z* | 1/4 | 1/4 | 1/4 |
| | $U$ (Å$^2$) | 0.0100(2) | 0.0166(2) | 0.0224(2) |
| $Si_{0.97}Mg_{0.03}$ | *x* | 0.4031(3) | 0.4037(3) | 0.4031(3) |
| 6*h* | *y* | 0.3732(3) | 0.3737(3) | 0.3738(3) |
| g(Si) = 0.970 | *y* | 1/4 | 1/4 | 1/4 |
| g(Mg) = 0.030 | $U$ (Å$^2$) | 0.0070(7) | 0.0137(7) | 0.0181(7) |
| O1 | *x* | 0.3237(7) | 0.3244(7) | 0.3252(7) |
| 6*h* | *y* | 0.4883(7) | 0.4883(6) | 0.4884(6) |
| g(O1) = 1.0 | *z* | 1/4 | 1/4 | 1/4 |
| | $U$ (Å$^2$) | 0.018(2) | 0.021(2) | 0.029(2) |
| O2 | *x* | 0.5971(7) | *0.5959(6)* | 0.5952(6) |
| 6*h* | *y* | 0.4757(7) | 0.4731(6) | 0.4724(6) |
| g(O2) = 1.0 | *z* | 1/4 | 1/4 | 1/4 |
| | $U$ (Å$^2$) | 0.008(1) | 0.016(2) | 0.022(2) |
| O3 | *x* | 0.3467(5) | 0.3441(4) | 0.3428(4) |
| 12*i* | *y* | *0.2566(4)* | *0.2578(4)* | *0.2577(4)* |
| g(O3) = 1.0 | *z* | 0.0714(5) | 0.0709(5) | 0.0708(4) |
| | $U_{11}$ (Å$^2$) | *0.056(4)* | *0.067(3)* | *0.079(3)* |
| | $U_{22}$ (Å$^2$) | 0.006(4) | 0.022(3) | 0.030(3) |
| | $U_{33}$ (Å$^2$) | *0.010(3)* | *0.017(3)* | *0.017(3)* |
| | $U_{12}$ (Å$^2$) | *0.019(3)* | 0.030(3) | *0.035(3)* |
| | $U_{13}$ (Å$^2$) | −0.020(2) | −0.020(2) | −0.022(2) |
| | $U_{23}$ (Å$^2$) | −0.014(2) | −0.014(2) | −0.015(2) |
| | $U_{eq}$ (Å$^2$) | 0.024 | 0.032 | 0.039 |
| O4 | *x* | 0 | 0 | 0 |
| 2*a* | *y* | 0 | 0 | 0 |
| g(O4) = 1.0 | *z* | 1/4 | 1/4 | 1/4 |
| | $U_{11}$ (Å$^2$) | 0.026(5) | 0.028(5) | 0.033(5) |
| | $U_{33}$ (Å$^2$) | 0.186(15) | 0.189(14) | 0.200(13) |
| | $U_{eq}$ (Å$^2$) | 0.079 | 0.082 | 0.089 |
| O5 | *x* | 0.102(6) | 0.080(10) | 0.094(9) |
| 12*i* | *y* | 0.162(5) | 0.142(9) | 0.144(8) |
| g(O5) = 0.031 | *z* | 0.811(9) | 0.852(13) | 0.834(13) |
| | $U$ (Å$^2$) | 0.006 | 0.013 | 0.013 |

Number of the formula in a unit cell, $Z = 1$.