Phase relationships in the quasi-ternary LaO$_{1.5}$–SiO$_2$–MgO system at 1773 K

Kiyoshi Kobayashi and Yoshio Sakka

Advanced Materials Processing Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan
E-mail: KOBAYASHI.Kiyoshi@nims.go.jp

Received 12 April 2012
Accepted for publication 28 June 2012
Published 5 September 2012
Online at stacks.iop.org/STAM/13/045006

Abstract
Phase relationships in the LaO$_{1.5}$–SiO$_2$–MgO quasi-ternary system at 1773 K were investigated by powder x-ray diffraction (XRD) analysis applying single- and multiple-phase Rietveld methods. Most of the formed phases satisfied the Gibbs’ phase rule, except for the samples containing LaO$_{1.5}$ and a liquid phase at 1773 K. The detection of segregated MgO phases was difficult in the XRD profiles of the compositional samples around the oxyapatite single phase because the MgO peaks were weak and heavily overlapped by peaks from the oxyapatite and La(OH)$_3$ phases. The solid solubility limit of MgO in oxyapatite was determined not only from the chemical composition of the oxyapatite phase, which was confirmed by XRD, but also from several phase boundary compositions among the two-phase and three-phase regions based on the Gibbs’ phase rule. Formation of a liquid phase at 1773 K was observed in a wide range of compositions and considered when constructing the phase diagram.

Keywords: ternary phase diagram, LaO$_{1.5}$–SiO$_2$–MgO system, oxyapatite solid solution, liquid phase formation

1. Introduction
Since its discovery by Nakayama et al., the high conductivity of oxygen ions in lanthanoid silicate oxyapatite [1–3] has attracted attention for applications in solid oxide fuel cells and chemical sensors. During research on improvement in oxygen ionic conductivity by chemical doping, Yoshioka and Tanase have reported the interesting result that magnesium is an effective element to increase ionic conductivity and that magnesium ions might substitute into not only the lanthanum ion sites but also silicon ion sites [4–6]. After these reports, the location and concentration of magnesium ions have been studied by neutron powder diffraction, synchrotron x-ray diffraction (XRD) and single-crystal XRD [7–10]. However, the amount of magnesium substitution in the La and Si sites as well as the magnesium dissolution reaction and defect chemistry have not been established, partly because of the lack of systematic research on the chemical compositional dependences for magnesium-doped lanthanum silicate oxyapatite. In particular, the phase relationship in the LaO$_{1.5}$–SiO$_2$–MgO system remains a fundamental, yet unexplored topic.

The compositional features of MgO-doped lanthanum silicate oxyapatites can be emphasized by plotting their elemental content on a Gibbs triangular graph [4–14] (figure 1). The oxyapatite phase is located on two compositional lines: horizontal line A that corresponds to the substitution of MgO for SiO$_2$ at a fixed LaO$_{1.5}$ concentration, and line B along which MgO was substituted for LaO$_{1.5}$ at a fixed SiO$_2$ concentration. Almost no oxyapatite single phase has been found in the hatched region between lines A and B. If these results were true, there is a possibility that two different phases having the oxyapatite structure existed and that two phase-regions, composed of two oxyapatite phases having different lattice parameters, did form in the hatched region, similar to the behavior of perovskite phases in the BaO–ZrO$_2$–YO$_{1.5}$ system [15, 16]. However, systematic research on the phase relationships in the LaO$_{1.5}$–SiO$_2$–MgO quasi-ternary system has not been reported before.
The difficulty in analyzing the phase relationships in this system by XRD is that many diffraction peaks overlap in the high-2θ region when more than two phases coexist in one sample, because many phases in the LaO$_{1.5}$–SiO$_2$–MgO system have low-symmetry crystal structures, such as hexagonal, monoclinic or orthorhombic [6–11, 14, 17–23]. Moreover, the XRD peak identification becomes difficult owing to the existence of many metastable phases and allotriomorphic phases in the MgO–SiO$_2$ system [24, 25]. Hence, another phase identification methodology is necessary for the phase analysis of the LaO$_{1.5}$–SiO$_2$–MgO system.

In this paper, we systematically investigated the phase relationships in LaO$_{1.5}$–SiO$_2$–MgO compositional samples by XRD, employing single- and multiple-phase Rietveld methods to overcome the analysis difficulties. Based on the experimental results, we derived an overall ternary phase diagram of this system at 1773 K.

2. Experimental procedures

All the samples were synthesized by a water-based sol–gel method as in previous reports [14, 26]. The raw materials were lanthanum nitrate hexahydrate (La(NO$_3$)$_3$ · 6H$_2$O, 99.9% purity, Nacalai Tesque Inc., Japan), amorphous silica (SiO$_2$, 99.9% purity, 200 m$^2$g$^{-1}$ specific surface area, 12 nm average grain size, Wako Chemical Industry Inc., Japan), magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$ · 6H$_2$O, ≥ 99% purity, Wako Chemical Industry Inc., Japan), citric acid (≥ 98% purity, Wako Chemical Industry Inc., Japan) and distilled water. Thermogravimetric-differential thermal measurements were performed between room temperature and 1473 K in air, and a negligible amount of adsorbed water in raw SiO$_2$ powder was detected [14], thus ignored for weighing. Lanthanum nitrate hydrate and magnesium nitrate hydrate were separately dissolved in distilled water to achieve a concentration of about 1–1.5 mol% of metal ions. The accurate concentrations of lanthanum and magnesium were determined by complexometric titration. An aqueous solution of ethylenediamine–N, N, N', N'-tetraacetic acid disodium salt (0.1 M, Tekiteieki, Dojindo Co., Japan) was used as the chelating agent in both titrations. The indicator and pH buffer were xylene orange (XO, Dojindo Co., Japan) and hexamethylenetetramine (reagent grade, Wako Pure Chemical Industry Inc., Japan) for the lanthanum titration and o-cresolphthalein complexone (PC, Dojindo Co., Japan) and dilute ammonia solution (reagent grade, Wako Pure Chemical Industry Inc., Japan) for the magnesium titration, respectively. The aqueous solutions of lanthanum nitrate hexahydrate and magnesium nitrate hexahydrate were kept in bottles and used as raw stocks.

Precursors were prepared by the following steps. The aqueous solutions of lanthanum nitrate hexahydrate and magnesium nitrate hexahydrate were pipetted and mixed in one beaker, then citric acid was added and the solution was stirred until it became clear. The added amount of citric acid was equal to the sum of the molar amounts of lanthanum and magnesium ions. The necessary amount of amorphous silica was then added to the solution, which became opaque due to the dispersion of amorphous silica. The opaque solution changed into a transparent viscous gel after being heated with stirring on a hot plate. The beaker was then placed in a heating mantle to pyrolyze the viscous gel. The ash-like residue was crushed into powder using an agate mortar and pestle and then used as a precursor. The dark-brown precursor was placed in an alumina boat and heated at 1273 K for 3 h in air to remove residual carbon. The resulting white samples were milled using an alumina mortar and pestle. Two or three pellets were fabricated using the sample powder by mechanical pressing at 63 MPa. The pellets were placed on a platinum or yttria-stabilized zirconia (YSZ) plate. To avoid the pellet attaching to or reacting with the plates, the sample powder was sandwiched between the plates and pellet. To avoid the sticking of pellets upon heating, a small amount of the sample powder was sandwiched between them. The pellets were reacted at 1773 K for 10 h in air in a tubular furnace and then cooled to room temperature.

One or two sample pellets were crushed into powder using an alumina mortar and pestle, and the XRD profiles of the sample were collected using a laboratory XRD instrument (RINT-2500, Rigaku Co. Japan) in a 2θ range of 5–100°. The formed phases were confirmed by single- and multiple-phase Rietveld methods using the RIETAN–FP software [27]. For the analysis of the MgO-dissolved oxypatite phase, we could not obtain a definitive proof that Mg was substituted into Si ion sites by the Rietveld analysis. The reason for this was that the effect of the substitution of Si by Mg on the XRD profiles was too weak because Mg and Si are both light elements. Furthermore, the XRD peak intensities collected by the laboratory x-ray diffraction instrument were insufficient to complete refinement for all of the parameters. Hence, we analyzed the XRD profiles of the MgO-dissolved oxypatite phase by a model in which Mg was substituted only into La ion sites while ignoring the average chemical composition. These procedures correspond to the case in...
which only the lattice parameters of the oxyapatite phase were refined using the Rietveld method. In the case of the multiple-phase Rietveld analysis, it was also difficult to refine all crystallographic parameters, and therefore only the lattice parameters were refined.

Parts of samples 9, 37 and 42 were heated at 1773 K for 70 h in air. The formed phases and their lattice parameters were confirmed to be the same as in the samples heated at 1773 K for 10 h.

3. Results and discussion

3.1. Oxyapatite solid solution

Previous reports in the fields of mineralogy and cement engineering suggest that alkali-earth ions substitute for lanthanoid ions in lanthanoid silicate oxyapatites [28, 29]. Typically, compositions of $Ln_9AE_2(SiO_4)_6O_2$, $Ln_6AE_4(SiO_4)_6O$ and $Ln_4AE_6(SiO_4)_6$ were reported as oxyapatite single phases, where $Ln$ and $AE$ were trivalent lanthanoid ions and alkali-earth ions, respectively [28].

In our previous studies, a single phase of lanthanum silicate oxyapatite was obtained with a composition of $La_9.50(SiO_4)_6O_2$ by heating at 1773 K [14, 26]. Using those results, here we first investigated the samples with compositions of $x$ mol% $La_{9.50}(SiO_4)_6O_2$ for $x = 0, 25, 50, 75, 100$. All the XRD peaks from the samples with compositions of $x$ mol% $La_{9.50}(SiO_4)_6O_2$ for $x = 0, 25, 50, 75, 100$, which correspond to line C in figure 2. The compositions, formed phases and lattice parameters are listed in table 1. The data for the $La_9Mg_3(SiO_4)_6O$ and $La_9Mg_3(SiO_4)_b$ samples are listed in table 2 because three phases coexisted in these samples. All the XRD peaks from the samples with compositions of $x$ mol% $La_{9.50}(SiO_4)_6O_2$ for $x = 0, 25, 50, 75, 100$ can be indexed to the oxyapatite structure as shown in figure 3. On the other hand, samples 11 ($La_9Mg_3(SiO_4)_6O$) and 12 ($La_9Mg_3(SiO_4)_b$) were mixtures composed of the oxyapatite (monoclinic clinocenstatite structure, symmetry group P21/c) [17], and $Mg_2SiO_4$ (orthorhombic forsterite structure, symmetry group Pnma) [18], as shown in figure 3. The $La_9Mg_3(SiO_4)_6O$ pellet slightly bended upon heating at 1773 K, suggesting that a part of the sample was melted.

![Figure 2. Magnified triangle graph around the oxyapatite single-phase region in the LaO$_1$–SiO$_2$–MgO system. The hatched region is the oxyapatite single-phase region. Line C corresponds to $x$ mol% $La_9.50(SiO_4)_6O_2$–$(100 – x)$ mol% $La_9Mg_3(SiO_4)_6O_2$ and line D to $8.4$ mol% $La_9O_{1.5}$–$(41.6 – x)$ mol% SiO$_2$–$x$ mol% MgO.

![Figure 3. XRD patterns of the samples with compositions of $(100 – x)$ mol% $La_{9.50}(SiO_4)_6O_2$–$x$ mol% $La_9Mg_3(SiO_4)_6O_2$ (a) $x = 0$, (b) $x = 50$, (c) $x = 100$, $La_9Mg_3(SiO_4)_6O$ (d, sample 11) and $La_9Mg_3(SiO_4)_b$ (e, sample 12). Short black, red, and blue bars indicate the oxyapatite, $La_9Si_2O_7$ and $Mg_2SiO_4$ peak positions, respectively. The differences between the collected and calculated patterns are shown at the bottom of each panel.

Table 1. List of a part of the synthesized single-phase oxyapatite samples. Values $x$, $y$ and $z$ refer to the formula $x$ mol% LaO$_{1.5}$–$y$ mol% SiO$_2$–$z$ mol% MgO.

| Sample No. | Composition | Lattice parameters |
|------------|-------------|--------------------|
| 1          | 61.3, 38.7, 0 | 0.9717(7), 0.7179(3) |
| 2          | 53.2, 37.7, 9.1 | 0.9613(9), 0.7029(1) |
| 3          | 52.5, 37.5, 10 | 0.9607(7), 0.7022(8) |
| 4          | 50, 37.5, 12.5 | 0.9610(0), 0.7023(2) |
| 5          | 58.4, 38.4, 3.2 | 0.9688(2), 0.7128(4) |
| 6          | 58.4, 37.4, 4.2 | 0.9694(7), 0.7137(6) |
| 7          | 58.4, 36.4, 5.2 | 0.9694(7), 0.7138(1) |
| 8          | 58.4, 36.4, 7 | 0.9710(9), 0.7167(8) |
| 9          | 61, 33, 6 | 0.9736(6), 0.7218(4) |

Figure 2. Magnified triangle graph around the oxyapatite single-phase region in the LaO$_1$–SiO$_2$–MgO system. The hatched region is the oxyapatite single-phase region. Line C corresponds to $x$ mol% $La_9.50(SiO_4)_6O_2$–$(100 – x)$ mol% $La_9Mg_3(SiO_4)_6O_2$ and line D to $8.4$ mol% $La_9O_{1.5}$–$(41.6 – x)$ mol% SiO$_2$–$x$ mol% MgO.

Figure 3. XRD patterns of the samples with compositions of $(100 – x)$ mol% $La_{9.50}(SiO_4)_6O_2$–$x$ mol% $La_9Mg_3(SiO_4)_6O_2$ (a) $x = 0$, (b) $x = 50$, (c) $x = 100$, $La_9Mg_3(SiO_4)_6O$ (d, sample 11) and $La_9Mg_3(SiO_4)_b$ (e, sample 12). Short black, red, and blue bars indicate the oxyapatite, $La_9Si_2O_7$ and $Mg_2SiO_4$ peak positions, respectively. The differences between the collected and calculated patterns are shown at the bottom of each panel.
Table 2. List of a part of the synthesized three-phase samples containing oxyapatite, $La_2Si_2O_7$, and $Mg_5SiO_4$. Changes in the shape of the pellets after heating at 1773 K for 10 h are noted. Values $x$, $y$, and $z$ refer to the formula $x$ mol% $LaO_1.5$–$y$ mol% $SiO_2$–$z$ mol% $MgO$.

| Sample No. | Composition $x$, $y$, $z$ | Formed phases and lattice parameters |
|------------|---------------------------|-----------------------------------|
|            | $La_2Si_2O_7$ | $Mg_5SiO_4$ |
|            | $a$, $c$ (nm), $\beta$ | $a$, $b$, $c$ (nm) |
| 10         | 0.9614(2) | 0.5405(5) | 1.018(8) |
|            | 0.7036(1) | 0.8787(6) | 0.597(8) |
|            | 1.426(8) | 0.475(4) | 112.74(9)$^\circ$ |
| 11         | 0.9625(4) | 0.540(8) | 1.019(8) |
| $La_4Mg_2(SiO_4)_6$O | 0.7042(7) | 0.8794(8) | 0.598(2) |
| Partly bended | 1.427(4) | 0.475(2) | 112.73(6)$^\circ$ |
| 12         | 0.9631(9) | 0.5407(5) | 1.0202(1) |
| $La_6Mg_6(SiO_4)_8$ | 0.7056(4) | 0.8797(5) | 0.5985(6) |
| Partly bended | 1.427(9) | 0.4753(7) | 112.76(1)$^\circ$ |

Table 3. List of the synthesized two-phase samples containing oxyapatite and $La_2Si_2O_7$. Values $x$, $y$, and $z$ refer to the formula $x$ mol% $LaO_1.5$–$y$ mol% $SiO_2$–$z$ mol% $MgO$.

| Sample No. | Composition $x$, $y$, $z$ | Formed phases and lattice parameters |
|------------|---------------------------|-----------------------------------|
|            | $La_2Si_2O_7$ | $Mg_5SiO_4$ |
|            | $a$, $c$ (nm), $\beta$ | $a$, $b$, $c$ (nm) |
| 13         | 0.9672(0) | 0.5405(3) | 1.018(8) |
|            | 0.7118(0) | 0.8789(1) | 1.0202(1) |
|            | 1.4269(0) | 0.4753(8) | 112.75(9)$^\circ$ |
| 14         | 0.9647(0) | 0.5404(8) | 1.0202(1) |
|            | 0.7079(0) | 0.8792(9) | 1.0202(1) |
|            | 1.4274(0) | 0.4753(7) | 112.77(6)$^\circ$ |
| 15         | 0.9610(4) | 0.5406(3) | 1.0202(1) |
|            | 0.7056(0) | 0.8791(9) | 1.0202(1) |
|            | 1.4278(0) | 0.4753(1)$^\circ$ | 112.74(5)$^\circ$ |

Figure 4. Oxyapatite lattice parameters as a function of MgO content in the (100 – $x$) $La_{9.50}(SiO_4)_6O_{25}$–$x$ mol% $La_2Mg_2(SiO_4)_6$O$_2$-$La_6Mg_6(SiO_4)_8$O$_2$-$La_4Mg_2(SiO_4)_6$O$_2$ samples.

Although the variation of the lattice parameters of the oxyapatite phase with MgO content in the quasi-binary system of $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ showed a linear decrease with increasing MgO concentration, the lattice parameters of the oxyapatite phase were almost the same in the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$–$La_4Mg_2(SiO_4)_6$O$_2$ samples (figure 4). Considering that the $La_2Mg_2(SiO_4)_6$O$_2$–$La_4Mg_2(SiO_4)_6$O$_2$ compositions are located in the three-phase coexisting region, the constant lattice parameters are consistent with the Gibbs’ phase rule in a quasi–ternary system, because no degrees of freedom exist in the three-phase region at a fixed temperature and total pressure [30]. The slight variation of the lattice parameters of the oxyapatite phase in the $La_2Mg_2(SiO_4)_6$O$_2$–$La_4Mg_2(SiO_4)_6$O$_2$ samples is related to the formation of a liquid phase as discussed in section 3.4. Considering the other phase relationship in the $LaO_1.5$–$SiO_2$–$MgO$ system discussed below, we conclude that the solid solubility limit of MgO substitution for $LaO_1.5$ in the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ system is about 12.5 mol%, which is smaller than the solubility limit of CaO, SrO or BaO in lanthanoid silicate oxyapatites [28].

In order to confirm the compositional width of the oxyapatite single-phase region around the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ line, two series of samples were prepared. One series consisted of samples with low $LaO_1.5$ and MgO concentrations compared to the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ line. The compositions of these samples (13, 14 and 15) are presented in table 3 and figure 2. The XRD peaks from these samples (figure 5) can be indexed to oxyapatite and high-temperature $La_2Si_2O_7$ structures with monoclinic symmetry (space group $P2_1/c$) [20]. The lattice parameters of the oxyapatite phases varied with the chemical composition and were within the values corresponding to the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ line. Although the composition of sample 14 is close to that of the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ line, we observed $La_2Si_2O_7$ segregation and therefore concluded that the oxyapatite solid solution region did not extend below the $La_{9.50}(SiO_4)_6O_{25}$–$La_2Mg_2(SiO_4)_6$O$_2$ line. Moreover,
Figure 5. XRD patterns of the samples with compositions of (a) 50 mol% LaO$_1$$_3$–45 mol% SiO$_2$–5 mol% MgO (sample 15 in table 3), (b) 55 mol% LaO$_1$$_3$–39 mol% SiO$_2$–6 mol% MgO (sample 14 in table 3), (c) 55 mol% LaO$_1$$_3$–42 mol% SiO$_2$–3 mol% MgO (sample 13 in table 3), (d) La$_8$Si$_3$Mg$_6$O$_{26.4}$ (62 mol% LaO$_1$$_3$–36.1 mol% SiO$_2$–1.9 mol% MgO, sample 16 in table 4) and (e) La$_8$Si$_3$Mg$_6$O$_{26.5}$ (62.5 mol% LaO$_1$$_3$–34.4 mol% SiO$_2$–3.1 mol% MgO, sample 17 in table 4). Black, red and blue bars mark the peak positions of the oxyapatite, La$_2$Si$_2$O$_5$ and La$_3$Si$_2$O$_7$ phases, respectively. The differences between the collected and calculated patterns are shown at the bottom of each panel.

The MgO solution limit in La$_2$Si$_2$O$_7$ would be very small because the lattice parameters of La$_2$Si$_2$O$_7$ were almost independent of the sample composition and were consistent with the reported data [20]. Additional samples were prepared to investigate the compositional solid-solubility limit of the oxyapatite phase in the high-LaO$_1$$_3$ concentration region. The formed phases were analyzed using samples 16 and 17 (see table 4 and figure 2). Although these compositions agree with the previous reports on the formation of oxyapatite single phase [7–9, 13], a La$_2$SiO$_3$ phase as well as the oxyapatite phase were segregated as shown in figure 5. The La$_2$SiO$_3$ segregation was due to the lower reaction temperature in this study (1773 K) than in the previous studies (1923–1873 K). The solubility limit of MgO in the La$_2$SiO$_3$ phase can also be ignored because the lattice parameters of the La$_2$SiO$_3$ phase in samples 16 and 17 have almost the same values, and furthermore, the values are almost the same as those reported for La$_2$SiO$_3$ [21]. On the other hand, the lattice parameters of the oxyapatite phase were much larger in samples 16 and 17 than in the samples corresponding to the La$_9$Si$_5$(SiO$_4$)$_6$O$_{26.5}$–La$_9$Mg$_3$(SiO$_4$)$_6$O$_2$ solid-solution line.

Figure 6. XRD patterns of the 58.4 mol% LaO$_1$$_3$–(41.6 – x) mol% SiO$_2$–x mol% MgO samples with (a) x = 3.2, (b) x = 4.2, (c) x = 5.2 and (d) x = 7. Short bars indicate the peak positions of the oxyapatite structure. The differences between the collected and calculated patterns are shown at the bottom of each panel. Insets magnify the 2θ = 41–64° region.

Table 4. List of the synthesized two-phase samples containing oxyapatite and La$_3$SiO$_7$. Values x, y and z refer to the formula x mol% LaO$_1$$_3$–y mol% SiO$_2$–z mol% MgO.

| Sample No. | Composition | Oxyapatite $x, y, z$ (nm) | La$_3$SiO$_7$ $a, b, c$ (nm), β |
|------------|-------------|---------------------------|--------------------------------|
| 16         | 62.0, 36.1, 1.9 | 0.9724(4) 0.7203(4)       | 0.9321(1) 0.7500(3) 108.67(1) |
| 17         | 62.5, 34.4, 3.1 | 0.9730(1) 0.7216(2)       | 0.9318(7) 0.7502(0) 108.68(4) |

The La$_9$Si$_5$(SiO$_4$)$_6$O$_{26.5}$–La$_9$Mg$_3$(SiO$_4$)$_6$O$_2$ line. These results indicate that the MgO solubility limit must expand in the higher LaO$_1$$_3$ concentration region compared to that on the La$_9$Si$_5$(SiO$_4$)$_6$O$_{26.5}$–La$_9$Mg$_3$(SiO$_4$)$_6$O$_2$ solid-solution line.

We confirmed the oxyapatite single-phase region as well as the formed phases and their lattice parameters using samples with a composition of 58.4 mol% LaO$_1$$_3$–(41.6 – x) mol% SiO$_2$–x mol% MgO (3.2 ≤ x ≤ 15) that corresponds to line D in figure 2. The XRD peaks of the samples with x = 3.2, 4.2, 5.2 and 7 (samples 5–8 in table 1, respectively) can be indexed to oxyapatite as shown in figure 6. In the samples with x = 8 and 10, a very weak but isolated XRD
Table 5. List of the synthesized three-phase samples containing oxyapatite, LaO1.5, and L2SiO5 phases. Values x, y, and z refer to the formula x mol% LaO1.5 – y mol% SiO2 – z mol% MgO.

| Sample No. | Composition | Oxyapatite | LaO1.5 | L2SiO5 |
|------------|-------------|------------|--------|--------|
| 18         | 67, 29.5, 2.5 | 0.9739(2)  | 0.3936(9) | 0.9322(1) |
|            |             | 0.7235(3)  | 0.6140(9) | 0.7502(9) |
|            |             |            | 0.7028(1) | 108.65(1) |

Figure 8. Relationships between the lattice parameters of the oxyapatite phase and MgO concentration in the 58.4 mol% LaO1.5 – (41.6 − x) mol% SiO2 – x mol% MgO (solid circles), 50 mol% LaO1.5 – (50 − x) mol% SiO2 – x mol% MgO (open circles) and 30 mol% LaO1.5 – (70 − x) mol% SiO2 – x mol% MgO (open squares). Dashed lines mark the phase boundaries. Ap and L2S5 stand for the oxyapatite and L2SiO5 phases, respectively.

3.2. LaO1.5 – L2SiO5 – oxyapatite and LaO1.5 – oxyapatite – MgO three-phase regions

Three phases, namely oxyapatite–LaO1.5 – L2SiO5 and oxyapatite–LaO1.5 – MgO, coexisted in the compositional sample 18 (table 5) and samples 19–28 (table 6), respectively. A comparison of the lattice parameters of the LaO1.5 and/or La(OH)3 phases in the LaO1.5 – oxyapatite–L2SiO5 and LaO1.5 – oxyapatite–MgO regions revealed that the values were almost constant in a wide range of compositions. Therefore, we concluded that the solid solubilities of MgO and SiO2 in the LaO1.5 phase were small enough to be ignored. The lattice parameters of the oxyapatite phases were similar, indicating that the compositional width of the two-phase region consisting of the LaO1.5 and oxyapatite phases must be narrow. In addition, the tie line connecting the LaO1.5 and oxyapatite phases must cross the compositional point between 67 mol% LaO1.5 – 29.5 mol% SiO2 – 2.5 mol% MgO (sample 18) and 67 mol% LaO1.5 – 28 mol% SiO2 – 5 mol% MgO (sample 19) points shown in figure 2, because these compositions were located in different three-phase...
regions. The lattice parameters of the oxyapatite phase in sample 09 are slightly smaller than those in the three-phase oxyapatite–LaO$_1$–MgO region (tables 5 and 6). This result indicates that the compositional point where oxyapatite, LaO$_1$, and MgO phases coexist must be located on the right side of the point corresponding to sample 09 in figure 2, because the lattice parameter of the oxyapatite phase increases with increasing MgO concentration, as shown in figure 8. The tie line connecting the LaO$_1$ and the oxyapatite phases was determined by employing these restrictions.

3.3. Oxyapatite–MgO and oxyapatite–MgO–Mg$_2$SiO$_4$ regions

The large difference in the lattice parameters of the oxyapatites coexisting in the LaO$_1$–(La(OH)$_3$)–oxyapatite–MgO and oxyapatite–MgO–Mg$_2$SiO$_4$ phase regions (tables 6 and 7) indicates that the existence of a wide compositional range between these three-phase regions. The oxyapatite lattice parameters in the oxyapatite–MgO–Mg$_2$SiO$_4$ region are close to those of La$_2$Mg$_2$Si$_2$O$_7$O$_2$ (sample 04). Moreover, the solubility limits of LaO$_1$ in MgO and Mg$_2$SiO$_4$ must be small enough to be ignored because the lattice parameters of MgO and Mg$_2$SiO$_4$ are independent of the sample composition.

To determine the compositional width of the two-phase region composed of oxyapatite and MgO, we prepared two series of samples: one had a fixed LaO$_1$ concentration of 50 mol% (line E in figure 9) and the other had a fixed LaO$_1$ concentration of 30 mol% (line F). The XRD peaks from the MgO phase were difficult to identify in the wide 2θ scans shown in figures 10 and 11 in the samples corresponding to lines E and F. Weak but isolated peaks from the MgO phase were observed in the insets in figures 10 and 11, and they were heavily overlapped with the peaks from the oxyapatite and La(OH)$_3$ phases. In particular, the peak positions of the oxyapatite phase shift depending on the equilibrium chemical composition, and hence, it is difficult to identify the MgO phase by particular diffraction peaks such as the 200 and 220 peaks. The Mg$_2$SiO$_4$ peaks were identified between 2θ = 22.5° and 24.5°. Hence, the identification of the MgO peaks became difficult without considering all of the phase equilibrium relationships.

From the relationships between the lattice parameters of the oxyapatite and MgO concentration in the 50 mol% LaO$_1$–(50 – x) mol% SiO$_2$–x mol% MgO and 30 mol% LaO$_1$–(70 – x) mol% SiO$_2$–x mol% MgO samples (figure 8) it can be seen that the lattice parameters of the oxyapatite phase increased with increasing x in the two-phase region composed of oxyapatite and MgO. In

---

**Table 6.** List of a part of the synthesized three- and four-phase samples containing oxyapatite, LaO$_1$, (La(OH)$_3$) and La$_2$SiO$_5$. Values x, y and z refer to the formula x mol% LaO$_1$_5–y mol% SiO$_2$–z mol% MgO.

| Sample No. | Composition Oxyapatite | LaO$_1$ | La(OH)$_3$ | MgO | Formed phases and lattice parameters |
|------------|------------------------|--------|------------|-----|-------------------------------------|
| 19         | 67, 28, 5              | 0.9744(9) | 0.3935(8) | 0.653(5) | 0.42(2) | Oxyapatite, MgO, LaO$_1$ |
| 20         | 67, 23, 10             | 0.9742(1) | 0.3934(0) | 0.6525(7) | 0.418(8) | Oxyapatite, MgO, LaO$_1$ |
| 21         | 62, 31, 7              | 0.9743(3) | 0.393(7)  | 0.653(8)  | 0.418(9) | Oxyapatite, MgO, LaO$_1$ |
| 22         | 58.4                   | 0.9743(4) | 0.392(6)  | 0.6529(2) | 0.4212(2) | Oxyapatite, MgO, LaO$_1$ |
| 23         | 58.4, 29.6, 12         | 0.9737(8) | 0.614(2)  | 0.385(6)  | 0.3851(7) | Oxyapatite, MgO, LaO$_1$ |
| 24         | 26.6, 15               | 0.7241(0) | 0.6139(9) | 0.3856(0) | 0.3856(0) | Oxyapatite, MgO, LaO$_1$ |
| 25         | 55, 15, 30             | 0.9746(7) | 0.6528(1) | 0.4211(9) | 0.4211(9) | Oxyapatite, MgO, LaO$_1$ |
| 26         | 50, 25, 25             | 0.9744(9) | 0.393(5)  | 0.6529(2) | 0.4208(0) | Oxyapatite, MgO, LaO$_1$ |
| 27         | 30, 15, 55             | 0.9742(9) | 0.3936(8) | 0.6529(2) | 0.4212(8) | Oxyapatite, MgO, LaO$_1$ |
| 28         | 30, 10, 60             | 0.9741(9) | 0.392(5)  | 0.6522(0) | 0.4210(9) | Oxyapatite, MgO, LaO$_1$ |

**Table 7.** List of a part of the synthesized three-phase samples containing oxyapatite, Mg$_2$SiO$_4$ and MgO. Values x, y and z to the formula x mol% LaO$_1$_5–y mol% SiO$_2$–z mol% MgO.

| Sample No. | Composition Oxyapatite | Mg$_2$SiO$_4$ | MgO | Formed phases and lattice parameters |
|------------|------------------------|---------------|-----|-------------------------------------|
| 29         | 30, 25, 45             | 0.9611(8)     | 1.019(4) | 0.4212(0) | Oxyapatite, Mg$_2$SiO$_4$, MgO |
| 30         | 27.8, 29.6, 43.2       | 0.9615(5)     | 1.019(7) | 0.4212(0) | Oxyapatite, Mg$_2$SiO$_4$, MgO |
| 31         | 10, 23, 67             | 0.9615(7)     | 1.0196(4) | 0.4211(7) | Oxyapatite, Mg$_2$SiO$_4$, MgO |

---

**Figure 9.** Partial phase diagram of the LaO$_1$–SiO$_2$–MgO system. Line E corresponds to 50 mol% LaO$_1$–(50 – x) mol% SiO$_2$–x mol% MgO and line F to 30 mol% LaO$_1$–(70 – x) mol% SiO$_2$–x mol% MgO. Phases: ●, oxyapatite; ○, oxyapatite +La$_2$SiO$_5$; △, oxyapatite +La$_2$SiO$_5$ + MgO; ▲, oxyapatite +La$_2$SiO$_5$ + MgO + Mg$_2$SiO$_4$; □, oxyapatite + Mg$_2$SiO$_4$ + La$_2$Si$_2$O$_7$.
None of the text is readable in the image provided.
Table 8. List of the synthesized three-phase samples containing La$_2$Si$_2$O$_7$, Mg$_2$SiO$_4$ and MgSiO$_3$. Values $x$, $y$ and $z$ refer to the formula $x$ mol% LaO$_{1.5}$–$y$ mol% SiO$_2$–$z$ mol% MgO. Changes in the shape of the pellets after heating at 1773 K for 10 h are noted.

| Sample No. | Shape change | Composition | Formed phases and lattice parameters |
|-----------|--------------|-------------|--------------------------------------|
|           |              | $x$, $y$, $z$ | $a$, $b$, $c$ (nm), $\beta$         | $a$, $b$, $c$ (nm), $\beta$ |
| 32        | Melted       | 25, 47, 28  | 0.5408(2) 1.019(4) 0.931(0)          | 0.8794(0) 0.5981(3) 0.889(7) |
|           |              |             | 1.428(2) 0.4755(3) 0.518(7)          | 112.75(4)$^\circ$ |
| 33        | Partly bended| 25, 43, 32  | 0.5409(7) 1.0194(4) 0.951(9)          | 0.8795(6) 0.5982(0) 0.857(0) |
|           |              |             | 1.4285(3) 0.4756(0) 0.521(9)          | 112.76(1)$^\circ$ |
| 34        | Melted       | 10, 45, 45  | 0.5411(4) 1.020(2) 0.937(0)          | 0.880(3) 0.598(5) 0.882(3) |
|           |              |             | 1.428(4) 0.4754(3) 0.518(1)          | 112.75(9)$^\circ$ |
| 35        | Partly bended| 4, 43, 53   | 0.5412(0) 1.020(2) 0.937(5)          | 0.880(2) 0.5983(3) 0.882(0) |
|           |              |             | 1.428(5) 0.4754(9) 0.517(3)          | 112.7(5)$^\circ$ |

lattice parameters was found for the MgSiO$_3$ phase in the La$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$–MgSiO$_3$ region (table 7). Moreover, the lattice parameters of the La$_2$Si$_2$O$_7$ and Mg$_2$SiO$_4$ phases are almost the same as those of the samples in the oxyapatite–La$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$ three-phase region, which are listed in table 2. These results indicate that the MgO solubility in the La$_2$Si$_2$O$_7$ and Mg$_2$SiO$_4$ phases can be ignored.

Complex relationships were observed among the La$_2$Si$_2$O$_7$, SiO$_2$ and MgSiO$_3$ phases. The XRD profiles of most samples in this region could be fitted by a four-phase mixture of the La$_2$Si$_2$O$_7$ [20], MgSiO$_3$ with a low-temperature forsterite form [17], and two polymorphic silica phases with low-temperature cristobalite form [32] and low-temperature tridymite form [19]. Based on the lattice parameters in this region (table 9), metastability generated by cooling the liquid phase seemed to be imposed on the low-temperature form cristobalite, low-temperature form tridymite and low-temperature form MgSiO$_3$ phases, because the lattice parameters showed scattering with the sample composition instead of the composition independent lattice parameters.
observed for the La$_2$Si$_2$O$_7$ phase. Changes in the lattice parameters with the composition were observed for samples corresponding not only to the La$_2$Si$_2$O$_7$–SiO$_2$–MgSiO$_3$ but also the La$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$–MgSiO$_3$ three-phase region implying that the MgO solubility in La$_2$Si$_2$O$_7$ and MgSiO$_3$ could be ignored.

3.5. Ternary phase relationships in the LaO$_{1.5}$–SiO$_2$–MgO system at 1773 K

Using all the obtained XRD results, we have summarized the overall phase relationships in the LaO$_{1.5}$–SiO$_2$–MgO system in figure 13. The phase boundary lines, including the metastable phases, are drawn by the dashed lines. Considering the compositions of the melted samples, marked by ⊕ symbol in figures 12 and 13, it can be seen that the liquid-phase region overlaps with three regions composed of the La$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$–MgSiO$_3$, La$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$–MgSiO$_3$ and La$_2$Si$_2$O$_7$–SiO$_2$–MgSiO$_3$ phases. The differences in the phase relationships between the formed phases at room temperature and at 1773 K are the existence of the liquid phase: two-phase regions connecting La$_2$Si$_2$O$_7$, Mg$_2$SiO$_4$, MgSiO$_3$ and SiO$_2$ with the liquid phase and three-phase regions containing the liquid phase. Considering the liquid-phase region inferred from the experimental results and the Gibbs’ phase rule, the isothermal section of the phase relationships in the LaO$_{1.5}$–SiO$_2$–MgO system at 1773 K in air is drawn in figure 14.

Surprisingly, the compositional region of the liquid phase expands up to not only the SiO$_2$–MgO side but also the high-LaO$_{1.5}$-concentration region. Referring to the phase diagram of the LaO$_{1.5}$–SiO$_2$ system [32], the lowest temperature of liquid-phase formation is the eutectic point (1898 K) at 60 mol% SiO$_2$, and for the MgO–SiO$_2$ system, the lowest eutectic temperature (about 1820 K) is reported at 54 mol% MgO [25]. These data are consistent with our results that the compositional width of the liquid phase decreases with increasing LaO$_{1.5}$ concentration due to the increasing melting temperature. Our data also agree with reports on the expansion of liquid-phase regions by the addition of CaO and MgO to the GdO$_{1.5}$–SiO$_2$ [33, 34] and YO$_{1.5}$–SiO$_2$ [34, 35] systems.

If the annealing temperature increased, the liquid-phase region would expand into the high-LaO$_{1.5}$-concentration
4. Conclusions

To clarify the phase diagram of the LaO$_{1.5}$–SiO$_2$–MgO system, we have investigated the phase relationships in 57 samples of different compositions by single- and multiple-phase Rietveld analysis. All the samples were heated at 1773 K for 10 h in air. The formed phases complied with the Gibb’s phase rule except for those containing the LaO$_{1.5}$ phase and liquid phase at 1773 K. Determination of the boundary composition between the oxyapatite single phase and oxyapatite–MgO dual phase was found to be difficult by XRD analysis of the profiles of the compositional samples around the oxyapatite single phase because most XRD peaks of the MgO phase were overlapped with the peaks of the oxyapatite phase. The oxyapatite single-phase region expanded in the compositional directions of MgO substitution into not only LaO$_{1.5}$ but also SiO$_2$ regions. The liquid phase exists in a wide range of compositions at 1773 K. Based on the experimental results, the phase diagram of the LaO$_{1.5}$–SiO$_2$–MgO system at 1773 K has been constructed.

Acknowledgments

The authors are grateful to Dr Takuji Ikeda at Tohoku University for his helpful suggestions on the single- and multiple-phase Rietveld analyses.

References

[1] Nakayama S 1995 Chem. Lett. 24 431
[2] Nakayama S, Kageyama T, Aono H and Sadaoka Y 1995 J. Mater. Chem. 5 1801
[3] Nakayama S and Sakamoto M 1998 J. Eur. Ceram. Soc. 18 1413
[4] Yoshio H 2004 Chem. Lett. 33 392
[5] Yoshio H and Tanase S 2005 Solid State Ion. 176 2395
[6] Yoshio H 2007 J. Am. Ceram. Soc. 90 3099
[7] Kendrick E, Sansom J E H, Tolchard J R, Islam M S and Slater P R 2007 Faraday Discuss. 134 181
[8] Ali R, Yashima M, Matsushita Y, Yoshioka H, Ohyama K and Izumi F 2008 Chem. Mater. 20 5203
[9] Ali R, Yashima M, Matsushita Y, Yoshioka H and Izumi F 2009 J. Solid State Chem. 182 2846
[10] Kinoshita T, Iwata T, Béchade E, Masson O, Julien L, Champion E, P. Yoshida H, Ishizawa N and Fukuda K 2010 Solid State Ion. 181 1024
[11] Okudera H, Masubuchi Y, Kikawa S and Yoshiasa A 2005 Solid State Ion. 176 1473
[12] Sansom J H E, Kendrick E, Torchard J R, Islam M S and Slater P R 2006 J. Solid State Electrochem. 10 562
[13] Guillot S, Beaudet-Savignat S, Lambert S, Roussel P and Vannier R-N 2011 Solid State Ion. 185 18
[14] Kobayashi K, Matsushita Y, Igawa N, Izumi F, Nishimura C, Miyoshi S, Oyama Y and Yamaguchi S 2008 Solid State Ion. 179 2209
[15] Imashuku S, Uda T, Nose Y and Awakura Y 2011 J. Phase Equilib. Diffus. 31 348
[16] Oyama Y, Kojima A, Li X, Cervera R B, Tanaka K and Yamaguchi S 2011 Solid State Ion. 197 1
[17] Duan W, Karki B, Wentzcovitch R M and Gu B L 2001 Am. Mineral. 86 762
[18] Kiefel A, Lippmann T, Blaha P, Schwarz K, Cox D F, Rosso K M and Gibbs G V 2005 Phys. Chem. Mineral. 32 301
[19] Graetsch H A 2003 Z. Kristallogr. 218 531
[20] Greis O, Bossemeyer H G, Greif P, Bredensterin B and Haase A 1991 Mater. Sci. Forum. 79–82 803
[21] Fukuda K, Iwata T and Champion E 2006 Powder Diffr. 21 300
[22] Koehler W C and Wollan E O 1953 Acta Crystallogr. 6 741
[23] Djerdi I, Granweighter G, Su D S and Niederberger M 2007 J. Solid State Chem. 180 2154
[24] Bowen N L and Andersen O 1914 Am. J. Sci. 187 487
[25] Swamy V, Saxena S K and Sundman B 1994 CALPHAD 18 157
[26] Kobayashi K, Suzuki T S, Uchikosh T and Sakka Y 2011 Solid State Ion. 204–205 91

Figure 14. Phase diagram of the LaO$_{1.5}$–SiO$_2$–MgO system at 1773 K in air. Liq stands for liquid phase. Phase boundaries and tie lines related to the liquid phase are shown by the dashed lines. Phases: •, oxyapatite; ◇, oxyapatite + La$_2$SiO$_5$; ◤, oxyapatite + La$_2$Si$_2$O$_7$; ▲, oxyapatite + MgO; △, oxyapatite + MgO + Mg$_2$SiO$_4$; □, oxyapatite + Mg$_2$SiO$_4$ + Li$_2$SiO$_3$; ◆, liquid phase: ○, La$_2$SiO$_5$ + Mg$_2$SiO$_4$ + MgSO$_4$; ■, La$_2$Si$_2$O$_7$ + MgSiO$_3$ + SiO$_2$ (L-tridymite + L-cristobalite).
[27] Izumi F and Momma K 2007 Solid State Phenom. 130 15
[28] Cockbain A G and Smith G M 1967 Miner. Mag. J. Miner. Soc. 36 411
[29] Jantzen C M and Glasser F P 1979 Am. Ceram. Soc. Bull. 58 459
[30] McHale A E 1998 Phase Diagrams and Ceramic Processes (New York: Chapman and Hall) pp 63 and 110
[31] Ozawa M, Onoe R and Kato H 2006 J. Alloys Compounds 408–412 556
[32] Kim Y-I, Im W B and Jeon D Y 2006 J. Mater. Sci. 41 1643
[33] Li L, Tang Z, Sun W and Wang P 1999 J. Mater. Sci. Technol. 15 439
[34] Fedorov N F, Andreev I F and Korneeva T F 1972 Inorg. Mater. 8 1919 (Engl. Transl.)
[35] Kuang S, Hoffmann M J, Lukas H L and Petzow G 1994 Key Eng. Mater. 89–91 399
[36] Shimizu F, Tokunaga H, Saito N and Nakashima K 2006 ISIJ Int. 46 388