Rudimental research progress of rare-earth silicate oxyapatites: their identification as a new compound until discovery of their oxygen ion conductivity

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Rudimental research progress of oxyapatite-type rare-earth silicates is reviewed based on the published papers mainly from 1959 to 1993 that have not yet been discussed in detail. The knowledge of oxyapatite-type rare-earth silicates significantly increased during this period. Chemical compounds of rare-earth oxides and silica were discovered around 1960. Because of the complex chemical composition of the oxyapatite phase, the composition was initially considered as $2\text{RE}_2\text{O}_3\cdot3\text{SiO}_2$, which was called orthosilicate. “RE” is the rare-earth elements. Different compositions of $2\text{RE}_2\text{O}_3\cdot3\text{SiO}_2$ have been proposed by crystal structure analysis based on the crystal chemistry and the leaping model. With respect to crystal structure analysis, knowledge has gradually improved step-by-step, including the implicit distinction between oxygen-stoichiometric apatite and oxygen-deficient apatite. Based on the published work, the rare-earth silicate oxyapatites are considered to have an apatite-like structure. Initially, application research focused on the optical properties of oxyapatite because rare-earth metals were constituent elements of the crystals, and on the use of oxyapatite as a stabilizer of unwanted radioactive waste produced in nuclear power reactors because oxyapatites can dissolve the actinide elements.

Key-words : Rare-earth silicate, Oxyapatite, Synthetic apatite, Phase diagram, Crystal structure

1. Introduction

Since Nakayama et al. reported high oxygen ion conductivity in lanthanoid silicate oxyapatites, many researchers have been interested in these materials because of their fundamentally different properties from typical oxygen ion conductors such as stabilized zirconia. One peculiar property is the presence of interstitial oxygen ions, which were first proposed in the literature at 2000. Some specialists in solid-state oxygen ionic conductors did not believe the initial reports. Lanthanoid silicate and rare-earth silicate compounds were first identified in 1959. However, the compounds corresponding to oxyapatites were identified as orthosilicate. On the other hand, lanthanoid silicate oxyapatites seemed to be recognized after 1995 in recent papers. In this review, we focused on the research of the rare-earth silicate oxyapatites before 1995. Furthermore, a part of the stacked knowledge until 1993 seemed not to be taken over after 1995.

In the early 1960s, there was research competition for clarification of the phase diagram of rare-earth oxides and silica between the USA and Soviet Union. Some rare-earth silicate compounds were discovered by Warshaw et al. and Toropov et al. The chemical composition of the apatite phase, however, was not correctly identified because of an anomalous property of the oxyapatite phase and the low resolution of the analytical instruments at that time. Therefore, the new compound was presented as orthosilicate.

Almost at the same time, the existence of rare-earth silicate oxyapatites was also recognized by mineralogists because of the similarity between rare-earth and silicon-containing minerals. However, the oxygen ion conductive function at high temperature was not identified until about 30 years later. Before the discovery of their good oxygen ion conductive properties, the main research focus was crystallographic analysis, their possible application as laser hosts, their fluorescent properties, and stabilizer host of unwanted radioactive waste. On the other hand, the accumulation and precision of the crystallographic data for rare-earth silicate oxyapatites and the similarities between the phase diagrams of rare-earth oxides and silica played an important role in the discovery of the oxygen ion conductivity. In this review, we summarize the research history of rare-earth silicate oxyapatites from the identification of the new compound (1959) up until the discovery of the oxygen ion conductivity (1993).

2. Identification of new compounds and the phase diagrams of rare-earth oxide and silica quasi-binary system

In the early 1960s, clarification of the chemical and physical properties of rare-earth element compounds was a very important scientific topic. Troprov and Bondar reported that the “U. S. Bureau of Mines planned a large program of fundamental research on the refractory properties of rare-earth oxides individually and in combination with other oxides” (See Appendix A), and “In the Institute of Silicate Chemistry, a large program of work has been planned for the study of phase diagrams of systems containing silica and oxides of rare and disperse elements, and the investigation of the physical and physicochemical properties of

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‡ This article was selected from the presentations at “STAC-7” (The 7th International Conference on the Science and Technology for Advanced Ceramics) held in Yokohama, Japan (2013), through the regular reviewing procedure.
crystalline and vitreous phases of these systems” in the Soviet Union. According to the large program in the Soviet Union, systematic research on the clarification of the phase diagrams of rare-earth oxide and silica quasi-binary systems was performed by Toropov’s group at the Institute of Silicate Chemistry and at the Leningrad Lensoviet Technological Institute.

From 1958 to 1959, three groups reported new rare-earth silicates with different compositions. Toropov’s group reported a new compound with composition 2La2O3·3SiO2. Roy’s group reported two new compounds with compositions of RE2O3·SiO2 and RE2O3·2SiO2 by studying the phase diagrams of silica and rare-earth (RE) oxide binary systems. In addition, Wannmaker’s group reported one lanthanum silicate compound, La2SiO4, in the same year. These studies were the initial research related to synthetic silicate-oxyapatites (See Appendix B).

In 1961, Keler et al.11–13 published three papers related to the phase diagrams of quasi-binary systems of praseodymium oxide, lanthanum oxide (La2O3), neodymium oxide (Nd2O3), gadolinium oxide (Gd2O3), and reduced cerium oxide (Ce2O3) with silica. In these papers, they discovered the three compounds RE2O3·SiO2 (RE=RE, La, Nd, Pr, Gd, and Ce). Based on the reported phase relationships, most of the samples might not be reached to the equilibrium state. Because the phase relationship in the La2O3–SiO2 system presented in reference11) (Fig. 1) does not satisfy the Gibbs’ phase rule,14 except for the La2O3–2SiO2 (La2Si2O5) composition at 1923 K for 1.5h. Based on the X-ray diffraction (XRD) patterns in,11–13 it is almost impossible to distinguish between single-phase samples and the two phases coexisting because of low diffraction angle accuracy and low intensity of XRD for the analysis of quasi-binary system in rare-earth oxide binary systems. In addition, the symmetry of the segregated crystal was determined from the shape of the precipitates. Although this method is too simple for today’s analysis, they surprisingly reached the conclusion that the unit cell of the La4Si3O12 crystal had hexagonal symmetry. However, the Miller indices of the XRD peaks and the calculated lattice constants (a = 1.123 nm, c = 0.467 nm) of their results were incorrect compared with the present data, for example, compared with the lattice constant of La6.33(SiO4)3O2 (a = 0.9714 nm and c = 0.7183 nm).

In the second to eighth papers,15–19 Toropov’s group also confirmed two compounds, RE2O3·2SiO2 and RE2O3·3SiO2 (RE = Y, Nd, Gd, Dy, Er, Sm, and Yb), discovered by Roy’s group. According to this confirmation, the phase diagrams of the RE2O3–SiO2 quasi-binary system were revised to the same as the data in the Phase Equilibria database21) (Fig. 3). A further revision was made that RE5Si5O12 (2RE2O3·3SiO2) was unstable below about 1873 K because the sample with composition 2RE2O3·3SiO2 was in the two phases RE2O3·SiO2 and RE2O3·2SiO2. However, the proof for the decomposition from 2RE2O3·3SiO2 to 2RE2O3·2SiO2 and RE2O3·SiO2 was only from one image observed by optical microscope (Fig. 4). In addition, the unit cell parameters of 2RE2O3·3SiO2 presented in these papers were different from today’s data. Although the phase boundary curves related to the liquid phases were investigated by thermodynamic modeling,24,25 the phase decomposition of 2RE2O3·3SiO2 below 1600°C has not been confirmed.

In 1964, Miller and Rase26) claimed that the phase diagram of the Nd2O3–SiO2 quasi-binary system proposed by Toropov27) [Fig. 5(a)] was incorrect [Fig. 5(b)]. The main differences were two eutectic reaction temperatures and the stability temperature region of Nd2O3·2SiO2 (Nd2Si2O7). The eutectic reaction temperature differences at 55 and 74 mol% SiO2 in the (100-x) mol% Nd2O3–x mol% SiO2 system were 130 and 35 K, respectively.
In addition, they reported that the melting temperature of the Nd$_2$O$_3$·2SiO$_2$ (Nd$_2$Si$_2$O$_7$) system was 1953 K, which was 70 K lower than Toropov's data. Comparing to these phase diagrams, temperature region where Nd$_2$O$_3$·2SiO$_2$ (Nd$_2$Si$_2$O$_7$) phase was stable, was different from each other. Miller and Rase concluded that Nd$_2$O$_3$·2SiO$_2$ (Nd$_2$Si$_2$O$_7$) phase was stable only above 1843 K because two phase formation was confirmed constructed by 2Nd$_2$O$_3$·3SiO$_2$ phase and SiO$_2$ phase was observed by the heating below 1843 K. Toropov reported that Nd$_2$O$_3$·2SiO$_2$ (Nd$_2$Si$_2$O$_7$) phase was stable between 2023 K and 1773 K. Existence of immiscibility of the liquid phase in the composition region higher than 80 mol% SiO$_2$ was reported by Glasser et al., Toropov, and Miller and Rase. With respect to the miscibility gap, thermodynamic modeling was performed based on the analytical expression of the Gibbs energy in the liquid phase.

In 1967, Roy's group published a paper on the preparation of Sm$_4$(SiO$_4$)$_3(2Sm$_2$O$_3$·3SiO$_2$) and Nd$_4$(SiO$_4$)$_6$ (2Nd$_2$O$_3$·3SiO$_2$). In this paper, they pointed out that this compound was stable below 1903 K, which corresponds to the decomposition temperature for Sm$_4$(SiO$_4$)$_3$ (2Sm$_2$O$_3$·3SiO$_2$) reported by Toropov's group. With respect to Nd$_4$(SiO$_4$)$_6$ (2Nd$_2$O$_3$·3SiO$_2$), Toropov did not report whether it was stable or not below 1903 K, because the Nd$_4$(SiO$_4$)$_6$ (2Nd$_2$O$_3$·3SiO$_2$) line was drawn as a broken line in the phase diagram. However, the results that Sm$_4$(SiO$_4$)$_3$ (2Sm$_2$O$_3$·3SiO$_2$) and Nd$_4$(SiO$_4$)$_6$ (2Nd$_2$O$_3$·3SiO$_2$) compounds were stable below 1903 K are not in the Phase diagram database because Roy's group did not publish the phase diagrams of the RE$_2$O$_3$·SiO$_2$ system (See Appendix C). A revised phase diagram of the La$_2$O$_3$·SiO$_2$ quasi-binary system was found in the invited review paper written in 1982 by Bondar, who was a research collaborator with Toropov (Fig. 6). This revised phase diagram was presented by referring to a textbook written in Russian in 1971 (See Appendix D). However, both the phase diagrams reported in the Russian textbook and in the Bondar's review are not in the phase equilibria database. In this review, the composition of 2RE$_2$O$_3$·3SiO$_2$ was revised to 7RE$_2$O$_3$·9SiO$_2$, and this compound is stable below 1873 K. Other important data reported by Roy's group in 1967 were the Miller indices and lattice constant values ($a = 0.94923$ nm and $c = 0.69394$ nm) for Sm$_4$(SiO$_4$)$_3$, which are close to the lattice parameters of oxyapatite ($a = 0.9497$ nm and $c = 0.6949$ nm) for Sm$_{9.33}$(SiO$_4$)$_6$O$_{2}$ even though it is now known that it was not possible to synthesize the oxyapatite single phase with the composition Sm$_4$(SiO$_4$)$_3$.

In 1971, Toropov and Kougiya revised the phase diagram of Nd$_2$O$_3$·SiO$_2$ quasi-binary system around oxyapatite composition (Fig. 7). Neodymium silicate oxyapatite phase has a compositionnal width with $x$ mol% SiO$_2$ range between $x = 54.5$ [corresponding to Nd$_{10.03}$(SiO$_4$)$_6$O$_{3.045}$] and $x = 60$ [corresponding to Nd$_{7.67}$(SiO$_3.9175$)$_6$] after the papers by Miller et al. and
Nd:Si indicates the mole fraction value of Nd$_2$O$_3$:SiO$_2$.

It was found that Nd$_2$Si$_2$O$_7$ compound was also revised by Toropov and Kougiya in 1971. This diagram was re-drawn from the Fig. 1 in reference. The labels in this figure are as follows: L: La$_2$O$_3$, LS: La$_2$O$_3$:SiO$_2$, L7S9: 7La$_2$O$_3$·9SiO$_2$, LS2: La$_2$O$_3$·2SiO$_2$, S: SiO$_2$, liq: liquid phase, and liq1 and liq2 are the liquid phase with different composition in the miscibility gap. Although L' and L'' might be two high temperature phases, there was no explanation in reference.

In 1982, Montorsi reported compounds of Ho$_2$O$_3$ and silica with the compositions Ho$_2$O$_3$:SiO$_2$, 2Ho$_2$O$_3$:3SiO$_2$, Ho$_2$O$_3$:5SiO$_2$, and Ho$_2$O$_3$:6SiO$_2$. In addition, the phase diagram of the Ho$_2$O$_3$–SiO$_2$ quasi-binary system was proposed in the limited temperature range below 1873 K. Furthermore, in this report the 2Ho$_2$O$_3$:3SiO$_2$ compound had hexagonal symmetry and was the stable high temperature phase above 1573 K.

Here, it is necessary to emphasize that all the groups that investigated the phase diagrams of rare-earth oxide-silica quasi-binary systems did not use the apatite or oxyapatite terms for the orthosilicate compounds $2$RE$_2$O$_3$:3SiO$_2$ (RE$_4$Si$_3$O$_{12}$) compound. For categorization of compounds by crystal structure in phase diagram research, it was necessary for ceramists to conform to the system used in mineralogy and crystal chemistry. Considering this fact, Bondar et al. used a different categorization to that normally used by ceramists, and the interdisciplinary research seemed to proceed smoothly in the Soviet Union.

In 1994, Tas and Akinc investigated the phase diagram of Ce$_2$O$_3$–Ce$_2$Si$_2$O$_7$ between 1423 K and 2243 K under Ar + 10% H$_2$ atmosphere to avoid CeO$_2$ formation. In this paper, Ce$_{4.67}$O(SiO$_4$)$_3$O phase was described as cerium oxygen apatite. Based on their results, the phase relationship between Ce$_2$O$_3$ and Ce$_2$Si$_2$O$_7$ were similar to the relationship of La$_2$O$_3$–SiO$_2$ quasi-binary system except for the phase transition of Ce$_2$Si$_2$O$_7$. The polymorphic transformation exists at 1547 K among tetragonal low-temperature form and monoclinic high-temperature form.

In 2003, Masubuchi et al. reinvestigated the phase diagram of the Nd$_2$O$_3$–SiO$_2$ quasi-binary system by single crystal growth of Nd$_{10.03}$(SiO$_4$)$_6$O$_{3.045}$ and partial dimerization of [SiO$_4$]$^{5-}$ unit. At present, the orthosilicate represents olivine, garnet, zircon, and etc. In addition, referring to the paper by Grisafe and Hummel, McCathy et al. seemed to consider that 2RE$_2$O$_3$:3SiO$_2$ orthosilicate had a similar but different crystal structure to apatite. In a review paper in 1982 by Bondar, the compound RE$_4.67$O(SiO$_4$)$_3$ (7RE$_2$O$_3$:9SiO$_2$) was introduced as an apatite-like silicate determined by Belov et al. Belov’s paper was published in 1965. Belov et al. solved the correct crystal structure and determined corresponding chemical composition of RE$_{4.67}$O(SiO$_4$)$_3$ (7RE$_2$O$_3$:9SiO$_2$) which had been identified as orthosilicate, 2RE$_2$O$_3$:3SiO$_2$ (RE$_4$Si$_3$O$_{12}$) compound. For categorization of compounds by crystal structure in phase diagram research, it was necessary for ceramists to conform to the system used in mineralogy and crystal chemistry. Considering this fact, Bondar et al. used a different categorization to that normally used by ceramists, and the interdisciplinary research seemed to proceed smoothly in the Soviet Union.

Before 1960, there had been considerable interest in the lanthanoid silicate system by mineralogists. Several mineralogists had already succeeded in solving the crystal structure and determining the chemical composition of fluorapatite.
(Ca10(PO4)6F2) before 1946.\(^{38}\) In addition, they already knew that several minerals, with different chemical composition to hydroxyapatite and fluorapatite, belonged to the apatite group. Based on early review-like papers,\(^{39,40}\) rare-earth silicate apatites were recognized to be isostructural to the natural minerals britholite, abukumalite, beckelite, and lessingite. The chemical formulae of these minerals are as follows:

- **Britholite**: \((\text{Ce}, \text{Ca}, \text{Th}, \text{La}, \text{Nd})_{10} (\text{SiO}_4, \text{PO}_4)_6 (\text{OH}, \text{F})_2\)
- **Abukumalite**: \((\text{Ca}, \text{Y})_{10} (\text{PO}_4, \text{Si}_4)_{6} (\text{OH}, \text{F})_2\)
- **Beckelite and Lessingite**: \((\text{Ce}, \text{Ca})_{10} (\text{Si}_3)_{3} (\text{OH}, \text{F})_2\)

Although these minerals contain rare-earth elements and silicon, all of the compounds seem to be categorized in the apatite group, in particular the hydroxyapatite or fluorapatite groups because they all contain the anions \(\text{OH}^-\) and \(\text{F}^-\). Mineralogist seemed to begin the artificial synthesis of apatite compounds inspired by the chemical compositions of these minerals.

Kuzmin and Belov focused on the similarity of the powder XRD pattern of the La and Sm silicates reported as orthosilicate \((2\text{RE}_2\text{O}_3 \cdot 3\text{Si}_2\text{O}_5)\) and britholite in 1965.\(^{34}\) The XRD patterns of britholite \([\text{Ce}, \text{Ca}, \text{Th}, \text{La}, \text{Nd})_{10} (\text{Si}_3, \text{PO}_4)_{3} (\text{OH}, \text{F})_2\) and \(\text{La}_{1.13} (\text{Si}_3\text{O}_9)_2 \text{O}_2\) calculated using the crystallographic data\(^{40,22}\) and RIETAN-FP software\(^{41}\) are shown in Fig. 9. From the host chemical composition of britholite \([\text{Ca}_{10} (\text{PO}_4)_{6\text{F}_2}]\) before 1946.\(^{38}\) In addition, they already knew that the lanthanum silicate and samarium silicate reported as orthosilicate \((2\text{RE}_2\text{O}_3 \cdot 3\text{Si}_2\text{O}_5)\) has a hexagonal symmetry and belongs to the space group \(P6_3/m\). Model (3) was confirmed to be the most adequate based on the XRD results. By their careful analysis, the chemical composition was determined as \(7\text{RE}_2\text{O}_3 \cdot 3\text{Si}_2\text{O}_5 \cdot 0.7\text{Si}_2\text{O}_5\), which corresponded to the \(7\text{RE}_2\text{O}_3 \cdot 9\text{Si}_2\text{O}_5\). The crystallographic data and the corresponding structure in this paper, which are fundamentally consistent with the present widely accepted oxygen-stoichiometric oxyapatite model, are shown in Table 1 and Fig. 10(a), respectively. According to Kuzmin and Belov’s results, the rare-earth ions at the 4\(f\) and 6\(h\) sites will be hereafter denoted as RE1(4\(f\)) and RE2(6\(h\)) or chemical

![Fig. 9. Simulated powder X-ray diffraction patterns of britholite\(^{40}\) (a) and \(\text{La}_{1.13} (\text{Si}_3\text{O}_9)_2 \text{O}_2\)\(^{22}\) (b) using the crystallographic data and the RIETAN-FP software.\(^{41}\) ](image)

**Table 1.** Coordinates of the atoms in \(\text{La}_{4\text{+}3/2} (\text{Si}_3\text{O}_9)_2 \text{O}_2\) and \(\text{Sm}_{4\text{+}3/2} (\text{Si}_3\text{O}_9)_2 \text{O}_2\) reported by Kuzmin and Belov in 1965.\(^{34}\) Both of the crystals have the hexagonal lattice with space group \(P63/m\). In the original paper, the La1(4\(f\)), La2(6\(h\)), Sm1(4\(f\)), and Sm2(6\(h\)) sites in this table were labeled as La1, La2, Sm1, and Sm2, respectively. In addition, site occupancy \((g)\) is included in the table.

| Site          | \(a = 0.953 \text{ nm} \) and \(c = 0.714 \text{ nm}\) | \(g\)  | \(x\)  | \(y\)  | \(z\)  |
|---------------|-----------------------------------------------|-------|-------|-------|-------|
| La1(4\(f\))  | 0.833                                        | 1/3   | 2/3   | 0     |
| La2(6\(h\))  | 1                                            | 0.233 | −0.013| 1/4   |
| Si(6\(h\))   | 1                                            | 0.400 | 0.368 | 1/4   |
| O1(6\(h\))   | 1                                            | 0.333 | 0.485 | 1/4   |
| O2(6\(h\))   | 1                                            | 0.592 | 0.468 | 1/4   |
| O3(12\(h\))  | 1                                            | 0.346 | 0.246 | 0.073 |
| O4(2\(a\))   | 1                                            | 0     | 0     | 1/4   |

| Site          | \(a = 0.933 \text{ nm} \) and \(c = 0.685 \text{ nm}\) | \(g\)  | \(x\)  | \(y\)  | \(z\)  |
|---------------|-----------------------------------------------|-------|-------|-------|-------|
| Sm1(4\(f\))  | 0.833                                        | 1/3   | 2/3   | 0     |
| Sm2(6\(h\))  | 1                                            | 0.232 | −0.009| 1/4   |
| Si(6\(h\))   | 1                                            | 0.394 | 0.370 | 1/4   |
| O1(6\(h\))   | 1                                            | 0.319 | 0.493 | 1/4   |
| O2(6\(h\))   | 1                                            | 0.595 | 0.470 | 1/4   |
| O3(12\(h\))  | 1                                            | 0.342 | 0.244 | 0.065 |
| O4(2\(a\))   | 1                                            | 0     | 0     | 1/4   |
element1(4f) and chemical element2(6h). The crystal structures were drawn by Kužmin and Belov’s model using the VESTA program. The difference between the results of Kužmin and Belov and those of recent studies22,34 is the RE1(4f) position: Kužmin and Belov’s analysis fixed the z position of the RE1(4f) site at 0, whereas the recent structural data have the z value slightly shifted from 0 [Fig. 10(b)]. Comparing the simulated XRD patterns of Kužmin and Belov’s original model and the modified model by changing the La1(4f) position and the lattice constants reported by Okudera et al.22 [Fig. 11] shows that the experimentally collected pattern is different from the simulated pattern by Kužmin and Belov. Hence, the accuracy of the Kužmin and Belov model seems to be insufficient. This might be because of the low analytical resolution of the instruments in 1965. The difference is mainly because of the lattice constants, as explained below.

One important conclusion by Kužmin and Belov was that 3 + 1/3 of the RE ions are statistically distributed in the RE1(4f) site35 and they determined the chemical composition of the rare-earth silicate oxyapatite from the crystal structure analysis. This methodology might be the opposite route to the chemists and ceramists. Chemists and ceramists at that time determined the chemical composition of new compounds from the nominal composition when the single phase was obtained because they did not have effective analytical method such as electron probe micro-analysis. Then, candidate crystal structure would be selected from the chemical composition. On the other hand, Kužmin and Belov determined the chemical composition of rare-earth silicate oxyapatites from the crystal structure. Considering that Belov had studied various types of silicates,43 the method would be based on both crystal chemistry and silicate chemistry.

The most important difference between the crystal model of Kužmin and the other studies is the assumption of the existence of statistical rare-earth deficiency. This indicates that the chemically stoichiometric composition does not indicate a perfect state compared with its crystal structure. This concept is significantly different from the model of disorder in crystals proposed by Frenkel44-46 and Wagner and Schottky.55-57 The concept of defects in crystal by Frenkel, and Wagner and Schottky is that defects are treated as components in thermodynamic system. Therefore, formation mechanism of defects is two types: one type of defects is formed by the thermal activation process to minimize the Gibb’s energy of the crystal system (or maximize the entropy of the crystal system); the second type is formed by doping of alien-valent ions to keep a charge neutrality of ionic crystals. In the latter case, the defects are formed to maintain charge neutrality in the crystals.48-51 However, the Kužmin and Belov model set the rare-earth deficiency as primitive existence. Although the structural model by Kužmin and Belov was derived from single-crystal XRD analysis, their suggestions seemed to not be widely accepted in the US and Europe during the 1960s.

For example, Ito agreed with the findings of Kužmin and Belov because the results were consistent with the lattice parameter dependences for a large number of the monovalent and divalent ion-doped lanthanoid silicate oxyapatites that he synthesized and analyzed.59 However, he stated that “The finding of cation-defect apatite opens the wide possibilities of cation deficiency in silicate apatites generally. Further investigation is indicated”. Ito synthesized a large number of samples, but the sample composition with RE9.33(SiO4)6O2 was not contained in his sample list. After the Kužmin and Belov’s paper, the RE9.33(SiO4)6O2 oxyapatites were followed in 1969 by Smolin and Shepelev52 and Felsche,53 and in 1972 by Belokoneva et al.54 and Felsche.55 The reason might be that the concept of primitive rare-earth deficiency was so far from the conventional knowledge.

Below we give the modern interpretation of Kužmin and Belov’s analysis logic. Keep in mind that systematic research on clarifying the physicochemical properties of rare-earth oxides started around 1960 and the possibility of the mixed valence state of La ion was not confirmed experimentally until 1965. If a mixed valence state of La ion was considered, it would be possible to explain why the rare-earth silicate oxyapatites were only formed at high temperature, as reported by Tropov et al.15 because the oxyapatites would be formed only when the lower valence rare-earth ions were formed, which would occur at high temperature.

Estimation logic of the chemical composition of rare-earth silicate oxyapatites was the main advance in the paper by Kužmin and Belov.34 They took into account the similarity of the XRD patterns of lanthanum silicate oxyapatite and britholite, and the chemical composition of lanthanum silicate oxyapatite was estimated from the host composition of britholite (Ca5(PO4)3·(F, OH)2). The explanation in the paper was that, referring to the similarity of the XRD patterns between the synthetic lanthanum silicate and britholite shown in Fig. 8, “This result led us to accept for the synthetic compounds a chemical formula close to the formula of britholite, Lax(SiO4)O, equal to the sum of the two silicates [La2SiO5 (La2O3·SiO2) and La2Si2O7 (La2O3·2SiO2)] initially assumed plus a minimum amount of a freer La2O3:

\[
\begin{align*}
\text{La}_{2}O_{3} \cdot \text{SiO}_{2} + \text{La}_{2}O_{3} \cdot 2\text{SiO}_{2} + 1/3\text{La}_{2}O_{3} \\
\quad \quad \rightarrow \text{La}_{5}\text{SiO}_{4} + \text{La}_{2}\text{Si}_{2}O_{7} + 1/3\text{La}_{2}O_{3}
\end{align*}
\]

(1)

This derivation of the formula seemed insufficiently dependable”. However, the explanation of the “minimum amount of a freer La2O3” was not given in detail, and, therefore, this equation might be incorrect as the equilibrium chemical reaction. Kužmin and Belov would know that the compound composition was close to equal amounts of La2SiO5 (La2O3·SiO2, 50 mol % of SiO2 in La2O3·SiO2 system) and La2Si2O7 (La2O3·2SiO2, 66.7 mol % of SiO2). In addition, they would notice that the La2(SiO3)O composition could not be given by a combination of La2O3 and

![Fig. 11. (a) Simulated powder X-ray diffraction patterns based on Kužmin and Belov’s original structure data and (b) modified data with the La1(4f) position changed from (1/3, 2/3, 0) to (1/3, 2/3, 0.0018) and the lattice parameters using the values of Okudera et al. (a = 0.9714 nm and c = 0.7183 nm). (c) The experimentally collected powder diffraction pattern for comparison. RIETAN-FP software41 was used for the pattern simulations.](image-url)
Ca₁₀(PO₄)₆O and Pb₁₀(PO₄)₆O, respectively. From this description, the chemical compositions of voelckerite and oxy-pyromorphite were introduced, namely, formation of oxyapatite, because we assumed the minimum La₂O₃ amount and changed the Ca₅(PO₄)₃(F, OH) composition to lanthanum and oxygen. If one wants to adjust the number of La atoms while ignoring the change in the number of oxygen atoms, 1/2La₂O₃ is necessary by following equation:

\[
\text{La}_2\text{O}_3 \cdot \text{SiO}_2 + \text{La}_2\text{O}_3 \cdot 2\text{SiO}_2 + 1/2\text{La}_2\text{O}_3 \rightarrow \text{La}_5(\text{SiO}_4)_5\text{O}_5. \tag{1'}
\]

This equation is also probable if the existence of excess oxygen is accepted. In this case, the additional La₂O₃ becomes 1/2. Comparing Eqs. (1) and (1'), the smallest amount of La₂O₃ necessary for apatite structure formation is 1/3 La₂O₃. This would be the meaning of “a minimum amount of a freer La₂O₃”. The meaning of this treatment is the estimation methodology of the compositional deviation of the rare-earth silicate oxyapatite from La₅Si₅O₁₂ (2La₂O₃·3SiO₂, 60 mol % of SiO₂). Therefore, Eq. (1) is not the chemical reaction equation. Actually, oxyapatite formation from La₅Si₅O₁₂ and La₅Si₅O₁₂ is simply given by

\[
10\text{La}_2\text{Si}_5\text{O}_3 + 4\text{La}_2\text{Si}_2\text{O}_7 = 3\text{La}_{4.5}\text{Si}_{4.5}\text{O}_6\text{BO}_2. \tag{2}
\]

The accuracy of Eq. (2) has been confirmed in papers from 2011 to 2013 by modified diffusion couple experiments. In contrast, if one tried to analyze the kinetics of rare-earth oxyapatite formation by considering Eq. (1) based on mass transport theory in solids, no solution can be derived because of thermodynamic inconsistency: Eq. (1) does not satisfy the phase rule. Kuzmin and Belov could reach the answer that the composition of the rare-earth silicate oxyapatites were RE₄+2/SiO₄O₂⁻ (7RE₂O₃·9SiO₂) by the viewpoint of the crystal chemistry. However, it would be impossible to find such a complex ratio between of La₂O₃ to SiO₂ (7 to 9) without Kuzmin and Belov’s research. Kuzmin and Belov wrote their logic in a simple way, and, therefore, it might be necessary to read it carefully. Furthermore, in Kuzmin and Belov’s paper the accuracy of the lattice constants is poor, as pointed out by McCarthy et al.²⁹ In the case of samarium silicate oxyapatite, the lattice parameters determined by Kuzmin and Belov were a = 0.933 nm and c = 0.685 nm, but the values reported by McCarthy et al.²⁹ were a = 0.9497 nm and c = 0.6949 nm. Compared with the recent data of Sm₃S₃O₁₇ (SiO₄)O₂ (-a = 0.94923 nm and c = 0.69394 nm), thirty-five McCarthy’s data is found to be more accurate than Kuzmin and Belov’s data. In contrast, McCarthy et al. did not solve the coordinates of the atoms because they measured the powder XRD pattern, not a single-crystal XRD pattern.

Cockbain and Smith reported their success of synthesizing a number of alkaline-earth–rare-earth silicates and germanateapatites in 1967.³⁸ The main analytical method they used was powder XRD by applying the space group P6₃/m to the hydroxyapatites and fluorapatites. In addition, an important possibility was introduced, namely, formation of oxyapatite, because we found the description “Attempts to confirm the presence of the hydroxyl ion in the calcium lanthanum silicate apatite by infra-red absorption spectroscopy have so far been unsuccessful, and an oxyapatite formula Ca₅La₃(PO₄)₂(OH)₂ such as has been suggested for voelckerite and oxy-pyroanphite could be proposed instead of Ca₅La₃(PO₄)₂(OH)₁⁻” in their paper. The chemical compositions of voelckerite and oxy-pyroanphite are Ca₆(PO₄)₂O and Pb₆(PO₄)₂O, respectively. From this description, Cockbain and Smith were careful to accept the existence of cation- and oxygen-deficient oxyapatites, whose crystal structure model was proposed by Kuzmin and Belov in 1965.³⁴

In the same year (1967), Schwarz reported the discovery of new oxyapatite single-phase compositions.²⁹ He systematically synthesized the solid solution of Sr₆(PO₄)₂ and La₆(PO₄)₆O with the molecular formula given by [Sr₉₋ₓLaₓ(PO₄)₁₆₋ₓ(PO₄)ₓ]. By this analysis, he found that the oxyapatite structure phase was obtained between x = 4.5 and x = 6. After further detailed analysis, he discovered the six non-doped and Sr-doped lanthanum silicate oxyapatite compositions: (1) La₉₊₂ₓ(PO₄)₁₆₋ₓ(OH)ₓ; (1a) Sr₇₋ₓLaₓ(PO₄)₁₆₋ₓ(OH)ₓ, 0 ≤ y ≤ 4; (1b) Sr₉₋ₓLaₓ(PO₄)₁₆₋ₓ(OH)ₓ; (2) La₉₊₂ₓ(PO₄)₁₆₋ₓ(OH)ₓ; (2a) Sr₇₋ₓLaₓ(PO₄)₁₆₋ₓ(OH)ₓ, 0 ≤ y ≤ 2; and (2b) Sr₉₋ₓLaₓ(PO₄)₁₆₋ₓ(OH)ₓ.

It was interesting that the oxyapatite type was distinguished by the number of oxygen atoms. This categorization indicated that Schwarz might consider that oxygen stoichiometric oxyapatite (2, 2a, and 2b) and oxygen-deficient oxyapatite (1, 1a, and 1b) were implicitly different phases.

Ito published a long paper in 1968 entitled “Silicate apatites and oxyapatites”.³⁹ In this paper, many compositional silicate hydroxyapatites and oxyapatites were synthesized mainly by hydrothermal and conventional solid-state reaction methods, respectively. XRD and thermal analyses were used for the characterization of the samples. From this research, the existence of silicate oxyapatites were clarified in the cases of monovalent ion-doped rare-earth silicates (RE₆A(SiO₄)₂O₇, RE = rare-earth elements and A = Na and Li) and divalent ion-doped rare-earth silicates [RE₂R₂(SiO₄)₂O₇, RE = rare-earth elements and R = Ba, Sr, Ca, and Pb]. In addition, it was clarified that cation and anion deficiencies were not the fundamental factor for formation of the lanthanoid silicate oxyapatites.

In 1969, Smolin and Shepelev³² determined the crystal structure of 7Gd₂O₃·3SiO₂ along with the Kuzmin and Belov analogy. Small 7Gd₂O₃·3SiO₂ single crystals (0.7 to 0.15 mm) were grown by the flux method using KF. Based on the single-crystal XRD analysis, they concluded that the 7Gd₂O₃·3SiO₂ compound had an apatite-like structure similar to 7La₂O₃·3SiO₂ (Ln = La, Sm, Eu, and Sm). The space group was P6₃/m. In the case of gadolinium silicate oxyapatite, it was concluded that 1/6 of the Gd(4f) sites were vacant.

In the same year as Smolin and Shepelev (1969),³² Felsche published a short paper reporting the success of solving the crystal structure of cerium (III) orthosilicate [Ce₆(PO₄)₂O₇].³³ He synthesized the sample at 1973 K under high vacuum conditions. The crystal structure was analyzed using a small plate-like single crystal (0.1 × 0.1 × 0.02 mm³) by XRD. The cerium (III) orthosilicate was found to be the oxyapatite structure with space group P6₃/m or P6₃/m. By the analysis of the cerium (III) orthosilicate structure, the adequacy of the structure model proposed by Kuzmin and Belov was confirmed.

Wannaker et al. synthesized a series of oxyapatite samples with compositions Me₂Ca⁺⁺, Me₃⁺⁺Me₄⁺⁺(SiO₄)₆₋₁(PO₄)₂O₂, Me₅⁺⁺Me₆⁺⁺(SiO₄)₆₋₁(PO₄)₃Me, and Me₇⁺⁺Me₈⁺⁺(SiO₄)₆₋₁(PO₄)₄O₆, with Me²⁺ = Ca, Sr, Ba, Mg, Zn or Cd and Me³⁺⁺ = Y or La in 1971.⁴⁰ In this research, the powder XRD method was used for the characterization of the samples. By analysis of the relationships between the chemical composition and lattice parameters, Vegard’s law was found to be well established when taking into consideration the ionic radii of the constituent ions.

Following Felsche’s work in 1969,³³ Belokoneva et al.⁴² successfully synthesized small single crystals (0.1 to 0.3 mm) of cerium (III) orthosilicate [Ce₆(PO₄)₂O₇] and dysprosium orthosilicate [Dy₆(PO₄)₂O₇] by the hydrothermal method. From crystal structure analysis using single-crystal XRD, both compounds were found to have the apatite structure with space group
In addition, it was reported that 1/6 of the REI(4f) sites were vacant.

Felsche examined systematic composition samples of lanthanoid-deficient oxyapatites [RE$_{33}$SiO$_{4}$O$_{2}$] and alkali-doped stoichiometric oxyapatites [RE$_{3}$A(SiO$_{4}$)$_{2}$]. RE = La–Lu, A = Na and Li between 1969 and 1973. These samples were synthesized and their crystal structures analyzed using small single crystals (10 to 200μm) by XRD. The single crystals were formed by cooling from the melted sample obtained by heating up to 2173 K. All of the samples were determined to have the space group $P6_3/m$. Felsche reported that a small deviation from the simple Vegard law was observed in the oxyapatite system in the small cell volume region for RE = La–Ho. Felsche discussed the deviation from Vegard’s law by the different distribution of RE vacancies and the site distribution of Na and Li on two RE sites: REI(4f) and REI(6h). In addition, Felsche recognized the existence of oxyapatites containing oxygen vacancies as well as lanthanoid vacancies such as Sr$_{2}$La$_{0.75}$SiO$_{4}$, Sr$_{2}$La$_{0.5}$SiO$_{4}$, Sr$_{2}$La$_{3.5}$SiO$_{4}$, Sr$_{2}$La$_{1.5}$SiO$_{4}$, and suggested that neutron diffraction was necessary for the crystal structural analysis of the oxygen-deficient oxyapatites. In the review paper by Felsche in 1973, he summarized the diagrams showing the relationships between the component ion radius and crystal structure types of various types of rare-earth silicate-based compounds including RE$_{33}$SiO$_{4}$O$_{2}$. It is necessary to note that the diagrams presented by Felsche were based on the crystal chemistry and/or silica chemistry of the title of his review paper: “Crystal chemistry of the rare-earth silicates”. The diagrams were not based on chemical thermodynamics, because the diagrams showed the relationship between crystal structure type and ionic radius of components. This means that the diagram was not contained the constraints generated from chemical thermodinamics. Hence, the diagrams described by Felsche were not the phase diagram as reported by Toropov et al. They succeeded to determine the space group, atomic arrangement, and oxygen coordination of the ordered arrangement of Ca on La$_{2}$SiO$_{4}$O$_{2}$ using the single crystal grown from solution in a melt. They succeeded to determine the space group $P6_3/m$. An important finding of this study was the existence of oxyapatite containing oxygen vacancies as well as lanthanoid vacancies.

In 1985, Fahey et al. reported that the crystal structures of the oxygen-deficient neodymium silicate oxyapatites Ca$_{2}$Nd$_{7.5}$(SiO$_{4}$)$_{2.5}O_{x}$ were analyzed by a combination of powder XRD and powder neutron diffraction analyses. Because of the powder diffraction analysis, they used the space group $P6_3/m$ for the pattern refinements. In this paper, they succeeded in clarifying the crystal structures of two samples: one was stoichiometric oxyapatite Ca$_{2}$Nd$_{7.5}$(SiO$_{4}$)$_{2.5}O_{x}$ and the other was oxygen non-stoichiometric oxyapatite Ca$_{2}$Nd$_{7.5}$(SiO$_{4}$)$_{2.5}O_{x}$. An important finding of this study was the existence of oxyapatite containing a non-integer number of oxygen atoms. Checking the previous research, all of the oxygen numbers in the oxygen-deficient oxyapatites were integer numbers. However, any explanation of this point was not found in Fahey’s paper. Instead, they clarified the two facts that calcium ions were preferably substituted in the NdI(4f) site rather than the NdI(6h) site, and oxygen vacancies was observed at the O4(2a) site. The former result was consistent with the results of Schroeder and Mathew for La$_{2}$Ca$_{2}$(SiO$_{4}$)$_{2}O_{2}$. Furthermore, it was not possible to synthesize the oxygen-deficient oxyapatites with the compositions of CaNd$_{6}$(SiO$_{4}$)$_{2}$O and CaNd$_{6}$(SiO$_{4}$)$_{2}$, owing to the coexistence of a glass-like calcium silicate phase, even though these compositions were reported to be the oxygen-deficient oxyapatite phase in previous papers. Based on their results, neodymium and oxygen deficiency was concluded to be very small in calcium.

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doped neodymium silicate oxyapatite. It was interesting that the sample composition presented by Fahey et al. (Ca$_{2+x}$Nd$_{6-x}$)$(SiO_4)_{6}O_3$ is equivalent to the modern description (Nd$_{10-x}$Ca$_x$(SiO$_4$)$_5$O$_3$) when $x$ is replaced by $y = 2$. This indicates that Fahey et al. had produced oxygen-excess oxyapatite. However, the oxygen-excess state was beyond the knowledge of crystallography at the time, and, therefore, they did not consider that possibility.

With respect to the RE ion ordering in RE$_{5.5}$SiO$_{4}$O$_3$, three research papers with different conclusions were published: one by Malinovskii et al. in 1990, the second by Yoshioka in 2007, and the third by Kobayashi et al. in 2012. Malinovskii et al. concluded that the crystal structure of La$_9$Nd$_{0.33}$SiO$_{4}$O$_2$ was given by La$_1$Nd$_{0.5}$SiO$_{3}$O$_3$ because of the ordering of the coordination of La and Nd ions even though the space group of La$_9$Nd$_{0.33}$SiO$_{4}$O$_2$ was the same as oxyapatite ($P6_3/m$). The La$_1$Nd$_{0.5}$SiO$_{3}$O$_3$ sample was synthesized by hydrothermal crystallization in La$_2$O$_3$–Nd$_2$O$_3$–SiO$_2$–Na$_2$O–H$_2$O at 723 K under 1.5 kbar. They used a well-faced isometric crystal (0.1 mm × 0.1 mm × 0.1 mm) for the crystal structure analysis. On the other hand, Yoshioka reported that no extra diffraction peaks owing to britholite-(RE) structure showed that britholite mineral mainly contained the (RE) elements. The crystal structure of this mineral was determined by single-crystal XRD. Although the crystal structure was close to the apatite structure with a hexagonal cell, the symmetry group was concluded to be $P6_3$. The reason for the lower symmetry compared with $P6_3/m$ was the distortion of the sevenfold coordination of RE–O.

From 1992 to 1993, Drexler’s group reported the crystal structure of monoclinic britholite-(RE) (RE = La, Gd, Y, and Ce) collected from Kipawa syenite gneiss complex and Suishoyama. Malinovskii et al. using the RIETAN-FP software were also listed for comparison. The britholite-(RE) structure showed that britholite mineral mainly contained the (RE) elements. Malinovskii et al. in 2007, and the third by Kobayashi et al. in 2012. Malinovskii et al. concluded that the crystal structure of La$_2$Nd$_7.33$(SiO$_4$)$_6$O$_2$ was synthesized by Kobayashi et al. (La$_0.46$Nd$_{0.54}$)$_{9.33}$SiO$_{4}$O$_2$ by Kobayashi et al. The Miller indices are also indicated for each structure model. Indices of the weak peaks, which cannot be confirmed by this figure, were omitted.

Fig. 12. Simulated powder X-ray diffraction patterns using the reported structure models: (a) La$_1$Nd$_{0.5}$SiO$_{3}$O$_3$ by Malinovskii et al., (b) (La$_{3.33}$Nd$_{0.33}$)SiO$_{3}$O$_2$ by Yoshioka, and (c) (La$_{0.46}$Nd$_{0.54}$)SiO$_{3}$O$_2$ by Kobayashi et al. The site relationships between the atomic coordination in the three models ($P6_3/m$, $P6_3$, and $P2_1$), tables of the atomic coordination in the three models ($P6_3/m$, $P6_3$, and $P2_1$), and the site occupancy factors based on the $P6_3/m$ model by Okudera et al. are also listed for comparison. Typical site labels are shown in the crystal structure Figs. 13(a)–13(c). The site relationships between $P6_3/m$, $P6_3$, and $P2_1$ (setting 2) are shown as a tree diagram in Fig. 14. From these
tables and figures, the symmetry lowering is found to be because of not only the slight deviation of RE coordination but also the coordination of the SiO4 tetrahedrons. Another question arose among mineralogists and physicists: Are the different polymorphs of oxyapatite the high pressure phase? This problem has been discussed in high pressure physics.88-90

| Table 2. Coordinates of the atoms in La9.33(SiO4)6O2 with different structure models: (a) P63/m, (b) P63/2m, and (c) P21 (setting 2).83 The site occupancy values were calculated based on the P63/m model.

(a) Symmetry: hexagonal
Space group: P63/m
a = b = c, α = β = γ = 90°, χ = 120°

| Sites | Occupancy | x   | y   | z   |
|-------|-----------|-----|-----|-----|
| RE1(4f) | 0.8580 2/3 | 1/3 | 1/4 |
| RE2(6h) | 0.983 0.01223 | 0.23921 | 1/4 |
| Si(6h) | 1 | 0.40290 | 0.37280 | 1/4 |
| O1(6h) | 1 | 0.32550 | 0.48730 | 1/4 |
| O2(6h) | 1 | 0.52670 | 0.12320 | 1/4 |
| O3(12i) | 1 | 0.34760 | 0.25640 | 0.06840 |
| O4(2a) | 1 | 0 | 0 | 1/4 |

(b) Symmetry: hexagonal
Space group: P63
a = b = c, α = β = γ = 90°, χ = 120°

| Sites | Occupancy | x   | y   | z   |
|-------|-----------|-----|-----|-----|
| RE1(2b) | 0.8580 1/3 | 2/3 | 0 |
| RE2(2b) | 0.8580 2/3 | 1/3 | 0.4977 |
| Si(6c) | 1 | 0.3730 | 0.3998 | 0.255 |
| O1(6c) | 1 | 0.486 | 0.318 | 0.264 |
| O2(6c) | 1 | 0.475 | 0.600 | 0.232 |
| O3(6c) | 1 | 0.262 | 0.362 | 0.064 |
| O4(6c) | 1 | 0.243 | 0.303 | 0.419 |
| O5(2a) | 1 | 0 | 0 | 0.155 |

(c) Symmetry: monoclinic
Space group: P21 (setting 2)
a ≠ b ≠ c, a/b = 1, α = β = γ = 90°, χ ≠ 120° ≈ 120°

| Sites | Occupancy | x   | y   | z   |
|-------|-----------|-----|-----|-----|
| RE1(2a) | 0.8580 | 0.33287 | 0.66656 | 0.0057 |
| RE2(2a) | 0.8580 | 0.33415 | 0.66678 | 0.5002 |
| RE3(2a) | 0.983 | -0.01483 | 0.23465 | 0.2513 |
| RE4(2a) | 0.983 | 0.23454 | 0.24946 | 0.7484 |
| RE5(2a) | 0.983 | 0.24944 | 0.01482 | 0.2506 |
| Si(2a) | 1 | 0.0289 | 0.6287 | 0.25 |
| Si(2a) | 1 | 0.3715 | 0.4004 | 0.248 |
| Si(2a) | 1 | 0.5997 | 0.9708 | 0.252 |
| O1(2a) | 1 | 0.8366 | 0.5165 | 0.245 |
| O2(2a) | 1 | 0.4821 | 0.3200 | 0.261 |
| O3(2a) | 1 | 0.6783 | 0.1623 | 0.243 |
| O4(2a) | 1 | 0.4068 | 0.8779 | 0.267 |
| O5(2a) | 1 | 0.4704 | 0.5033 | 0.238 |
| O6(2a) | 1 | 0.1230 | 0.5304 | 0.267 |
| O7(2a) | 1 | 0.6364 | 0.8985 | 0.0618 |
| O8(2a) | 1 | 0.6811 | 0.9258 | 0.422 |
| O9(2a) | 1 | 0.2615 | 0.3625 | 0.063 |
| O10(2a) | 1 | 0.2443 | 0.3189 | 0.425 |
| O11(2a) | 1 | 0.0747 | 0.7546 | 0.083 |
| O12(2a) | 1 | 0.1017 | 0.7373 | 0.444 |
| O13(2a) | 1 | -0.0007 | -0.0009 | 0.225 |

Fig. 13. Crystal structure of La9.33(SiO4)6O2 with different models. Models using the space groups P63/m, P63/2m, and P21 (setting 2) are shown in (a), (b), and (c), respectively. Typical atomic sites are also shown in the figures. To compare the structural features, all the crystal structures are drawn within the fractional coordinate range from -0.2 to 1.2 of the x, y, and z axes.

The important fact was that before 1995, the consensus was that point defects in the silicate oxyapatites were only vacancies of lanthanoid and oxygen, and the understanding of the defect model suddenly and drastically changed after 1995, and various defects are now accepted. These changes will be explained in a further.

4. Initial application research of oxyapatites

4.1 New laser hosts
In the 1960s, the main research topics of the lanthanoid silicate oxyapatites were at the fundamental science stage. In the 1970s,
however, the interests of scientists were gradually shifting from fundamental research to the applications of oxyapatites.

The first research papers suggesting applications of the silicate oxyapatites were published in 1971 by Hopkins et al., who belonged to the Westinghouse Research Laboratory. The initial applications of the oxyapatites were alternative materials to fluorapatite \(\text{Ca}_10(\text{PO}_4)_6\text{F}_2\) as solid laser hosts. Although fluorapatite was known to be an extremely efficient host for both rare-earth ion fluorescence and laser action at 1.06 \(\mu\)m, and as a candidate as a host for the activator ion (Ho\(^{3+}\)), the drawback was the low solubility limit of sensitizer ions (Er\(^{3+}\)) and the activator ion (Ho\(^{3+}\)). Therefore, they focused on oxyapatites with the same crystal structure as fluorapatite. In addition, various lanthanoid ions were known to be structural constituents of oxyapatites. Hence, it was suggested that co-doping of Ho\(^{3+}\), Er\(^{3+}\), and Tm\(^{3+}\) in oxyapatite hosts was a candidate for new laser hosts. Based on this strategy, Hopkins et al. successfully grew single crystals of \(\text{Ca}_y\text{Y}_z(\text{SiO}_4)_3\text{O}\) and \(\text{Ca}_y\text{Y}_z\text{Er}_x\text{Tm}_y\text{Ho}_z(\text{SiO}_4)_3\text{O}\) with size greater than 100 \(\mu\)m by Czochralski’s method. Although the quality of the single crystal was not very good because of the low angle boundary development and secondary phase precipitation, it was confirmed that energy transfer from the Er\(^{3+}\) and Tm\(^{3+}\) ions to the Ho\(^{3+}\) ion was efficient and complete in the silicate oxyapatite by spectroscopic measurements. In addition, they pointed out that the most promising application for the oxyapatite host would be in high energy per pulse \(Q\)-switch systems because of the broad fluorescence line width of Ho\(^{3+}\).

In the second paper, they grew single crystals of Nd\(^{3+}\)-doped \(\text{Ca}_y\text{La}_z(\text{SiO}_4)_3\text{O}\) and Sr\(_2\text{La}_2(\text{SiO}_4)_3\text{O}\) by Czochralski’s method. In this paper, surprisingly large single crystals (0.64 cm diameter and 4.6 cm length but including a 3 \(\mu\)m to 5 \(\mu\)m sized second phase) were shown in the image (Fig. 15). The quality of the single crystals were quite good compared with the single crystals of \(\text{Ca}_y\text{Y}_z(\text{SiO}_4)_3\text{O}\). With respect to the spectroscopic data, they carefully discussed that oxyapatite might be superior to fluorapatite at a high pumping power level because of the high hardness. From the viewpoint of the mechanical properties, the thermal and elastic properties of Ho\(^{3+}\)-doped \(\text{Ca}_y\text{La}_z(\text{SiO}_4)_3\text{O}\) single crystals were reported in 1973. The interesting results were that the temperature dependence of the thermal conductivity was large compared with the conductivity of fluorapatite. In addition, the thermal conductivity did not show crystallographic anisotropy. The elastic, thermal expansion, and heat capacity behaviors could be explained by the Debye solid model. Further studies by the same group reported that the damage threshold of Nd\(^{3+}\)-doped \(\text{Ca}_y\text{La}_z(\text{SiO}_4)_3\text{O}\) was 20 to 30 percent higher than the threshold of Nd\(^{3+}\)-doped yttrium aluminum garnet (YAG). With respect to the long-pulse properties, the gain per excited Nd ion in \(\text{Ca}_y\text{La}_z(\text{SiO}_4)_3\text{O}\) was at least 3.5 times lower than in YAG. Overall, it can be concluded that oxyapatites have an advantage over YAG as laser host materials.

In 1989, de la Fuente et al. were successful in growing a single crystal of \((\text{La}_{1-\alpha}\text{Nd}_\alpha)_{9.33}(\text{SiO}_4)_3\text{O}_2\) and \((\text{Gd}_{1-\alpha}\text{Nd}_\alpha)_{9.33}(\text{SiO}_4)_3\text{O}_2\) by the floating zone method. The absorption and fluorescence spectra were measured at 18 K and room temperature. Based on the spectra, the energy level diagram of Nd\(^{3+}\) in \((\text{La}_{1-\alpha}\text{Nd}_\alpha)_{9.33}(\text{SiO}_4)_3\text{O}_2\) was given for the 806 nm absorption band and laser transition state. As a result, they concluded that lanthanum silicate oxyapatite could be used as a Nd host with potential applications in diode-pumped solid-state lasers.

In 2002, Druon et al. announced first success of diode-pumped laser oscillation using Yb\(^{3+}\)-doped \(\text{Sr}_2\text{Y}_3(\text{SiO}_4)_2\text{O}\) oxyapatite single crystal. They focused on the simpler electronic structure of Yb\(^{3+}\) ions and oxyapatite system could be dissolved various kind of lanthanoid species. It was explained that single crystal growth of Yb\(^{3+}\) doped \(\text{Sr}_2\text{Y}_3(\text{SiO}_4)_2\text{O}\) was relatively easy by the Czochralski method from the melt around 2173 K (Fig. 16). They reported that Yb\(^{3+}\)-doped \(\text{Sr}_2\text{Y}_3(\text{SiO}_4)_2\text{O}\) exhibits very broad emission and absorption bands compared to the bands of Yb\(^{3+}\) doped \(\text{Sr}_2\text{Y}_3(\text{BO}_3)_2\) and \(\text{Ca}_4\text{Gd}(\text{BO}_3)_3\) single crystals and Yb\(^{3+}\)-doped glass in range of wavelength between 850 and 1150 nm. Due to this broad emission and absorption bands, they succeeded that 1.05 W of output power at 1071 nm with an incident power of 3.6 W in the continuous wave (cw) laser regime, and sub-100-femt second (fs) pulses were generated near 1070 nm with an average power of 110 mW in the fs regime. In the case of cw regime, laser operation was observed wide wavelength range of 75 and 1095 nm. Additional interesting result was the anisotropic thermal conductivities, 2.85 W m\(^{-1}\) K\(^{-1}\) along

![Fig. 14. Schematic tree diagram of the relationships of the atomic sites among the models for the space groups P6\(_3\)/m, P6\(_3\), and P2\(_1\) (setting 2). The O atoms enclosed in the dashed boxes are the constituents of the SiO\(_4\) tetrahedron.](image)

![Fig. 15. Photo of the 3% Nd-doped \(\text{Ca}_y\text{La}_z(\text{SiO}_4)_3\text{O}\) single crystal copied from reference.](image)
to c-axis and 1.6 W m⁻¹ K⁻¹ for perpendicular to the c-axis. This anisotropy was different from the thermal conductivity of Nd³⁺-doped La₃Ca₂(SiO₄)₂O₁₀ single crystal.⁹⁰) After this paper, Druon et al. reported the self-compression and Raman soliton generation in a photonic crystal fiber using a diode-pumped Yb-doped oscillator in 2003.⁹⁰) and pulse-compression down to 20 fs using a photonic crystal fiber seeded by a diode-pumped Yb:SYS laser in 2004.⁹⁰)

### 4.2 Phosphor Materials

Although lanthanoid silicates were already expected to be phosphor materials by Wannmaker et al. in 1958⁹⁹) and Toropov and Bondar in 1961,⁹¹) the early luminescent experiments of oxyapatites were carried out by Itou⁹⁹) in 1968 and Maksimov et al.⁹²) in 1969 as pure scientific research. The optical spectra were sometimes reported with respect to the crystal structure and local coordination of the activator ions.⁹³)-⁹⁵)

In 1973, Isaacs¹¹¹) reported systematic data of the emission and excitation spectra of Eu³⁺-doped Ca₃Gd₅(SiO₄)₁₂O₂, Ca₃La₇(SiO₄)₂O₂, Ca₃Y₅(SiO₄)₂O₂, Mg₃La₃(SiO₄)₂O₂, and Mg₃Y₅(SiO₄)₂O₂ by comparing the spectra with the spectrum of Eu³⁺-doped Y₂O₃ at room temperature. This was the first report on material engineering of oxyapatite phosphors. Through detailed interpretation of the spectra of these materials, the main emission peak intensity at 253.7 nm excitation of oxyapatites was found to be much lower than the intensity of Eu³⁺-doped Y₂O₃.

In 1987, Lammers and Blassé¹²²) reported the luminescence properties of Tb⁺⁺ and Ce⁺⁺-activated Gd₈.₃₃(SiO₄)₁₂O₂, La₉.₃₃(SiO₄)₁₂O₂, and Gd₃SiO₅ excited by ultra-violet (UV) light and X-ray. The quantum efficiency of all the oxyapatites were reported to be low by interpretation of the energy transition of the emission spectra by the UV excitation. The local structure of the Tb⁺⁺ and Ce⁺⁺ ions was discussed combined with the crystal structural information. On the other hand, Tb⁺⁺- and Ce⁺⁺-activated oxyapatites were concluded to be inefficient phosphors.

Lin and Su¹³) reported a systematic study of the luminescence properties of Ca₃Gd₅(SiO₄)₁₂O₂ doped with Eu⁺⁺, Tb⁺⁺, Dy⁺⁺, Sm⁺⁺, Y⁺⁺, Ce⁺⁺, Pr⁺⁺, Bi⁺⁺, and Pb⁺⁺ ions in 1994. They concluded that Pb⁺⁺ and Dy⁺⁺ coactivated Ca₃Gd₅(SiO₄)₁₂O₂ was a potential candidate for white emission under excitation by 254 nm light, which corresponds to excitation by a low-pressure mercury discharge. After this work, they reported a systematic luminescent properties of M₃RE₅(SiO₄)₁₂O₂ (M = alkali earth elements) prepared by sol–gel method and solid state reactions.¹¹⁴)-¹¹⁹)

After Lin’s paper, Han et al.¹²⁰) reported the luminescence properties of Eu⁺⁺-, Ce⁺⁺-, and Tb⁺⁺-doped La₈.₃₃(SiO₄)₁₂O₂ phosphor thin films fabricated by a sol–gel soft lithography technique in 2002. They succeeded in making a pattern array with linewidths of 50 μm and 20 μm, and found that strong emission with red (615 nm), green (542 nm) and blue (350–450 nm) colors were obtained by the doped Eu⁺⁺, Tb⁺⁺, and Ce⁺⁺ ions, respectively. Even though the film seems not to be the oxyapatite single phase because many peaks from the impurity phase were found by careful checking of the XRD patterns in the paper, the luminescence properties are interesting.

In 2006, Yamane et al.¹²¹) reported the luminescence properties of Tb-activated rare-earth oxyapatite silicate MLn₄SiO₁₃ (M = Ca or Sr, Ln = La or Gd). The molecular formula corresponds to Ln₂M₂(SiO₄)₂O₂. They reported the vacuum UV radiation excited photoluminescence spectra of Tb-doped MLn₄SiO₁₃. It was clarified that Tb-doped MLn₄SiO₁₃ showed the green luminescence due to the ⁵D₂→⁷F₂ transition of Tb⁺⁺. Furthermore, the photoluminescence peak intensity of the Tb⁺⁺ emission from SrGd₄SiO₁₃ was found to be comparable to the peak intensity of Mn-doped Zn₂SiO₄, which was the commercial phosphor material for plasma display panels. Hence, they concluded that Tb-doped SrGd₄SiO₁₃ is a candidate for a green phosphor material of plasma display panels excited by Xe discharged plasma.

Improvement of the luminescent properties of Ca₂(La₂Eu₁)₉(SiO₄)₁₂O₂ by lithium treatment was reported by two research groups in 2009 and 2013.¹²²) Shen et al. reported that efficient bright red emission was observed by excitation of near-UV to blue light. In addition, the emission intensity was improved by addition of Li₂CO₃ flux. Shen et al. suggested that the reason for the luminescent improvement was that the Li₂CO₃ flux might decrease at the oxyapatite formation temperature and improve the crystallinity. After Shen’s paper, Li et al. also reported the luminescent properties of a similar composition, Ca₂La₇.₆₃(Tb₁ₓEu₀.₄ₓ)₈(SiO₄)₁₂O₂, EuₓLa₉(M₃+L₄+)-(SiO₄)₂O₂, EuₓMg₉(SiO₄)₂O₂, Li₄ₓEuₓCa₉(Y₃+La₃+)₋ₓ(SiO₄)₂O₂.¹²₃) In contrast to the report by Shen et al.¹²²) Li et al. proposed that the improvement of the luminescent properties by lithium ion doping was related to oxygen ion vacancy formation.¹²₃)

Between 2011 and 2012, Lin’s group and Lu’s group reported the color tuning luminescence of Ce⁺⁺/Mn⁺⁺/Tb⁺⁺-triaxivated phosphor using oxyapatite.¹²⁴)-¹²₆) They used Mg₃₂₅(Y₃+La₃+)₋ₓ(SiO₄)₂O₂,¹²₄),¹²₅) and Ca₃₂₅(SiO₄)₂O₂,¹²₆) as the phosphor host. The interesting results of these studies were that the luminescent color can be changed by a dual energy transfer mechanism between the activator ions. These oxyapatites were concluded to have potential as single-phase trichromatic white-emitting phosphors under UV and low-voltage electron beam excitation. Furthermore, they succeeded in fabricating a microfiber of Ce, Eu, and Tb-doped La₇.₆₃(SiO₄)₁₂O₂ using electrospinning synthesis that has a potential application in field emission displays.¹²₇) After this study, their target materials seem to shift from silicate oxyapatites to phosphate oxyapatites and/or solid solutions of silicate oxyapatite and phosphate oxyapatite.¹²₈),¹²₉) With respect to the silicate oxyapatite and phosphate oxyapatite solid solution system, two papers were published by Yu et al.¹³⁰) and Tao et al.¹³¹) Recalling the fact that the solid solution of silicate oxyapatite and phosphate oxyapatite was initially recognized as minerals,³₀),³⁹),⁴₅),¹₁₂) it is interesting that the phosphor host seems to have changed from artificial materials back to natural compounds.

### 4.3 Other applications

The silicate oxyapatite and quasi-ternary rare-earth oxide–silica–alkali earth oxide system was studied as a candidate as a...
stabilizer of unwanted radioactive waste materials (radwastes) produced in nuclear power reactors. The studies by de Alleluia et al. and Fahey et al. seemed to be motivated by the fact that de Alleluia belonged to Karlsruhe Nuclear Research Center, School of Nuclear Technology and Institute of Radiochemistry, and we found the explanation “The structure and stability of rare earth silicate isomorphs of natural apatite, $\text{Ca}_5(\text{PO}_4)_3(F, \text{OH})_2$, are of interest in nuclear management because they can occur as actinide host phases in several high-level nuclear waste forms” in Reference. 

In addition, the quasi-ternary $\text{Y}_2\text{O}_3\text{SiO}_2\text{MgO}$ system and $\text{RE}_2\text{O}_3\text{SiO}_2\text{Al}_2\text{O}_3$ (RE = Y, Sc, La, Ce, Nd, Sm, Gd, Dy, Er, and Yb) system were investigated as sintering additives for Si$_3$N$_4$, SiAlON, Sic, and AlN.

5. Summary

Although research of the rare-earth silicate oxyapatites focused on their oxygen ion conductivity since 1956, many studies were carried out from 1959 to 1993. Before 1993, research on the rare-earth silicate oxyapatites was separately carried out in the fields of ceramics and crystal chemistry. After the fusion of the accumulated knowledge of the ceramists and crystal chemists, the existence of rare-earth silicate oxyapatites was recognized.

The idea of the rare-earth vacant model was an important advance for the identification of the rare-earth silicate oxyapatites and understanding their crystal structures. Although this structural model has now been accepted, the model was carefully treated from 1965 to 1980. Oxygen defective rare-earth silicate oxyapatite was first reported as $\text{Ca}_2\text{Nd}_7\text{SiO}_4\text{O}_1.9$ in 1985. Before this paper, the oxygen number of rare-earth silicate oxyapatites was fixed at integer numbers.

The engineering of rare-earth silicate oxyapatites started in 1973 for their application as optical materials such as laser and phosphor hosts. Before 1995, other applications were also considered, such as stabilizer hosts of radwaste elements and phosphor hosts. Before 1995, all other applications were separately carried out in the fields of ceramics and crystal chemistry. Development of phosphor materials based on rare-earth silicate oxyapatites continues.

Acknowledgement Authors are grateful to Dr. Takui Ikeda at National Institute of Advanced Industrial Science and Technology for helpful suggestions on the crystallography and the RIETAN-FP software.

Appendix A

Although Toropov and Bondar introduced the US atmosphere referring to the paper “Smith K M and Doningnes L P, 1938 J. Am. Ceram. Soc. 37 4”, we could not find the corresponding literature in the American Ceramics Society Bulletin or the Journal of the American Ceramics Society in 1958. However, we did find the report entitled “Thermal expansion and phase inversion of rare-earth oxides” in the United States Department of Energy (DOE) office of scientific and technical information (OSTI) in the United States. The sponsoring and research organizations were credited as the DOE and Bureau of Mines, respectively. http://www.osti.gov/scitech/biblio/4840970

Appendix B

According to the papers by Warshaw and Roy (Warshaw I and Roy R, 1964 Prog. Sci. Tech. Rare Earths, vol. I (Ed. Eyring L, Pentagonon Press) pp 201–221), and Smolin and Shepelev (Smolin Y I and Shepelev Y F 1970 Acta Cryst. B26 484), first investigation of rare-earth silicates were carried out by Giuscià in 1934 (Giuscià D 1934 Bull. Labor. Miner. Univ. Bucuresti. 1 27). Although we could not obtain a copy of the Giuscià’s paper, the brief abstract of the Giuscià’s research was found in the Warshaw’s one: they explained that crystallographic data accuracy was poor due to low resolution of their XRD instrument and low purity of the raw materials.

Appendix C

Kuzmin and Belov explained in their paper that “The most complete investigations of the phase diagrams of the La$_2$O$_3$–SiO$_2$ system have been made at the University of Pennsylvania and at the Institute for the Chemistry of Silicates of the Academy of Sciences of USSR (Leningrad)”. The research groups at the University of Pennsylvania and at the Institute for the Chemistry of Silicates are suggested to be Roy’s group and Toropov’s group, respectively. However, we could not find the phase diagram of the La$_2$O$_3$–SiO$_2$ quasi-binary system reported by Roy’s group.

Appendix D

The latest phase diagram of the La$_2$O$_3$–SiO$_2$ system in Bondar’s review paper referred the textbook entitled “Rare-earth silicates and their analogues” (Nauka, Leningrad, 1971). Compared with the phase diagram of the La$_2$O$_3$–SiO$_2$ system presented in Felsche’s review, the difference was found in the La$_2$O$_3$ and liquid coexisting region, even though Felsche specified that the phase diagram was the same as the textbook. In the phase diagram in Bondar’s review, he seemed to consider that two different polymorphs of La$_2$O$_3$ appeared at about 2323 K and 2373 K.

Appendix E

We could not obtain a copy of the textbook entitled “Rare-earth silicates and their analogues” (Nauka, Leningrad, 1971) written in Russian. Although we could not confirm whether they used the term apatite and/or oxyapatite, we confirmed that the term apatite-like structure was used in Bondar’s review in 1982 by referring to the above textbook.

Appendix F

Although the space group was presented as $P2_1$ setting 1 in the original papers, the subgroup of Pb$m/n$ is $P2_1$ setting 2 ($P112_2$) correctly. Hence, we employed the correct description of the space group.

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