Reaction mechanism on the formation of (Sr, Ba)TiO₃ and Ba(Zr, Ti)O₃ at near room temperature by using A(OH)₂·nH₂O (A = Sr, Ba) and BO₂·nH₂O gel (B = Zr, Ti, Zr₀.₄₅Ti₀.₅₅)

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ABSTRACT
Recently, our group synthesized perovskite-type oxide ABO₃ (A = Sr, Ba; B = Ti, Zr, Hf) with high crystallinity simply by leaving a powder mixture of A(OH)₂·nH₂O and BO₂ hydrdgel at room temperature to 323 K for 3–10 days. In this study, perovskite solid solution (Ba, Sr)TiO₃ and Ba(Zr, Ti)O₃ were synthesized to investigate the reaction mechanism in this synthesis method in detail. The perovskite solid solution (Ba, Sr)TiO₃ was obtained by using barium hydroxide, strontium hydroxide and TiO₂ hydrgel as the starting materials. On the other hand, in the case of using barium hydroxide and the mixture of TiO₂ hydrgel and ZrO₂ hydrgel as the starting materials, a mixed phase of BaTiO₃ and BaZrO₃ was obtained. B-site-substituted perovskite solid solution Ba(Zr₀.₄₅Ti₀.₅₅)O₃ was obtained by using barium hydroxide and (Zr₀.₄₅ Ti₀.₅₅)O₂ hydrgel as the starting materials. From the above, it was clarified that in this synthetic method, the Sr and Ba ions diffuse into the water part of hydrgel and then slowly react with Ti(OH)₄ to form a perovskite lattice.

1. Introduction
In the perovskite-type oxide ABO₃, a relatively large A cation occupies the cage formed by vertices shared BO₆ octahedra framework [1,2]. The perovskite structure can accommodate various elements, and compounds containing multiple types of ions at each site can also be synthesized. Perovskite-type Pb(Zr, Ti)O₃ [3] are industrially important materials due to the structural-related properties such as ferroelectricity and piezoelectricity [4].

Recently, our group developed a low-temperature synthesis method for perovskite-type ABO₃ (A = Sr, Ba; B = Ti, Zr, Hf) with high crystallinity. The process was simply by leaving a powder mixture of A(OH)₂·8H₂O and BO₂ hydrgel (hereafter described as BO₂·nH₂O) at room temperature to 353 K [5–8]. The reaction temperature was related to the tolerance factor t, given by t = (rA + rO)/2(rB + rO), where rA, rB, and rO were ionic radii of the respective ions. SrTiO₃, BaZrO₃ and BaHFO₃, which all have t ~ 1 and cubic structure, were obtained at room temperature [8]. In particular, SrTiO₃ exhibited very sharp X-ray diffraction (XRD) peaks due to its high crystallinity, which was comparable to that synthesized by the solid-state reaction at 1373 K [6]. The crystallinity was affected by the reaction temperature. When the reaction proceeded rapidly at a relatively high temperature of 383 K, a sample with low crystallinity was obtained [5]. Dehydration occurs with the progress of the reaction, which was clearly observed as the sample in the reaction vessel getting wet [5]. Unlike other low-temperature synthesis method such as hydrothermal synthesis, this method does not need to add solvents or additional reagents, and the by-product is only water. In addition, high crystallinity was obtained even at low temperatures.

In the hydrothermal synthesis method which is a widely used as low-temperature process, the dissolution-precipitation has been widely proposed as the reaction mechanism [9]. On the other hand, it is considered that the synthesis method we developed have a reaction mechanism different from the dissolution-precipitation in following points [5]. In the powder mixture of starting materials, Sr(OH)₂ dissolves in a small amount of water to make a strong alkali solution. However, TiO₂·nH₂O did not dissolve even in the strong alkali solution of pH14 [5]. Therefore, so-called dissolution-precipitation seems to be not suitable for this process. In addition, the reaction temperature to produce AtiO₄ was dependent on the kind of A ion. If Ti component in the gel dissolves into a water, the reaction temperature should be similar regardless of the kind of A ion. On the synthesis of SrTiO₃, the reaction did not proceed when n value in TiO₂·nH₂O was 0.97 or less [5]. TiO₂·nH₂O contains OH groups and water molecules in the structure, and is more accurately described as TiO₂·(OH)₂·(n-x)H₂O [10,11].
The internal water in hydrous titania gel TiO\textsubscript{2}·nH\textsubscript{2}O was decreased by the addition of Sr(OH)\textsubscript{2} saturated solution, preventing the reaction [5]. Hence, the existence of the internal water in the gel is important for the reaction. It is expected from those results that A ions diffuse into the water part of hydrous titania gel and then slowly react with partially polymerized Ti(OH)\textsubscript{4} (body of the gel) to form a perovskite lattice.

As shown in Equation (1), driving force of this reaction is neutralization, in which A(OH)\textsubscript{2} acts as base and BO\textsubscript{2}·nH\textsubscript{2}O as acid (H\textsubscript{4}BO\textsubscript{2}·nH\textsubscript{2}O).

\[ A(OH)\textsubscript{2} \cdot 8H\textsubscript{2}O + BO\textsubscript{2} \cdot nH\textsubscript{2}O \rightarrow ABO\textsubscript{3} + (n + 9)H\textsubscript{2}O \] (1)

In this study, the reaction mechanism proposed above has been verified by the syntheses of (Ba, Sr)TiO\textsubscript{3} and Ba(Zr, Ti)O\textsubscript{3} solid solutions. In the powder mixture of Ba(OH)\textsubscript{2}·8H\textsubscript{2}O, Sr(OH)\textsubscript{2}·nH\textsubscript{2}O and TiO\textsubscript{2}·nH\textsubscript{2}O, if Ba ions and Sr ions equally diffuse all over the TiO\textsubscript{2}·nH\textsubscript{2}O, (Ba, Sr)TiO\textsubscript{3} solid solution will be formed. In addition, on the synthesis of Ba(Zr, Ti)O\textsubscript{3} solid solution, (Zr, Ti)O\textsubscript{2}·nH\textsubscript{2}O should be used as gel material. When the mixture of TiO\textsubscript{2}·nH\textsubscript{2}O and ZrO\textsubscript{2}·nH\textsubscript{2}O is used as gel materials, the mixed phase of BaTiO\textsubscript{3} and BaZrO\textsubscript{3} would be obtained.

2. Materials and methods
A(OH)\textsubscript{2}·8H\textsubscript{2}O (A = Ba, Sr) (Fujifilm Wako Pure Chemical, 98%), and BO\textsubscript{2}·nH\textsubscript{2}O (B = Ti, Zr, Zr\textsubscript{0.45}Ti\textsubscript{0.55}) were used as starting materials for the synthesis of perovskite phase. BO\textsubscript{2}·nH\textsubscript{2}O (B = Ti, Zr) were prepared using TiCl\textsubscript{4} (Fujifilm Wako Pure Chemical 16% in HCl aq.) and ZrCl\textsubscript{4} (Fujifilm Wako Pure Chemical, 95%), respectively. 5 mL of BCl\textsubscript{4} was added to 250 mL of ice-cooled pure water. Subsequently, concentrated ammonia water was added until the pH reached 8.5 to precipitate the BO\textsubscript{2} hydrous gel. When the ZrCl\textsubscript{4} was used, these operations were performed in a glove box filled with Ar gas. The obtained precipitation was filtered, washed with distilled water, and dried at 373 K for 12 hours.

The n value was measured by TG analysis and found to be 1.68 for the TiO\textsubscript{2}·nH\textsubscript{2}O gel and 1.46 for the ZrO\textsubscript{2}·nH\textsubscript{2}O gel. To prepare the Zr\textsubscript{0.45}Ti\textsubscript{0.55}O\textsubscript{2}·nH\textsubscript{2}O solid solution hydrous gel (n = 2.50), a mixture of TiCl\textsubscript{4} and ZrCl\textsubscript{4} in a volume ratio of 1:9 was used.

The perovskite-type ABO\textsubscript{3} was synthesized by the following procedure. The starting materials were mixed with stoichiometric ratio in an alumina mortar. The mixture was placed in a vial and sealed with a cap. These operations were performed in an Ar-filled glove box to prevent the formation of carbonate. The vial was kept at 296 K – 323 K in a constant temperature bath and then left for 1–5 days. The reacted powder was washed with 1.0 M acetic acid and pure water.

Table 1 shows the target composition, starting materials, and reaction conditions.

Powder XRD measurement was performed using a RIGAKU MiniFlex600 X-ray diffractometer (CuK\textsubscript{α} radiation). The program VESTA was used for drawing crystal structures [12]. To check the n value in BO\textsubscript{2}·nH\textsubscript{2}O, thermogravimetric (TG) analysis was performed (heating rate of 5 K/min in air, and α-Al\textsubscript{2}O\textsubscript{3} as standard sample). The particle shape of the powder samples was observed with a field emission scanning electron microscope (FE-SEM) JEOL JSM-7600. The composition analysis was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a SHIMADZU ICPE-9000. The solution for composition analysis was prepared by the following procedure. A few milligrams of powder sample and 5 mL of concentrated HCl were placed in a vial vessel and then heated to near 373 K on a hot plate. Once the sample was dissolved, it was diluted to 100 mL with ultrapure water.

3. Results and discussion
The perovskite-type SrTiO\textsubscript{3}, BaTiO\textsubscript{3}, and BaZrO\textsubscript{3} were synthesized by conditions shown in Table 1. Similar to the previous report [5,7], all were obtained as cubic perovskite phases. The lattice constants of the samples
synthesized in 5 days of reaction were 0.39292(11) nm for SrTiO$_3$, 0.40447(3) nm for BaTiO$_3$, and 0.42176(3) nm for BaZrO$_3$. Figure 1 shows SEM images of TiO$_2$·nH$_2$O and SrTiO$_3$. If a perovskite phase was formed by diffusion of Sr$^{2+}$ and Ba$^{2+}$ ions into the hydrous gel, the grain shape of perovskite phase should be similar to initial hydrous gel. However, it has not been confirmed because no clear particle size was observed from SEM in both the hydrous gel and perovskite due to agglomeration of particles. Therefore, we verified that the reaction process of this synthesis method was due to diffusion of Sr$^{2+}$ and Ba$^{2+}$ ions in hydrous gel by synthesizing perovskite solid solution using various starting materials.

Synthesis of (Ba, Sr)TiO$_3$ solid solution was performed by using Ba(OH)$_2$·8H$_2$O, Sr(OH)$_2$·8H$_2$O and TiO$_2$·nH$_2$O as starting materials. Figure 2 shows the XRD patterns of the products synthesized by leaving at 323 K for 1–5 days. Single phase of cubic perovskite phase (Space group $Pm3m$) was obtained on the first day, and the peak intensity became stronger day by day. The peak position was between SrTiO$_3$ and BaTiO$_3$, suggesting the formation of perovskite solid solution. The solid solution obtained was found to be (Ba$_{0.60}$Sr$_{0.40}$)TiO$_3$ by ICP-AES. Ba and Sr were considered to have disordered arrangement because superlattice peaks due to the ordering of Ba and Sr in perovskite A-site were not observed.

Next, the synthesis of $(Ba_{1-x}Sr_x)TiO_3$ series were performed by leaving at 323 K for 5 days. Table 2 shows composition of Ba and Sr of the starting materials and products measured by ICP-AES. The ratio of Ba and Sr of the starting materials and products were in substantial agreement. Figure 3 shows the XRD patterns of the obtained samples. Cubic perovskite phase (Space group $Pm3m$) was obtained in all compositions. Figure 4 shows the relationship between the lattice parameter and composition. The lattice parameter increased with increasing Ba content. This relationship appears to follow the Vegard’s law, based on the 12-coordinated ionic radii [13] of Ba$^{2+}$ (0.161 nm) and Sr$^{2+}$ (0.144 nm). From the above results, it was found that A-site-substituted perovskite solid solution (Ba, Sr)TiO$_3$ was synthesized by starting materials of Ba(OH)$_2$·8H$_2$O, Sr(OH)$_2$·8H$_2$O and TiO$_2$·nH$_2$O.

Ba(Zr, Ti)O$_3$ containing multiple ions at the perovskite B-site, was attempted to synthesize using two kinds of starting materials (mixture of ZrO$_2$·nH$_2$O + TiO$_2$·nH$_2$O, and $\left(Zr_{0.45}Ti_{0.55}\right)O_2$·nH$_2$O). Figure 5 shows the XRD patterns of the products synthesized by using 2 Ba(OH)$_2$·8H$_2$O + ZrO$_2$·nH$_2$O + TiO$_2$·nH$_2$O at 323 K for 3–5 days. Diffraction peaks showing a two-phase

![Figure 1. SEM images of TiO$_2$·nH$_2$O (a) and SrTiO$_3$ synthesized at 323 K for 5 days (b).](image-url)
A mixture of perovskite phases were observed. The lattice parameters calculated for each phase were 0.40555(3) nm and 0.42091(3) nm, which were close to those of end members of BaTiO$_3$ (0.40447 nm) and BaZrO$_3$ (0.42176 nm), respectively. This result indicated that BaTiO$_3$ and BaZrO$_3$ were individually generated when the mixture of ZrO$_2$·$n$H$_2$O and TiO$_2$·$n$H$_2$O were used as starting materials. However, the XRD peak intensity of BaTiO$_3$ was much smaller than that of BaZrO$_3$. This may be due to the difference in atomic

**Figure 2.** XRD patterns of (Ba, Sr)TiO$_3$ synthesized at 323 K for 1–5 days. 0.5 Ba(OH)$_2$·8H$_2$O, 0.5Sr(OH)$_2$·8H$_2$O, and TiO$_2$·$n$H$_2$O were used as starting materials. The ratio of Ba : Sr in product measured by ICP-AES was 0.6:0.4.

**Table 2.** Composition of Ba and Sr in starting mixture and obtained product.

| Starting materials | Products |
|--------------------|----------|
| Ba/(Ba+Sr) | Sr/(Ba+Sr) | Ba/(Ba+Sr) | Sr/(Ba+Sr) |
| 0.1 | 0.9 | 0.07 | 0.93 |
| 0.2 | 0.8 | 0.19 | 0.81 |
| 0.3 | 0.7 | 0.27 | 0.73 |
| 0.4 | 0.6 | 0.42 | 0.58 |
| 0.5 | 0.5 | 0.60 | 0.40 |
| 0.6 | 0.4 | 0.63 | 0.37 |
| 0.7 | 0.3 | 0.75 | 0.25 |

**Figure 3.** XRD patterns of (Ba, Sr)TiO$_3$ synthesized at 323 K for 5 days. (1-$x$)Ba(OH)$_2$·8H$_2$O, $x$ Sr(OH)$_2$·8H$_2$O, and TiO$_2$·$n$H$_2$O were used as starting materials. The $x$ values represent value in the starting materials. The composition of products is summarized in Table 2.
scattering factors of X-rays between Zr and Ti, as well as the difference in reactivity between Ba(OH)$_2$•8H$_2$O and BO$_2$•nH$_2$O (B = Ti, Zr). Yamaguchi and coworkers reported the minimum temperature required for synthesizing each perovskite compound by this method as 303 K for BaZrO$_3$ and 313 K for BaTiO$_3$ [8]. BaZrO$_3$ can be formed at the lower temperature than BaTiO$_3$. It is considered that crystallization of BaZrO$_3$ proceeded faster than that of BaTiO$_3$ and as a result, BaZrO$_3$ exhibited higher XRD peak intensity.

Next, we attempted to synthesize single-phase Ba(Zr, Ti)O$_3$ by using (Zr$_{0.45}$Ti$_{0.55}$)O$_2$•nH$_2$O as a starting material. Figure 6 shows the XRD patterns of products. Unlike the case using ZrO$_2$•nH$_2$O + TiO$_2$•nH$_2$O, single phase of cubic perovskite (Space group Pm3m) was obtained. The lattice parameter, 0.41274(10) nm, was almost in the middle of the end members of BaTiO$_3$ (0.40447 nm) and BaZrO$_3$ (0.42176 nm). ICP-AES measurement revealed that the ratio of Ti and Zr in product did not change from starting material of (Zr$_{0.45}$Ti$_{0.55}$)O$_2$•nH$_2$O. In addition, superlattice peak due to the ordered arrangement of Zr and Ti ions in perovskite B-site was not observed, indicating that Zr and Ti ions were disorderly arranged in perovskite B-site. It was found that the use of (Zr, Ti)O$_2$•nH$_2$O hydrous gel was important for the formation of Ba(Zr, Ti)O$_3$ solid solution in this method.

From the above results, the reaction mechanism in this synthesis method is considered. Ba(OH)$_2$ and Sr(OH)$_2$ dissolve in water to show strong alkaline, respectively. As described above, B component in BO$_2$•nH$_2$O gel is insoluble in strong alkaline water. It is
deduced that the reaction proceeds in the gel, as shown in Figure 7. On the other hand, in the hydrothermal synthesis method, which is a similar low-temperature process, so-called dissolution-precipitation mechanism is proposed. In this mechanism, B component must dissolve in water to react with \( A^{2+} \) ion, precipitating a perovskite [9]. If B component dissolved slightly, there would be a possibility to form (Ba, Sr)TiO\(_3\) solid solution perovskite via dissolution-precipitation. Ba(Zr, Ti)O\(_3\) also could be obtained from (Zr, Ti)O\(_2\)·nH\(_2\)O gel via dissolution-precipitation. However, in this study, when two kinds of gel (ZrO\(_2\)·nH\(_2\)O and TiO\(_2\)·nH\(_2\)O) were used, BaZrO\(_3\) and BaTiO\(_3\) were obtained as clearly separated two phases. These two phases never be formed via dissolution-precipitation, as shown in Figure 7(c). Therefore, it is verified as the reaction mechanism in this method that A ions of Ba\(^{2+}\) and Sr\(^{2+}\) diffuse into the hydrous gel to react slowly with BO\(^{2-}\)·nH\(_2\)O to form a perovskite lattice. More precisely, A ions diffuse all over the inner water channel in the gel, because the reaction does not proceed without inner water. This is also supported by the fact that in synthesis of Ba(Zr\(_{0.45}\)Ti\(_{0.55}\))O\(_3\), the ratio of B cation was unchanged between starting hydrous gel and perovskite product.

4. Conclusion

The perovskite solid solutions (Ba, Sr)TiO\(_3\) and Ba(Zr, Ti)O\(_3\) were synthesized by leaving the mixture of A(OH)\(_2\)·8H\(_2\)O (A = Ba, Sr) and BO\(^{2-}\)·nH\(_2\)O (B = Ti, Zr, Zr\(_{0.45}\)Ti\(_{0.55}\)) at 323 K for 5 days. The reaction mechanism
of this synthesis process was verified by investigating the relationship between the starting materials and the obtained perovskite phase. A-site substituted perovskite solid solution (Ba, Sr)TiO$_3$ were formed by using Sr(OH)$_2$·8H$_2$O, Ba(OH)$_2$·8H$_2$O, and TiO$_2$·nH$_2$O as starting materials, indicating that Ba and Sr ions diffused all over the TiO$_2$·nH$_2$O even at a low temperature of 323 K. In the Ba(Zr, Ti)O$_3$ system, mixed phase of BaTiO$_3$ and BaZrO$_3$ was obtained by using Ba(OH)$_2$·8H$_2$O and a mixture of TiO$_2$·nH$_2$O and ZrO$_2$·nH$_2$O as starting materials. On the other hand, when (Zr$_{0.45}$Ti$_{0.55}$)O$_2$·nH$_2$O solid solution hydrous gel were used as starting material, B-site substituted perovskite solid solution Ba(Zr$_{0.45}$Ti$_{0.55}$)O$_3$ was obtained. The reaction process in this study is not based on the dissolution-precipitation, but on the long-range diffusion of Ba$^{2+}$ and Sr$^{2+}$ ions in the inner water channel of hydrous gel.

**Disclosure statement**

There is no potential competing interest in this work.

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