Next-generation ceramic devices will have to be fabricated by novel sintering techniques if they are to obtain the requisite properties such as lightness, robustness, and flexibility. To bind with polymer materials, ceramics must be sintered at temperatures of under 300 °C. In this study we developed a number of low-temperature sintering techniques to synthesize complex oxides by exploiting the chemical reactions among the raw material components. We also developed a number of novel low-temperature synthesis processes to utilize the aforesaid synthesis reactions in sintering. Complex oxides can be prepared at low-temperature using hydroxide and peroxide raw materials. Notably, we found that perovskite oxides, including alkaline earth oxides, can be prepared at temperatures below 100 °C using hydroxide raw materials. (Ba,Sr)(Co,Fe)O3 can be sintered as a cathode material on solid oxide fuel cells at 700 °C by reactive sintering using the solid state synthesis reaction among the peroxide-and-hydroxide mixtures. Cells produced by this method show superior electrochemical performance attributable to an improved interface on the cathode layer derived from reactive sintering. We also found that the novel low-temperature synthesis method effectively yields bulk bodies of perovskite materials such as BaZrO3 at temperatures below 100 °C in atmospheric pressure.

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esses such as sputtering, pulse laser deposition, and chemical vapor deposition can deposit dense ceramic layers while controlling the substrate temperature. These dry processes are less effective, however, in fabricating large samples and thick films, as the deposition rate is slow and the vacuum chamber is limited in size. Dry processes are much more costly than conventional wet processes as a consequence. They also have the demerit of unwieldy performance in the preparation of bulk ceramics. For these reasons, ceramic devices for industrial use are still fabricated by wet processes such as tape casting and screen printing.

Fine powder and additive sintering aids are the conventional means used to lower the sintering temperature. While these methods achieve their purpose, the high temperature of the heat treatment still makes it difficult to combine the ceramic and metal. And in some cases, the addition of sintering aid leads to a degradation of the material’s properties. A novel sintering process capable of reducing the sintering temperature without additional reagents is therefore required.

Many researchers are now pursuing the development of low-temperature sintering and solidification for ceramic-based materials. The cold sintering process (CSP) can sinter ceramic materials at temperatures under 300 °C by exploiting the hydrothermal reaction.7-11) CSP promotes the diffusion of ions under the high-pressure conditions of a hydrothermal system, which makes it suitable as a process to sinter ceramic materials for ferroelectrics or lithium ion batteries at low-temperature. The films and bulk ceramics composed of BaTiO₃, meanwhile, can be prepared by solvothermal solidification.12),13) The reaction required for these processes must take place in high pressure at a temperature above 100 °C. Once again, the limitations in the size of the equipment make it difficult to prepare samples of a large size. Meanwhile, the aerosol deposition method14),15) and non-firing process16)-18) are attracting widespread attention as low-temperature solidification techniques performed at around room temperature.

In this study we developed a number of low-temperature sintering techniques for application in functional ceramic devices. The low-temperature sintering techniques developed in this study use the synthesis reactions to drive the ion diffusion, processes of key importance for the sintering behavior. A reduction of the sintering temperature can be expected by applying the ion diffusion and lattice reconstruction of the synthesis reaction. A low-temperature sintering process that exploits the chemical reaction requires the development of a synthesis process that takes place at a temperature much lower than the conventional sintering process. Further, the synthesis reactions must produce the intended complex oxides without any by-products. Hence, a novel low-temperature synthesis method suitable for the sintering must be developed.

2. Low-temperature synthesis of complex oxides using hydroxide and peroxides

Complex oxides are conventionally prepared by solid state reaction synthesis with heat treatment at a temperature above 1000 °C. While this process can easily produce complex oxides, it has difficulty in obtaining small particles. In contrast, solution methods such as the sol-gel,19),20) co-precipitation,21) and Pechini22),23) processes can synthesis complex oxides with small particle sizes at temperatures below 1000 °C. The use of solutions in these methods enables a homogeneous mixing of all of the ions. The methods can therefore synthesize the products at lower temperature than that of a conventional solid-state reaction process while precisely controlling control the composition of the complex oxides. Hydrothermal and solvothermal methods, meanwhile, can produce nanoparticles of ceramic materials with high crystallinity below 300 °C.24)-27) These processes, however, require large amounts of solvent and cannot easily yield powder products in large amounts.

We know, on the other hand, that complex oxides can be synthesized at a temperature below 500 °C by heat-treating the hydroxide raw materials in a closed vessel without the use of solvents. In the case of a conventional solid-state reaction process, oxides and carbonates are normally used as raw materials for the synthesis of complex oxides. In that process, a high temperature is required to decompose the carbonates before the raw materials react. The hydroxides, in contrast, are more unstable than the oxides and carbonates, and decompose at a lower temperature in air. When the hydroxides decompose in a closed vessel at a temperature below 500 °C, the raw materials are converted into various active intermediate states and generate water as a by-product.28),29) Products can thus be obtained through a hydrothermal-like reaction in a closed vessel. Figure 1 shows the X-ray diffraction (XRD) patterns of complex oxides prepared from hydroxide materials by heating in a closed vessel. As the figure demonstrates, all of the products can be obtained as a single phase under 400 °C, with good crystallinity. The products were also found to have small particle sizes, as shown in Fig. 2.

Fig. 1. XRD patterns of complex oxides prepared by heating the hydroxide raw materials in a closed vessel. The respective samples were prepared at different temperatures, as appropriate: MgAl₂O₄ at 400 °C, NiFe₂O₄ at 350 °C, CoFe₂O₄ at 300 °C, LiCoO₂ at 200 °C.
The solid-state reaction can therefore be promoted using hydroxide raw materials and heating in a closed vessel. The schematic in Fig. 3 shows the mechanism of the synthesis reaction of MgAl₂O₄. MgAl₂O₄ is normally prepared at more than 1400 °C by the conventional solid-state reaction. In the present reaction, Al(OH)₃ and Mg(OH)₂ are used as raw materials and heated at 500 °C. When Al(OH)₃ is heated in an air atmosphere, it decomposes into γ-AlOOH at 300 °C and changes into γ-Al₂O₃ at around 400 °C. Mg(OH)₂, meanwhile, decomposes at 350 °C in air. Thus, a high temperature comparable to that required in a solid state reaction is a necessary condition for synthesis when hydroxide raw materials are heated in open air. In a closed space, these hydroxide raw materials can remain in a hydroxide state at high temperature. Mg(OH)₂ actually remains in its initial state after heat treatment at 500 °C in a closed vessel. Al(OH)₃, on the other hand, seems to change to α-Al₂O₃ via γ-AlOOH and γ-Al₂O₃. Hence, a low-temperature solid state reaction occurs when one raw material remains a hydroxide and another hydroxide decomposes or changes into another phase. This reaction seems to be an example of the “Hedvall effect.” A phenomenon which the reactivity of substance increases by crystal transition is known as the Hedvall effect. The transition promotes the diffusion of elements in the raw materials and the reaction temperature becomes lower. A small amount of water by-product generated is thought to additionally promote the ion diffusion, dissolution and precipitation in the synthesis reaction. When the functional oxide materials were prepared from the hydroxides by heating in a closed vessel, products inclusive of the alkali or alkaline earth elements can be prepared at 200 °C. This is a much lower temperature than that applied for other oxides. LiCoO₂, for example, was synthesized at 200 °C, as shown in Fig. 1. As a result, some perovskite oxides can be prepared at 100 °C by leaving the hydroxide raw material mixtures without any solvent. In our study, SrTiO₃ was synthesized at room temperature, proving that this process can synthesize products under atmospheric pressure. Figure 4 shows an XRD pattern and SEM image of SrTiO₃ prepared at room temperature. A highly crystallized SrTiO₃ product was obtained by the
reaction of Sr(OH)$_2$·8H$_2$O and hydrous titania gel in spite of the room temperature synthesis. The crystallinity of the SrTiO$_3$ in the present process was as high as that prepared by solid state reaction at 1100 °C, judging from the FWHM of the XRD pattern shown in Fig. 4(a). The products of this have a small particle size of 100 nm. The mechanism is assumed to occur based on a kind of acid-base reaction. Strontium hydroxide works as a strong base and reacts with the titania hydrous gel, which is assumed to be a titanic acid (H$_4$TiO$_4$). The amount of internal water in the gel is quite important. A considerable amount of water promotes the diffusion of the Sr ion and acidity of (H$_4$TiO$_4$)$_n$.

$\text{ABO}_3$ (A = Ca, Sr, Ba, B = Ti, Zr, Hf) were successfully prepared by this process without high-temperature heat treatment. Considering the high crystallinity and reaction mechanism based on this process, the products resembled a kind of ionic crystal. These products can be described as salts consisting of A$^{2+}$ and BO$_3$$^{2-}$. Turning to the synthesis temperature of the products, the tolerance factor $t$ was found to be strongly linked to these temperatures. The tolerance factor $t$ is an indicator for the distortion in crystal structure of perovskite oxides. When $t$ of a perovskite oxide is 1, it has ideal cubic structure. The synthesis temperature increases with $t$ of perovskite products, when $t$ is equal to or larger than 1. These results demonstrate the importance of the electronegativity of the A site ions. From the above assumption, the thermodynamic stability of $\text{ABO}_3$ is thought to be strongly correlated with the Madelung energies of the products. The Madelung energies of the products were calculated from data on the lattice parameter. The MADEL program (packaged in RIETAN-FP·VENUS system) was used to calculate the change of the Madelung energy before and after the synthesis reaction. Figure 5, a plot of the change of the Madelung energy, $\Delta E_M$, against the synthesis temperature, shows a linear relationship between the two. We can assume, based on this relationship, that the crystal structure and electronegativity of the elements are important. The A site ions, which have low electronegativity, become stable by connecting with the coordinated oxide ions. Thus, the A site ions pull the oxide ions in the BO$_6$ octahedra, and the minimum structure of the perovskite oxides is constructed, in the present synthesis reaction (see Fig. 6). When the distortion is introduced into the lattice, it becomes unstable. Perovskite oxides, which have a high-symmetry structure, can be prepared at around room temperature.

Attempts have been made to produce cathode materials for SOFCs by low-temperature synthesis processes using hydroxide and peroxide materials. Cobaltite- and ferrite-based perovskite oxides, such as (La,Sr)(Co,Fe)O$_3$ (LSCF), (La,Sr)CoO$_3$ (LSC), (La,Ca)FeO$_3$ (LCF), and Sm,SrCoO$_3$ (SSC), are widely used as cathode materials in SOFCs. (Ba, Sr)(Co,Fe)O$_3$ (BSCF) is attracting attention as a material for intermediate-temperature...
SOFCs. BSCF has an ideal cubic perovskite structure and includes strong base elements of Ba and Sr. These properties have prompted speculation that BSCF can be prepared at low-temperature by a similar process using hydroxide raw materials. In the synthesis of cobaltite- and ferrite-based oxides, the acidity of raw material was slightly weak, and the reaction was difficult to achieve under 100 °C. The hydroxides of Ba and Sr, however, immediately reacted with CO2 when heated in air. The generation of carbonates in the raw materials thus necessitates heat treatment at a high temperature in excess of 800 °C. The process therefore requires non-hydroxide raw materials without generating carbonates. To meet this condition, we focused on alkaline earth peroxides as raw materials for low-temperature solid state synthesis. Barium peroxide (BaO2) and strontium peroxide (SrO2) are more stable against CO2 than the monoxides of BaO and SrO. These peroxides can react among raw materials without the carbonation. In addition, a synthesis reaction assisted by the Hedvall effect is expected, as the BaO2 changes to liquid at around 450 °C. When BaO2 and SrO2 are used as raw materials, the intermediate compound was formed at around 300 °C, as shown in the XRD patterns and differential thermal analysis (DTA) curve (see Fig. 7). When the raw materials were heated to over 400 °C, the BSCF was synthesized as hexagonal phase. At the higher temperature of 700 °C, moreover, the BSCF changed from hexagonal to cubic phase. The particle size of the BSCF prepared at 400 °C was around 100 nm, as measured by nitrogen adsorption-desorption measurement and estimation by Scherrer’s equation. The low-temperature synthesis enables the production of BSCF in a fine powder form. The use of peroxide raw materials allows us to reduce the synthesis temperature.

These results demonstrate that many complex oxides can be obtained by low-temperature solid state synthesis in active raw materials such as hydroxides and peroxides using the decomposition and phase transition in these processes. The processes are also clean, as they yield complex oxides without additive reagents and produce only water as by-product. Better still, small particles with high
crystallinity can be obtained by designing a synthesis route promoted by the acid-base reaction. The crystal structure and electronegativity were both found to be important, and to correlate with the synthesis temperatures.

3. Reactive sintering of cathode materials using peroxide raw materials

Ceramic-based electrochemical devices such as SOFCs and all-solid-state batteries are attracting widespread attention as promising solutions for energy and environmental problems. The layered structures of these novel devices can only be obtained by applying sintering processes effective in producing fine interfaces. A lower sintering temperature is crucial for the binding of the ceramics with other materials such as metals or polymers. Low-temperature sintering will be crucial, for example, for developing the upcoming generation of metal-supported SOFCs (MSCs) designed with high robustness and tolerance for vibration and shocks.\textsuperscript{44−47} MSCs are expected to be applied in systems for mobility devices such as electric vehicle and drones. MSCs generally consist of ceramic layers fabricated upon porous metal substrates. The conventional co-sintering process by high-temperature heat treatment in air is ill-suited to fabricate such a structure. Most MSCs are fabricated by dry-processes,\textsuperscript{48,49} which tend to be rather costly when preparing larger cells. MSCs can also be fabricated by co-sintering processes performed in a reducing atmosphere. Most of the SOFC cathode materials, which include the cobalt and iron ions, however, decompose when heat-treated under a reducing atmosphere. The cathodes on MSCs must therefore be sintered in air at a temperature lower than the oxidation temperature of the metal substrate. A reactive sintering technique performed at a temperature lower than 700 °C using peroxide raw materials was developed to enable the use of stainless steel substrate materials. By sintering and synthesizing the cathode material on the cell at the same time, this technique decreases the number of steps in the process. The technique also decreases the sintering temperature by promoting ion diffusion in the synthesis reaction. To exploit these advantages, we decided to apply the reactive sintering method to fabricate a cathode fabrication at a temperature under 700 °C by synthesizing BSCF from peroxide and hydroxide raw materials via a low-temperature solid-state reaction.\textsuperscript{50} As shown in Fig. 7, the intermediate compound was generated at around 300 °C when the BSCF was synthesized from the peroxide raw materials. The cathode was then fabricated on the cell using this intermediate compound as a starting material for the reactive sintering of the BSCF. A BSCF prepared at 400 °C was also used as a starting material for the cathode in a parallel experiment for comparison. The cathode slurry was printed on the cell and heated at 700 °C. Figure 8 shows the impedance spectra and cross-sectional SEM images of the cells. The cell with the cathode prepared from BSCF synthesized at 400 °C (BSCF4070) had an ohmic resistance ($R_{\text{ohm}}$) of 488 and polarization resistance ($R_p$) of 2312 mΩ cm$^2$. In contrast, the cathode prepared from the intermediate compound (BSCF3070) had a lower $R_{\text{ohm}}$ of 128 and a lower $R_p$ of 390 mΩ cm$^2$. As Fig. 8(c) shows, delamination was observed at the interface of the cathode and gadolinium doped ceria (GDC) interlayer in the BSCF4070 cell. In contrast, the BSCF3070 cathode layer was connected to the GDC interlayer. The reactive sintering

![Fig. 8.](image_url)
appeared to improve the sinterability of the BSCF3070. With such an improvement, a lower cathode resistance might also be expected. Figure 9 shows the $I$–$V$ characteristics and power densities for the anode-supported SOFCs of BSCF3070 and Com-70. Com-70 is an anode supported cell sample equipped with a cathode prepared from a commercial BSCF powder. The power density of the BSCF3070 was confirmed to be higher than that of the Com-70. From these results, we confirmed that reactive sintering can sinter the BSCF as a cathode on the cell in spite of the lower sintering temperature of 700 °C. This process can improve the sinterability of BSCF and the connection between the cathode and interlayer.

4. Acid-base chemical sintering by a room-temperature synthesis reaction

Reactive sintering requires heat treatment to synthesize complex oxides via a solid state reaction, as mentioned above. Sintering at temperatures under 100 °C is thought to occur when the ions can diffuse in the crystal structure with the application of low-temperature synthesis. An acid-base chemical (ABC) sintering technique performed at temperatures under 100 °C has therefore been developed using the reaction for the synthesis of perovskite oxide materials. BaZrO$_3$ (BZO) with a small particle size and high crystallinity can be prepared at around room temperature, as mentioned earlier. BZO shows promise as a potential electrolyte material for protonic ceramic fuel cells (PCFCs). PCFCs are being widely studied in the expectation that they will be adopted as highly efficient next-generation SOFC systems. The development of BZO-based PCFCs still has an important roadblock, however, as BZO has a high sintering temperature of about 1700 °C. The high-temperature heat treatment required makes it difficult to fabricate the cell by a co-sintering technique. While the sintering temperature of BZO can be lowered by adding sintering aids to the anode and electrolyte layers, the addition of sintering aids degrades the efficiency by facilitating hole conduction in the electrolyte layer. The crucial challenge, therefore, is to develop low-temperature sintering techniques for BZO electrolyte without sintering aids. Figure 10 shows a schematic image of this ABC sintering process as we performed it. First, the precursor powder was prepared by introducing a ZrO$_2$ hydrous gel at the surface of the BZO particles by a wet process. This precursor powder was then pressed into pellets and immersed in a concentrated barium hydroxide solution at 75 °C. Figure 11 shows the internal morphology of BZO bulk ceramics prepared by the ABC sintering process at 75 °C. These results demonstrate that dense ceramics of perovskite oxides can be prepared using the acid-base reaction for synthesis at temperatures under 100 °C. This ABC sintering process is effective in preparing dense ceramics without high-temperature heat treatment or additive reagents. Products of high purity that
seem to show the essential properties can be obtained. The materials are sintered or solidified under atmospheric pressure, and the process produces large-size products more easily than other low-temperature processes. The process can also be used to prepare ceramic-based multi-materials.

5. Conclusion

A number of low-temperature synthesis and sintering processes by exploiting the high reactivity of raw materials such as hydroxides and peroxides were developed. The raw materials used in the processes can reduce the synthesis temperature of solid-state reactions by controlling the decomposition and phase transition temperature. The raw materials and atmosphere can both be adjusted to control the synthesis temperature. Several perovskite oxides can be prepared at temperatures under 100 °C via an acid-base reaction. The products synthesized via the acid-base reaction behaved like ionic crystals. Therefore, it was found that the crystal structure and electronegativity of the ions strongly affect the stability of the crystal and the synthesis temperature. The Madelung energy change in the synthesis reaction increased proportionally with the synthesis temperature. We developed a number of low-temperature sintering processes by applying the above low-temperature synthesis to promote the diffusion of ions.

The BSCF cathode was fabricated on the cell at 700 °C by reactive sintering using an intermediate compound prepared from peroxide raw materials. The cell showed high electrochemical performance, as the reactive sintering enabled the formation of a fine interface between the cathode and GDC interlayer. We also prepared bulk and film BZO-based ceramics by ABC sintering processes at temperatures under 100 °C. The acid-base reaction for the synthesis of perovskite oxides was applied to the sintering. The chemical reactions in the synthesis of these complex oxides can be used to promote the sintering of ceramics.

These processes can be used to make new ceramic-based multi-materials. The development of these low-temperature sintering processes will promote the innovation of next-generation ceramic devices.

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