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Nonstoichiometrically Activated Sintering for $Ca_{1-x}Sr_xTiO_3$ Compound by Creating Point Defects

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According to both first principle and materials chemistry, an innovative method for fabricating $Ca_{1-x}Sr_xTiO_3$ ceramics was investigated. $Ca_{1-x}Sr_xTiO_3$ was sintered at temperatures as low as 980 °C by adding 1.0 wt % $Li_2Si_2O_5$ without forming a grain boundary phase. It was considered that the sintering was promoted by self-accelerated diffusion due to the formation of point defects caused by doping with $Li_2Si_2O_5$. Consequently, a new concept of nonstoichiometrically activated sintering, which is enhanced by point defects without the help of a grain boundary phase, is systematically studied for the first time in the $Ca_{1-x}Sr_xTiO_3-Li_2Si_2O_5$ system.

Introduction

The fabrication step in ceramics involves the synthesis of starting materials, mixing, molding, and subsequent sintering of the materials to convert them into dense solids. Sintering is the process by which a powder compact is transformed into a strong and dense ceramic body upon heating. It is known that the fabrication of ceramics requires high-temperature sintering. This is because the driving force for sintering is quite small, i.e., usually only a few joules per mole, whereas that of the chemical reaction is a few kilojoules per mole.[1] Of major interest for the production of sintered materials are the mechanisms and processes which control densification and grain coarsening. High temperature can greatly promote sintering and grain growth,[2] but it requires high-energy consumption. Consequently, enhanced sintering is widely used because it provides an opportunity to improve the properties of the sintered body, increase sintering rate, and lower the firing temperature of traditional systems.[3] Usually, liquid-phase sintering is characterized by the presence of a liquid phase; alternatively, the absence of a liquid phase is thus referred to as solid-state sintering.[4] Liquid-phase sintering is one of the enhanced sintering methods and is of commercial importance since a majority of ceramic products are fabricated via this route. If the properties required in the target material are not adversely affected by the presence of a grain boundary phase, it is the preferred route. However, for many applications, the presence of a second phase at the grain boundaries can have detrimental effects on the properties, e.g., creep resistance and permittivity. Additionally, in contrast to metallic materials, the study of enhanced sintering for ceramic materials is still being conducted. There is not a universal theory developed in previous studies because several processes occur simultaneously during enhanced sintering, making its mechanisms too difficult to identify clearly.

To explore the basic theory, a new concept of enhanced sintering, i.e., nonstoichiometrically activated sintering, was developed in the present study. This method of sintering proceeds with the creation of point defects in the lattice without forming a grain boundary secondary phase. It is the first time for this argument to be proposed systematically based on both the first principle and solid-state chemistry and is supported with corroborating experimental results. Both doping and enhanced sintering were achieved simultaneously during the heating of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \le x \le 0.4$) with 1.0 wt % $Li_2Si_2O_5$ additive. It was possible to sinter this ceramic at temperatures as low as 980 °C because of the intrinsic self-accelerated diffusion characteristic of nonstoichiometrically activated sintering. Thus, nonstoichiometrically activated sintering may result in not only the promotion of sintering but also an improvement in the functionality of ceramic materials by eliminating detrimental secondary phases.

Classic Studies of Enhanced Sintering

Enhanced sintering includes both liquid-phase sintering and solid-state sintering. In general, both of them require the use of an additive to form a second-phase binder γ (the minor phase) as shown in Figure 1,[1,3,5,6] where the composition of a_1 (in the two phase field of $\gamma + \beta$) is the normal practice for enhanced sintering so far. This binder γ is a solid solution of the additive and the base materials and may be either a solid or a liquid during sintering. The base

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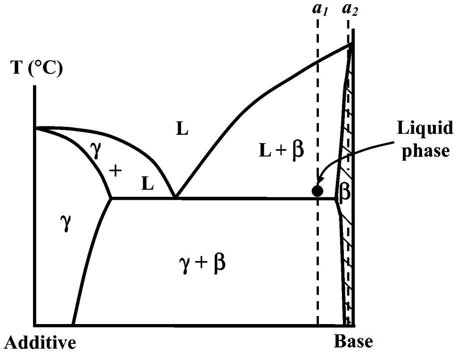

Figure 1. Ideal binary phase diagram for enhanced sintering.[3,5]

material should have a low solubility to accommodate the additive; conversely, the binder phase has a high solubility for the base phase at the sintering temperature. Such a situation can provide a short-circuit mass flow path at the interparticle contacts and thereby enhance sintering. Accordingly, the diffusion rate in the segregated binder phase must be higher than that in the base.[5] The amount of additive may vary from 0.1 to 10 wt %.[7] Therefore, enhanced sintering is viewed in terms of fast diffusion through a binder phase between grains. Although liquid-phase sintering is not an equilibrium process, phase diagrams do provide useful information with respect to the behavior of mixed components during sintering. It could guide the selection and understanding of a sintering process.

Liquid-phase sintering is widely used for the fabrication of both ceramic and metallic materials. Just as described above, a common composition is a_1 for the liquid-phase sintering shown in Figure 1. This sintering process is actually composed of four stages. Initially, during heating, solid-state densification occurs by chemical potential gradients. When the liquid phase is formed, additional densification occurs. Since the volume of liquid increases rapidly, the liquid spreads rapidly, penetrating along interparticle contacts where it lubricates the sliding of particles. This allows the pores to be filled by both solid and liquid flow. Subsequently, a solution-reprecipitation reaction occurs; i.e., a small grain dissolves in its surrounding liquid and precipitates on the large grains.[5]

Consideration of Enhanced Sintering without a Binder Phase

As noted above, enhanced sintering occurs in the presence of a binder phase, γ; this fact has resulted in many important insights being made into the behavior of enhanced sintering in both ceramic and metallic materials, especially for the latter. It is not, however, the only way to enhance sintering for ceramic compounds. In contrast to pure metals, it is easy to make point defects in ceramics through processing or chemical adjustments. During the latter half of the last century, the capacity to improve in the functionality of ceramics was shown through precise control of nonstoichiometry, dependent on the doping techniques, etc. For the most part, however, enhanced sintering with an additive and doped ceramics with a dopant are considered individually. This is because the dopant (in the case of the doping) must enter the host lattice to form a single solid solution β (the major phase) which is similar in composition to a_2 (in single-phase field of β) shown in Figure 1, whereas the additive (in the case of enhanced sintering) should form a second phase γ during the sintering as it does in the composition of a_1 in Figure 1. As a consequence, the doped powder is generally synthesized first, followed by other fabrication processes such as mixing, compacting, and sintering.[8,9] However, is it impossible for the processes of both doping and enhanced sintering to be conducted simultaneously during heating.

Theoretically, the first principle for an atomic or ionic diffusivity D_{ion} is given by[1]

$$D_{\text{ion}} = \alpha\lambda^2\rho\zeta\nu_0 \exp(\Delta S_{\text{m}}/k) \exp(-\Delta H_{\text{m}}/kT) = D_0 \exp(-Q/kT) \quad (1)$$

where α is a geometric constant that depends on the crystal structure, λ is the elementary jump distance, ρ is a fraction of vacancies, ζ and ν_0 are the coordination number and vibration of the atoms, respectively, ΔS_{m} is the entropy, k is Boltzmann's constant, ΔH_{m} is the enthalpy, T is the migration enthalpy, T is the temperature, and Q is the activation energy.

At sufficiently high temperatures, that is, $kT \gg \Delta H_{\text{m}}$, the barrier ceases and every vibration would result in a jump. The temperature is not, however, the only means to improve the diffusion for an atom or ion according to eq 1. It is suggested that the diffusivity of an ion in a crystal depends on the fraction of vacancy, ρ. The vacancy concentration is proportional to the concentration of the dopant.[1] This means that the diffusivity of an ion in a crystal can be tailored by controlling the dopant concentration.

It is known that sintering is described by atom and/or ion diffusion, which happens when an atom gains sufficient energy to leave its mooring and migrate. There are essentially three mechanisms by which atoms will diffuse. First is the vacancy mechanism, which involves the jump of an atom or ion from a regular site into an adjacent vacant site. Second is interstitial diffusion, which requires the presence of interstitial atoms or ions. Third and least common is the interstitialcy mechanism, i.e., an interstitial atom pushes an atom from a regular site into an interstitial site. Accordingly, the sintering process will be enhanced through increasing the amount of vacancies based on either the first principle or the first diffusion mechanism; meanwhile, the presence of interstitial atoms can also improve diffusion during heating.

In previous studies, the mechanism by which the vacancy acts as a diffusion path has been depicted by Kingery[10] and Barsoun.[1] However, no experimental proof has been demonstrated for the enhanced sintering of bulk ceramics. Hwang et al. discussed that a silver additive, which existed as a grain boundary phase, could improve the densification of Pb(Zr,-

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Ti)O_3. The reasoning was that this silver would create vacancies in the base material; however, there was no description of related theory.[11]

The perovskite compounds of the general formula ABO_3 have been tailored to modify crystallographic, electronic, and physical properties by replacing the A or B ions by other cations with different radius/charge. The normal sintering of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$), in which $CaTiO_3$ and $SrTiO_3$ are completely miscible to form a solid solution,[12−15] is conducted at 1400−1600 °C. This conventional method of sintering needs such a high temperature due to the lack of sufficient driving force for the sintering. Because of the same ionic valence of Ca^{2+} and Sr^{2+}, the substitution of Ca^{2+} by Sr^{2+} results in no vacancy or interstitial ions on the lattice structure. It is possible to tailor the point defects in $Ca_{1-x}Sr_xTiO_3$ by doping differently charged species, such as $Li_2Si_2O_5$, i.e., when it is accommodated into the $Ca_{1-x}Sr_xTiO_3$ structure; both the vacancy and interstitial ions should be formed for charge compensation. It is expected that these defects can enhance diffusion on the basis of eq 1, as well as the first and second diffusion mechanisms.

In a previous paper,[16] it was reported that liquid-phase sintering could efficiently decrease the sintering temperature of $Ca_{1-x}Sr_xTiO_3$ from 1400 to 1200 °C by using $Li_2Si_2O_5$, which possesses the low melting temperature of ca. 1030 °C, as a sintering additive. Moreover, the solubility of this additive in $Ca_{1-x}Sr_xTiO_3$ reaches 1.0 wt %, and then $Li_2Si_2O_5$ segregates at the grain boundaries as a secondary phase.[16] This means that the highest solubility of this additive in the β phase is 1.0 wt % as is indicated in Figure 1. Consequently, it is reasonable to perform the sintering process in the single-phase field of β, i.e., no formation of the secondary phase for $Ca_{1-x}Sr_xTiO_3$ by adding less than 1.0 wt % $Li_2Si_2O_5$, which is similar in composition to a_2 shown in Figure 1. Thus, considering the intersolubility, both the partial substitution of $CaTiO_3$ by $SrTiO_3$ and the formation of the point defects by doping are able to increase the sintering driving force for mass flow during heating.[5]

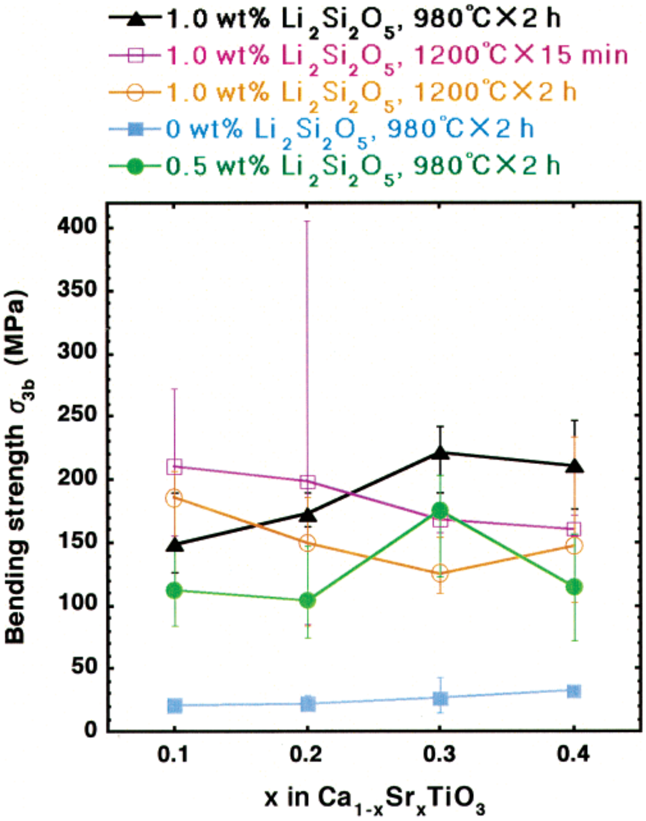

Figure 2. Three-point bending strength of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with and without $Li_2Si_2O_5$ followed by three sintering schedules, i.e., 980 °C for 2 h, 1200 °C for 2 h, and 1200 °C for 15 min.

Experimental Section

$Li_2Si_2O_5$ was prepared by a conventional solid-state reaction using the reagent grade (99.9%) powders of Li_2CO_3 and amorphous SiO_2. They were mixed by ball milling for 16 h and were calcined at 1010 °C for 10 h and then re-milled for 40 h with zirconia balls in a polyethylene bottle. $CaTiO_3$ and $SrTiO_3$ powders were supplied by the Sakai Chemical Industry Co. Appropriate quantities of $CaTiO_3$, $SrTiO_3$, and $Li_2Si_2O_5$ were wet-mixed in a polyethylene bottle with ZrO_2 balls and ethanol for 16 h. The mixtures were dried at 85 °C and then ground by an agate mortar. Two different sintering routes were adapted in order to clarify the role of point defects. The first one used the above-mentioned mixed powder directly for sintering. In an alternate method route the mixed powder was calcined at 900 °C for 10 h and then was ground prior to sintering. After uniaxially pressing the powders into 20 × 20 × 5 mm^3 specimens at 20 MPa, the samples were subjected to cold isostatic pressing under a pressure of 200 MPa and sintered at 980 and 1200 °C for different times in air. The heating rate was controlled at 2 °C/min, and temperature variations were kept to ±2 °C.

The sintered body was polished to a mirrorlike finish and sliced to measure the three-point bending strength; i.e., fracture strength was determined at a crosshead speed of 0.5 $mm\cdot min^{-1}$ and a span width of 10 mm (Shimadzu, Autograph AG-20kNG).

The crystallographic phase constitution was characterized by X-ray diffraction (XRD) analysis using graphite monochromatized Cu Kα radiation (Shimadzu, XD-01). The microstructure was observed using a scanning electron microscope (Hitachi, S-4100L) and transmission electron microscope (JEOL, JEM-2000EX).

Results and Discussion

Material properties depend on the microstructure after sintering. Generally, the strength is a comprehensive reflection of the densification and sinterability of a material. Figure 2 shows the three-point bending strengths of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with 0−1.0 wt % $Li_2Si_2O_5$ followed by three sintering schedules, i.e., 980 and 1200 °C for 2 h and 1200 °C for 15 min. The bending strengths of $Ca_{1-x}Sr_xTiO_3$ sintered at 980 °C without additives were very low, indicating that the sintering of $Ca_{1-x}Sr_xTiO_3$ without use of an additive at such a low temperature as 980 °C is impossible. It was observed that sintering was slightly promoted by increasing

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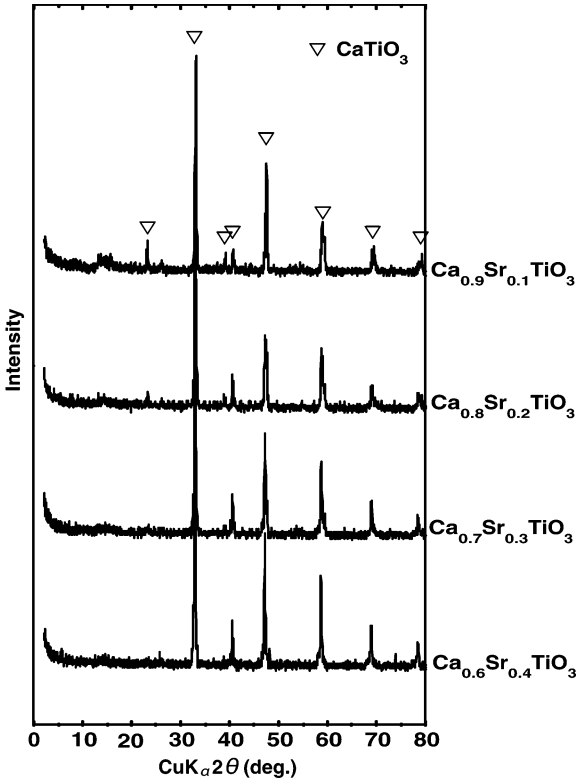

Figure 3. XRD patterns of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with 1.0 wt % $Li_2Si_2O_5$ sintered at 980 °C for 2 h in air.

$SrTiO_3$ content, x, and greatly promoted by increasing $Li_2Si_2O_5$ content. The slight promotion of sintering by replacing smaller Ca^{2+} with larger Sr^{2+} may be due to enhancement of the thermal vibration of the atoms.[17] The sintering at 980 °C may be classified as solid-state sintering because the melting point of $Li_2Si_2O_5$ is 1030 °C. In a previous paper,[16] it was reported that $Li_2Si_2O_5$ is soluble in $Ca_{1-x}Sr_xTiO_3$ up to 1.0 wt %. Therefore, it is considered that the primary influence promoting sintering by doping with $Li_2Si_2O_5$ was caused by nonstoichiometrially activated sintering by the lattice defects. The increase in the sintering temperature up to 1200 °C greatly increased the fracture strength of $Ca_{1-x}Sr_xTiO_3$ ($x = 0.1$), but the fracture strength tended to decrease with increasing sintering time and $SrTiO_3$ content, x, as shown in Figure 2. Therefore, little benefit is obtained by firing the specimens at such a high temperature as 1200 °C for time as long as 2 h, probably due to excess grain growth.[18] Similar phenomena have been found in the previous study, i.e., the densification and sintering prior to the liquid formation for enhanced sintering of Al_2O_3.[19]

$Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with 1.0 wt % $Li_2Si_2O_5$ sintered at 980 °C consisted of a single-phase $CaTiO_3$ orthorhombic structure, as shown in Figure 3 by XRD analysis. It is in agreement with prior reports.[12−16] However, a comparison of the fracture surfaces for $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with 1.0 wt % $Li_2Si_2O_5$ sintered at 980 °C for 2 h demonstrates that there existed some residual additive at the grain boundaries of $Ca_{1-x}Sr_xTiO_3$ ($x = 0.1$ and 0.2) with 1.0 wt % $Li_2Si_2O_5$. However, no grain boundary phase existed in the case of $x = 0.3$ and 0.4 as shown in Figures 4a and 4d, indicating that $Li_2Si_2O_5$ remained at the grain boundary for the samples with $x = 0.1$ and 0.2, but was completely doped in the $Ca_{1-x}Sr_xTiO_3$ lattice for $x = 0.3$ and 0.4. The grain boundary phase is amorphous according to the identification by the electron diffraction pattern (EDP) as shown in Figures 4b and 4c. Additionally, an orthorhombic $CaTiO_3$ structure was determined by EDP for $Ca_{0.7}Sr_{0.3}TiO_3$ with 1.0 wt % $Li_2Si_2O_5$ as is shown in Figures 4e and 4f. The same result has been presented by Howard et al.[20]

According to the chemical composition, ionic radii, coordination number, and Pauling's Rules, the chemical formula of $Li_2Si_2O_5$-doped $Ca_{1-x}Sr_xTiO_3$ nonstoichiometry may be written as $[(Ca_{1-x}Sr_x)_{2-2y}\square_{2y}](Ti_{2-2y}Li_{2y})Si_{2y}O_{6-y}\square_y$ ($\square$: vacancy). This presupposes a partial substitution of Li^+ onto Ti^{4+} sites together with the creation of interstitial Si^{4+} ions, A site vacancy, and oxygen vacancy.[21−24] Further study is necessary to confirm the chemical formula of this material.

Based on the above experimental results, the densification of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with $Li_2Si_2O_5$ at 980 °C might be attributable to both the vacancy and interstitial diffusions, together with the thermal vibration of the atoms enhanced by the partial substitution of smaller Ca^{2+} with larger Sr^{2+}.[17] Alternatively, the existence of some unconsumed additive at the grain boundaries in $Ca_{1-x}Sr_xTiO_3$ ($x = 0.1$ and 0.2) with 1.0 wt % $Li_2Si_2O_5$ might be attributed to the lack of sufficient thermal vibration of the atoms because of insufficient Sr^{2+} content. As a consequence, it is necessary to increase the sintering temperature to compensate for the lack of the sintering driving force, and thereby temperatures as high as 1200 °C are more valid for the sintering of $Ca_{0.9}Sr_{0.1}TiO_3$ and $Ca_{0.8}Sr_{0.2}TiO_3$. Moreover, besides the grain boundary phase for $Ca_{0.9}Sr_{0.1}TiO_3$, its grain size is also smaller than that of $Ca_{0.7}Sr_{0.3}TiO_3$ by comparing Figures 4a and 4d; these results also imply that the sintering was stopped at some primary stage for $Ca_{0.9}Sr_{0.1}TiO_3$ sintered at 980 °C for 2 h.

To clarify the effects of the point defects in $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) on the densification and sinterability, sintering at 980 °C was undertaken after forming $[(Ca_{1-x}Sr_x)_{2-2y}\square_{2y}](Ti_{2-2y}Li_{2y})Si_{2y}O_{6-y}\square_y$ by calcining the mixed powders at 900 °C for 10 h. As shown in Figure 5 by XRD analysis, the alloying of $CaTiO_3$ and $SrTiO_3$ was completed during the calcination at 900 °C; therefore, it was expected that alloying $Li_2Si_2O_5$ was also completed during the calcination process.

Figure 6 shows the photographs of $Ca_{0.8}Sr_{0.2}TiO_3$ and $Li_2Si_2O_5$-doped $Ca_{0.8}Sr_{0.2}TiO_3$, $[(Ca_{1-x}Sr_x)_{2-2y}\square_{2y}](Ti_{2-2y}Li_{2y})Si_{2y}O_{6-y}\square_y$ ($x = 0.2$), sintered at 980 °C for 2 h after

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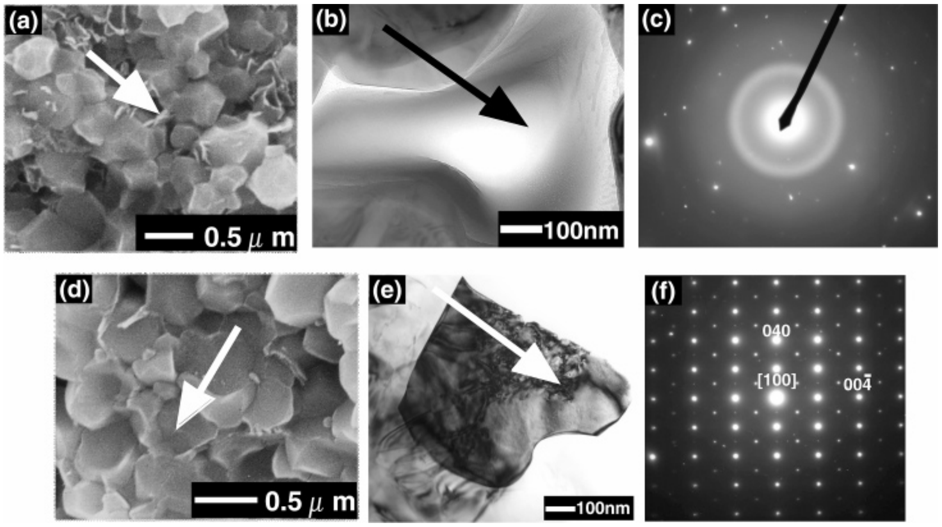

Figure 4. SEM images of fracture surfaces ((a), (d)), TEM images ((b), (e)), and electron diffraction pattern (EDP) images ((c), (f)). The images of (a)−(c) belong to the compound of $Ca_{0.9}Sr_{0.1}TiO_3$, and (d)−(f) are of $Ca_{0.7}Sr_{0.3}TiO_3$ with 1.0 wt % $Li_2Si_2O_5$ sintered at 980 °C for 2 h in air.

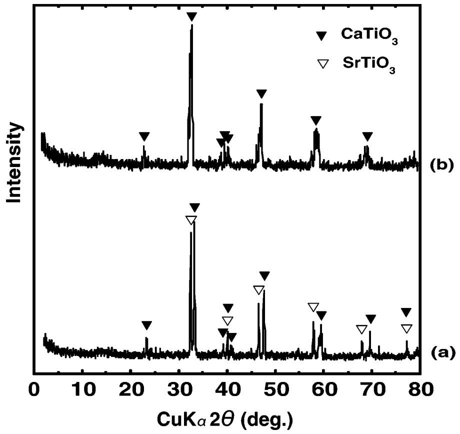

Figure 5. XRD patterns of $Ca_{0.8}Sr_{0.2}TiO_3$ powder with 1.0 wt % $Li_2Si_2O_5$ (a) before and (b) after a calcination at 900 °C for 10 h.

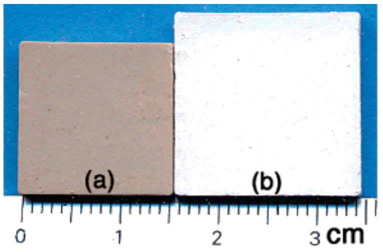

Figure 6. Photographs of $Ca_{0.8}Sr_{0.2}TiO_3$ (a) with 1.0 wt % and (b) without $Li_2Si_2O_5$ sintered at 980 °C for 2 h after calcination at 900 °C for 10 h.

calcination at 900 °C for 10 h. It is obvious that doping with $Li_2Si_2O_5$ before sintering is also quite an effective method to promote sintering; i.e., nonstoichiometrically activated sintering occurred equally in the powders both with and without calcinations.

Fracture test shown in Figure 7 also indicates similar results. That is to say, the point defects formed by doping with $Li_2Si_2O_5$ were effective to promote sintering for the powders both without and with calcinations at 900 °C, although the fracture strengths of the samples prepared using calcined powders were a little smaller than those without calcinations. It may be due to the agglomeration of the powder during calcination.

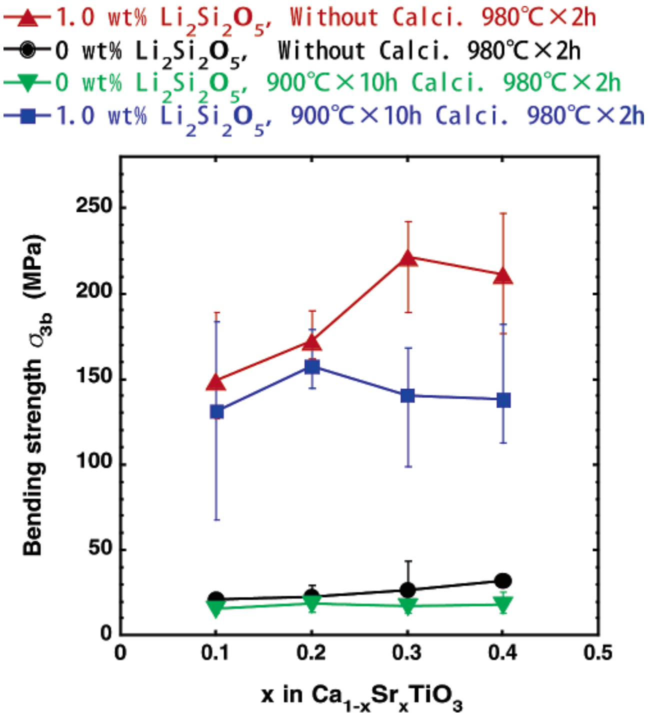

Figure 7. Three-point bending strengths of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) with 1.0 wt % and without $Li_2Si_2O_5$ sintered at 980 °C for 2 h with and without calcination at 900 °C for 10 h.

Nonstoichiometrically Activated Sintering Model

The above discussions provide a basis for describing a more realistic theory of nonstoichiometrically activated sintering. In this vein, a model of consolidation is formulated. Initially, the solid-state dissolution of the $Li_2Si_2O_5$ additive together with $SrTiO_3$ in $CaTiO_3$ occurs by chemical potential gradients during heating. The important feature to note is that the diffusion is a self-accelerated process. The more the additive dissolves, the more rapidly the diffusion proceeds due to the introduction of both the vacancies and interstitial silicon ion. In addition, the partial substitution of the Ca^{2+} by Sr^{2+} ion also improves the self-diffusion due to the vigorous thermal vibration of atom.

With use of this model, the experimental results mentioned above might be explained; namely, the sintering of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) can be improved by increasing $Li_2Si_2O_5$ content as well as $SrTiO_3$ content, x. When the value of x in $Ca_{1-x}Sr_xTiO_3$ is less than 0.2, the promotion of sintering was not large enough because of insufficient atom vibration resulting from $SrTiO_3$ diffusion. Consequently, the samples of $x = 0.1$ and 0.2 consisted of smaller grains than those of $x = 0.3$ and 0.4, and the additive remained in the amorphous phase at the grain boundary.

Conclusions

Based on the present results, the following conclusions may be drawn. (1) $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) ceramics could be sintered at temperatures as low as 980 °C by adding 1.0 wt % $Li_2Si_2O_5$. (2) The sintering of $Ca_{1-x}Sr_xTiO_3$ ($0.1 \leq x \leq 0.4$) was slightly promoted by increasing $SrTiO_3$ content, x, and greatly promoted by increasing $Li_2Si_2O_5$ content. (3) The primary influence promoting the sintering of $Ca_{1-x}Sr_xTiO_3$ by doping with $Li_2Si_2O_5$ seems to be caused by the nonstoichiometrially activated sintering by creating point defects.

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