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Low-Temperature Sintering of Apatite-Type Lanthanum Silicate with Fluoride Additives

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Abstract

Various fluorides (3 - 8 wt%) were added to a $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ (LSO) powder synthesized by calcining the corresponding oxides mixture at 1100°C for 4 h. The addition of BaF_2 , AlF_3 or $\text{Ba}_3\text{Al}_2\text{F}_{12}$ caused an appreciable and substantial increase in bulk density after sintering at 1400° and 1450°C , respectively. These fluorides melt below 1400°C to form liquid phase which could assist the densification at low temperatures. Abnormal grain growth was observed for LSO samples with the addition of AlF_3 and $\text{Ba}_3\text{Al}_2\text{F}_{12}$, but it was effectively suppressed by stepwise sintering at 1400° and 1450°C . The BaF_2 addition brought about the simultaneous promotion of densification and moderate grain growth, leading to the production of a densified LSO sample showing a conductivity of $1.5 \times 10^{-2} \text{ Scm}^{-1}$ at 800°C with an activation energy of 1.23 eV.

Introduction

Apatite-type lanthanum silicates are promising candidates for SOFC electrolytes at an intermediate temperature range (600° - 800°C). Since Nakayama et al. reported high oxide ion conductivities in the apatite-type rare-earth (RE) silicates [1, 2], a lot of study have been conducted on the conduction mechanism [3 - 5] and doping effect on their ion conductivities of bulk RE-silicate samples [6, 7]. In most of the studies using conventional solid state reaction of oxide mixtures, very high temperatures above 1550°C was required to obtain densified samples [7 - 10] because sintering at a lower temperature caused the production of a less dense sample consisting of small grains with a considerably lower conductivity. However, the production of secondary phase(s) and unexpected doping of some impurity element contaminated during powder processing might be enhanced by high-temperature sintering. Therefore, it is desirable that energy efficient processing enabling accelerated mass transport at temperatures as low as possible is developed. One approach leading to low-temperature sintering is to utilize a liquid phase formed during sintering. For lanthanum silicates, fluoride additives would be expected to assist sintering at lower temperatures, because they generally melt at relatively lower temperatures and liquefied fluorides have high resolution capability against lanthanum compounds. In this study, the sintering characteristics of the fluoride-added $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ (LSO) were examined in 1350° - 1450°C in air to find out the appropriate additive(s) which can bring about the densification and controlled microstructure in low-temperature sintering.

Experimental

Fixed amounts of La_2O_3 and SiO_2 powders were mixed in a wet state for 24 h and calcined at 1100°C for 4 h to prepare a stoichiometric powder of LSO. Fluoride additives, BaF_2 , CaF_2 , NdF_3 , AlF_3 , NaF , KF and $\text{Ba}_3\text{Al}_2\text{F}_{12}$ with the amount of 3 – 8 wt%, were added to the calcined LSO powder. Each fluoride-added powder was then formed into disks and sintered in air under various conditions (1350° – 1500°C, 2 – 20 h). Sintered products were characterized by density measurement, solid phase identification and lattice parameter evaluation with X-ray powder diffractometry (XRD), microstructure observation with scanning electron spectroscopy (SEM), and electrical conductivity measurement for Pt-coated samples.

Results and Discussion

Effect of Fluoride Additives on Sintering Behavior of LSO at 1450°C

Figure 1 shows bulk densities of LSO samples with some selected fluoride additives (5 wt%) sintered at 1450°C for 2 h. These fluorides melt around or below 1400°C to form each liquid phase which would be expected to promote the densification of LSO. However, as can be seen in Fig. 1, the addition of BaF₂ and AlF₃ only resulted in a substantial increase in the bulk density, whereas CaF₂ and NaF were found to have a detrimental effect on the densification. Results obtained by XRD and microstructure observation for sintered LSO samples with different fluorides are given in Figs. 2 and 3, respectively. From the XRD analysis, the LSO samples consisting of the apatite-type single phase could be produced with the BaF₂ and NaF additions. The formation of secondary phases was detected when AlF₃ (La₂Si₂O₇), NdF₃ (La₂SiO₅) and CaF₂ (La₂O₃) were added. These results indicated that a liquid phase having different nature of reactivity and solubility to LSO was formed from each fluoride during sintering, resulting in different sintering characteristics.

Substantially different microstructures were observed for LSO samples sintered with fluoride additives (Fig. 3). A SEM image of the non-additive LSO sample shows that it consisted of relatively small grains ranging from 1 to 5 μm. Substantially larger grains could be recognized for sintered samples with the addition of BaF₂ (Fig. 3(B)) and CaF₂ (D), indicative of the promotion of grain growth in the presence of these additives. On the contrary, the addition of AlF₃ considerably altered the microstructure, bringing about abnormal grain growth (Fig. 3(C)). Liquid phase has been cited as a major causes of this kind of abnormal grain growth [11]. An enhanced densification rate was also observed with the AlF₃ addition. Therefore, when AlF₃ was added to LSO, a very reactive liquid was formed in a compact and accelerated mass transport via solution-precipitation process would give substantially increased grain size and density of the sintered LSO sample.

In order to control such an accelerated mass transport through a reactive liquid phase, Ba₃Al₂F₁₂ (BAF) in the BaF₂-AlF₃ system was selected as an additive for promoting moderate grain growth despite of AlF₃. Results are summarized in Table 1 where bulk density, solid phase formed, and electrical conductivity are indicated for LSO samples sintered under different conditions and with different amounts of BAF addition. As has been expected, sintering with the BAF addition caused the promotion of densification of the LSO samples at lower temperature. Typical microstructures can be seen in Fig. 4 (A) and (B) where SEM

images of LSO samples with 5 wt% of BAF addition, sintered at (A) 1400°C for 20 h and (B) 1450°C for 2 h. It was found that a temperature difference by 50°C led to considerably different microstructure, suggesting that sintering temperature is very critical to the resulting microstructure. So a modified sintering method was applied to the BAF-added samples. As can be seen in Fig. 4(C), a stepwise sintering consisting of the 1st heating at 1400° for 5 h followed by the 2nd heating at 1450°C for 5 h effectively suppressed the abnormal grain growth occurring at 1450°C. This might be explained by the fact that a major part of solution - reprecipitation process proceeded during sintering at 1400°C. Sintering and grain growth behaviors of the samples with 3 wt% of BAF addition were almost the same as those obtained with 5 wt% BAF. As shown in Table 1, LSO samples with different amounts of the BAF addition had similar conductivities irrespective of considerably different microstructures. Lower values of the conductivity than that of the non-additive sample could be attributed to the formation of the second phase, $\text{La}_2\text{Si}_2\text{O}_7$. Therefore, it was concluded that the application of the AlF_3 -related fluorides as a densification promoter in an attempt of low-temperature sintering of LSO inevitably led to very rapid densification with simultaneous occurrence of the second phase formation and abnormal grain growth (without applying a specified sintering process) because of very highly reactive and soluble capability of the AlF_3 species in a liquid form.

Effect of BaF_2 Addition

Detailed examination was conducted for the BaF_2 addition because it successfully affected both the densification (Fig. 1) and grain growth (Fig. 3) of the LSO sample after sintering at 1450°C. Figure 5 shows density changes with sintering time at 1400° and 1450°C. It can be clearly seen that enhanced densification was achieved by the BaF_2 addition at both temperatures. However, its densification behavior with sintering time was essentially different from that observed commonly in liquid-phase sintering, i.e. rapid densification in the initial stage of the sintering. The observed densification characteristic of the BaF_2 -added LSO samples revealed that a liquid phase of BaF_2 , which melts at 1353°C, was not as reactive as those containing the AlF_3 species and hence caused moderate rates of densification and grain growth. The effect of the amount of BaF_2 addition was also studied. The addition of 3 wt% BaF_2 resulted in a considerable decrease in the bulk density at 1400° and 1450°C. With an increasing amount of BaF_2 , say 8 wt%, the formation of a second phase (La_2SiO_5) as well as density decrease was detected after sintering at 1450°C. Thus, the addition of 5 wt% BaF_2 was

optimum to produce a densified LSO sample with fairly grown grains at 1450°C.

As clearly deduced from shifting of the XRD peaks identified with the apatite-type LSO to lower diffraction angles in Fig. 2, the unit cell dimension of the LSO samples would be changed by the doping of larger Ba²⁺ cations. Figure 6 shows lattice parameter changes with the amount of BaF₂ addition for LSO samples sintered at 1450°C for 20 h. They almost linearly increase with an increasing amount of BaF₂ addition. In this study, Ba²⁺ cations could be considered to be incorporated into the apatite structure in different ways. One is that they simply substitute for the La³⁺ sites and the other is they occupy the available but vacant cation sites in the structure, for the latter of which a final chemical formula would be La_{9.33}Ba_{0.67}Si₆O_{26.67}. Based on the lattice parameter change with an increasing Ba²⁺ occupancy reported for the oxygen stoichiometric samples of (La_XBa_Y)Si₆O₂₆ (8 ≤ X ≤ 9.33, 0 ≤ Y ≤ 2) [7], the composition of larger cations (A = La³⁺ plus Ba²⁺) in the BaF₂-added LSO samples obtained in this study could be estimated to be, in the order of increasing amount of BaF₂ (3 → 5 → 8 wt%), A_{9.54} → A_{9.67} → A_{9.88} (on *a*-axis base) or A_{9.38} → A_{9.54} → A_{9.67} (*c*-axis base). This result indicated that some portion of the incorporated Ba²⁺ cations could occupy the vacant sites for larger cations and the rest of them would replace the La³⁺ cations on the regular lattice sites. Further quantitative examination is needed for detailed discussion.

Selected conductivity data reported in literature and measured in this study are given in Table 2. Activation energy for conduction of the LSO samples with 5 wt% BaF₂ addition was calculated from an Arrhenius plot. LSO samples doped with alkaline earth cations (M = Ba, Sr, or Ca) while maintaining oxygen stoichiometry showed that as M content increased, i.e. the number of cation vacancies decreased, the conductivities considerably decreased (those of the sample No. < 1 > → < 4 > → < 5 > in Table 2). On the contrary, samples with cation stoichiometry but containing oxygen excess (Sample No. < 3 > and < 6 >) and those containing both cation vacancies and oxygen excess (No. < 2 >) showed very high conductivities with lower activation energies. Thus, it was found that cation vacancies did not appear to be important but the incorporation of additional interstitial oxide ions should be essential to achieve high oxide ion conductivities in the apatite-type LSO samples. The BaF₂-added sample fabricated by sintering at 1450°C for 20 h (No. < 7 >) showed a fairly high conductivity at 800°C with a relatively high activation energy corresponding to that of No. < 5 >. Activation energy for oxide ion conduction tended to increase as the number of cation vacancies decreased for the LSO samples with oxygen stoichiometry (No. < 1 > → < 4 > → < 5 >). An opposite tendency was recognized for samples with decreasing cation

vacancies and increasing oxygen excess (No. $\langle 1 \rangle \rightarrow \langle 2 \rangle \rightarrow \langle 3 \rangle$). Considering oxide ion conduction data reported, it could be deduced that the occupancy of the vacant cation sites with Ba^{2+} and the corresponding formation of oxygen excess would cause a fairly high conductivity for the BaF_2 -added LSO sample obtained in this study (No. $\langle 7 \rangle$). Its relatively high activation energy could be attributed to the temperature-dependent contribution of vacancy and interstitial mechanisms, which are predominant at lower and higher temperature regions, respectively, to oxide ion conduction.

Conclusion

Some selected fluorides were added to a calcined $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ (LSO) powder to produce densified LSO samples by low-temperature sintering. Among the fluoride additives examined in this study, BaF_2 and AlF_3 were found to promote the densification of LSO samples at 1450°C . The addition of AlF_3 resulted in a highly enhanced densification rate and abnormal grain growth with the formation of a second phase ($\text{La}_2\text{Si}_2\text{O}_7$). $\text{Ba}_3\text{Al}_2\text{F}_{12}$ additive had similar effects on the densification and grain growth but a stepwise sintering ($1400^\circ\text{C}/5 \text{ h} \rightarrow 1450^\circ\text{C}/5 \text{ h}$) brought about the inhibition of abnormal grain growth at 1450°C . On the contrary, the BaF_2 addition positively assisted both the densification and grain growth. The LSO sample sintered at 1450°C for 20 h, to which 5 wt% BaF_2 was added, showed a fairly high conductivity of $1.5 \times 10^{-2} \text{ Scm}^{-1}$ at 800°C with an activation energy of 1.23 eV. Ba^{2+} cations incorporated into the apatite structure would occupy not only the cation vacancies but also the La^{3+} sites substitutionally, leading to temperature-dependent oxide ion conduction by vacancy (predominant at lower temperature) and interstitial (higher temperature) mechanisms.

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Table 1 Characterization of LSO sample sintered with Ba₃Al₂F₁₂ addition

Samples (Amount of BAF / wt%)	Sintering conditions (°C / h)	Bulk density (gcm ⁻³)	Phase	Conductivity at 800°C (Scm ⁻¹)
Non	1450 / 20	4.90	Single	6.0 x 10 ⁻³
5 wt%	1450 / 2	4.93	La ₂ Si ₂ O ₇ *	3.6 x 10 ⁻³
5 wt%	1400 / 20	5.06	La ₂ Si ₂ O ₇ *	2.1 x 10 ⁻³
3 wt%	1400 / 20	5.02	La ₂ Si ₂ O ₇ *	3.0 x 10 ⁻³

* very small XRD peak of La₂Si₂O₇

Table 2 Conductivities and activation energies for LSO samples reported in references and measured in this study

Sample No. and composition	σ (Scm ⁻¹) at 500°C	Ea (eV)	Reference
< 1 > La _{9.33} Si ₆ O ₂₆	1.1 x 10 ⁻⁴	0.74	[12]
< 2 > La _{9.67} Si ₆ O _{26.5}	1.3 x 10 ⁻³	0.62	[12]
< 3 > La ₁₀ Si ₆ O ₂₇	4.3 x 10 ⁻³	0.38	[1]
< 4 > La _{8.33} Ba _{1.5} Si ₆ O ₂₆	6.6 x 10 ⁻⁵	0.75	[13]
< 5 > La ₈ Ba ₂ Si ₆ O ₂₆	5.4 x 10 ⁻⁷ *	1.21	[12]
< 6 > La ₉ BaSi ₆ O _{26.5}	6.6 x 10 ⁻³	0.58	[12]
< 7 > La _{9.33} Ba _{0.54} Si ₆ O _{26.5} **	1.5 x 10 ⁻² *	1.23	This study

* at 800°C; ** 5 wt% BaF₂ added

Figure captions

Fig. 1 Effect of various fluoride additives (5 wt%) on bulk densities of LSO samples sintered at 1450°C for 2 h.

Fig. 2 XRD patterns of LSO samples sintered at 1450°C for 2 h (A) without additive and with 5 wt% of (B) BaF₂, (C) AlF₃, (D) NdF₃, (E) CaF₂ and (F) NaF, showing (○) LSO, (□) La₂Si₂O₇, (■) La₂SO₅ and (Δ) La₂O₃.

Fig. 3 Microstructures of LSO samples sintered at 1450°C for 20 h with (A) non-additive and the addition of 5 wt% (B) BaF₂, (C) AlF₃ and (D) CaF₂.

Fig. 4 Microstructure evolution of LSO samples with 5 wt% BAF sintered at (A) 1400°C for 20 h, (B) 1450°C for 2 h and (C) 1400°C for 5 h plus 1450°C for 5 h.

Fig. 5 Densification behaviors of LSO samples with 5 wt% BaF₂ addition (solid lines) and non-additive (broken lines) sintered at 1400° and 1450°C.

Fig. 6 Lattice parameter changes with an increasing amount of BaF₂ addition for LSO samples sintered at 1450°C for 20 h.

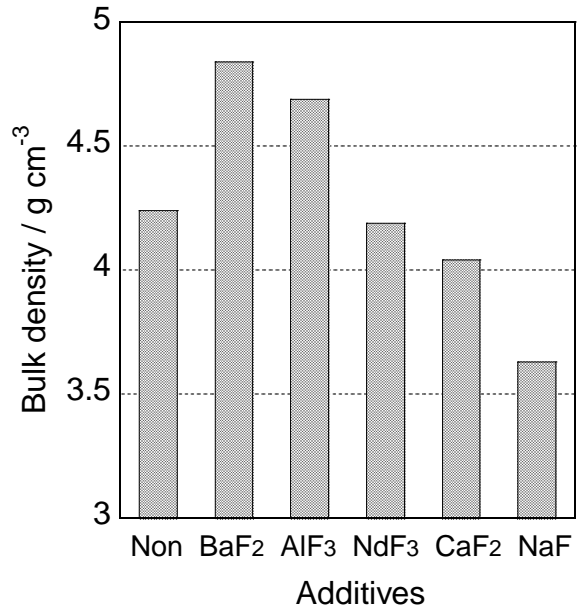


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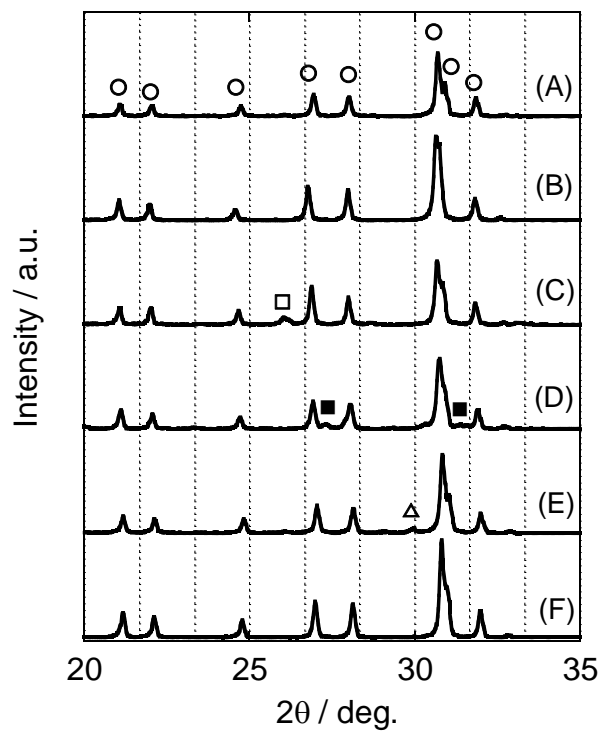


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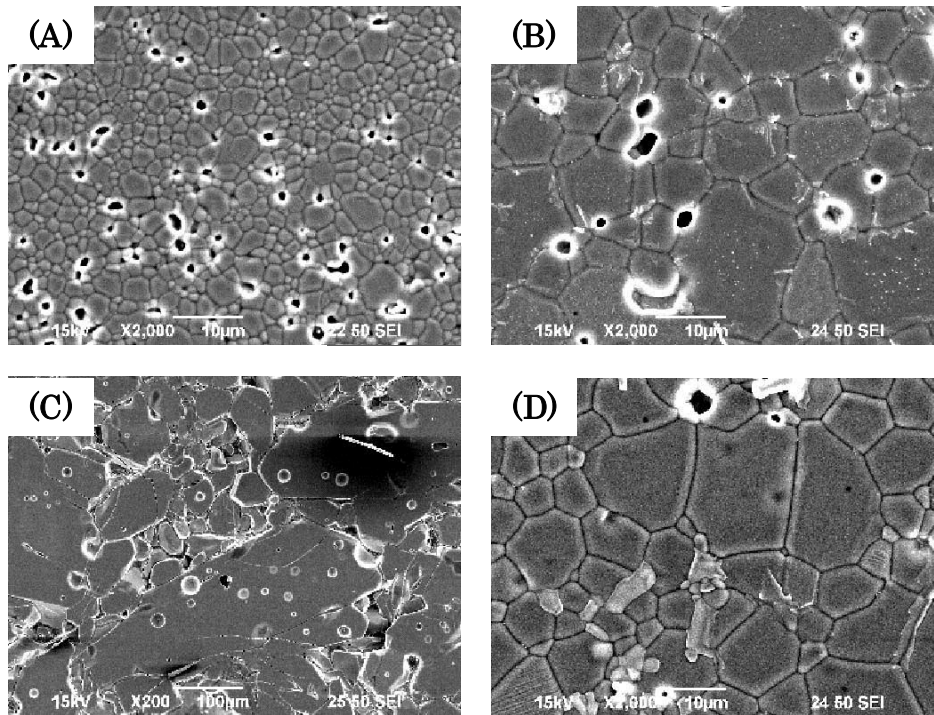


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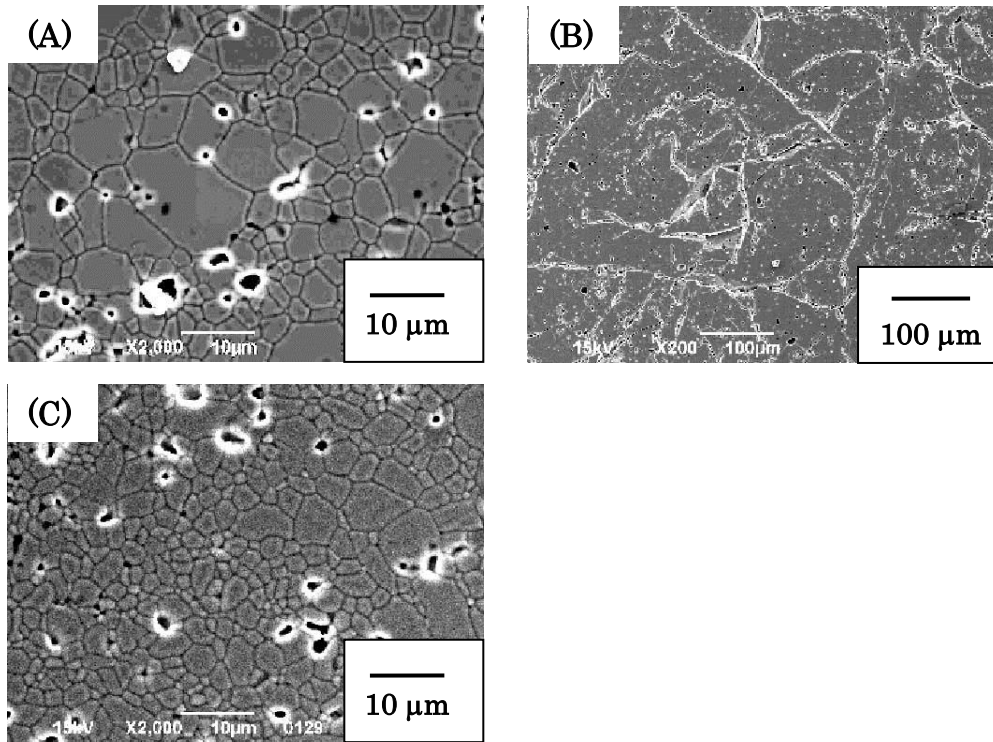


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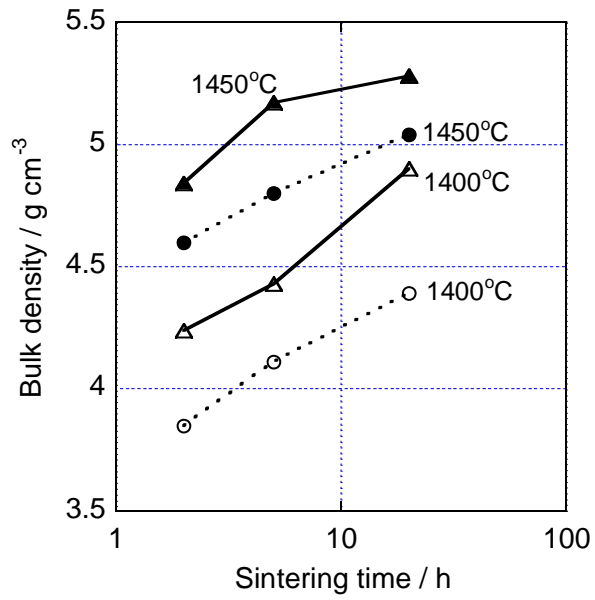


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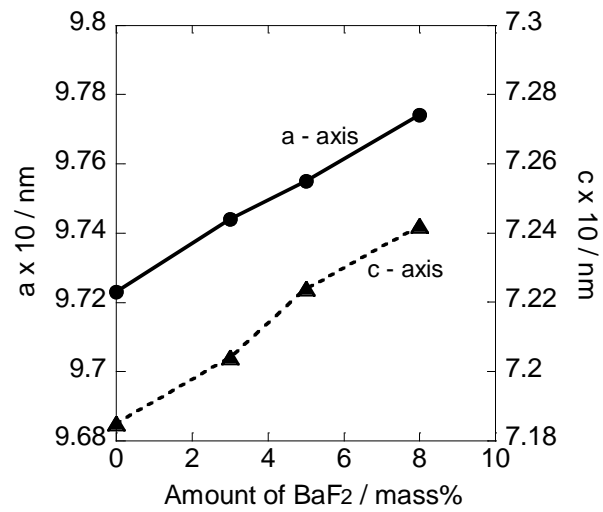


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