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Effect of B_2O_3–Li_2O on microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ ceramics

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Abstract

Effect of B_2O_3–Li_2O on the sintering behavior and the microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ ceramics were investigated as a function of B_2O_3–Li_2O content and sintering temperature. Densities of the specimens were enhanced with an increase of $B_2O_3{\cdot}Li_2O$ up to 0.5 wt.% and then decreased. The sintering temperature of the specimens could be reduced to 1200 °C without the degradation of the microwave dielectric properties of the specimens. For the same content of $B_2O_3{\cdot}Li_2O$, the dielectric constant (ε_r) and Q_f value of the specimens were increased, while the temperature coefficient of resonant frequency (TCF) was not changed drastically with sintering temperature. The specimens with 0.5 wt.% B_2O_3–Li_2O sintered at 1200 °C for 3 h showed ε_r of 98.7, Qf value of 5930, and TCF of −3.7 ppm/°C.

Keywords: B_2O_3–Li_2O; (Ca,Sm,Li) TiO_3; Microwave ceramics; Dielectric properties; Powders-solid state reaction; Sintering

1. Introduction

With the great increase of interest in the microwave telecommunication system, the development of the dielectric ceramics has accelerated to meet the demand for miniaturization of communication systems. The dielectric resonator has the advantages of the compactness and ease of matching to the microwave integrated circuits. The desired ceramic characteristics for microwave resonators are a high dielectric constant (k), low dielectric loss and a near zero temperature coefficient of the resonant frequency (TCF).

Generally, it is not easy to find materials which simultaneously satisfy the three required characteristics for microwave dielectric applications because the materials with high dielectric constant have a high dielectric loss and large TCF. After the dielectric characteristics of $(A^{+1}_{1/2}A^{+3}_{1/2})TiO_3$ were first reported,[1] various dielectric ceramic compositions with high dielectric constant based on the $(Li_{1/2}Ln_{1/2})TiO_3$ (Ln = Sm, Nd) system were investigated.[2–6] Among these compositions, CaO–Li_2O–Sm_2O_3–TiO_2 ceramics exhibit superior microwave dielectric properties.[4–6] On the other hand, several studies were done to lower the sintering temperature, using sintering aids for the practical applications [7–10] B_2O_3–Li_2O was suggested as a promising sintering aid for the densification at relatively low sintering temperatures.[10]

In this study, the effect of B_2O_3–L_2O content on the microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})$-$TiO_3$ ceramics was investigated as a function of sintering temperature.

2. Experimental procedure

Mixed oxide powders were prepared from reagent grade $CaCO_3$, Sm_2O_3, Li_2CO_3 and TiO_2. They were batched to the desired composition and then wet mixed for 24 h in ethanol with ZrO_2 balls. After drying, the reagent was calcined at 1000 °C for 2 h. Prepared powders were pressed uniaxially at 700 kg/cm^2 and cold isostatic pressed at 1450 kg/cm^2. These pellets were sintered at 1200–1250 °C for 3 h with a heating rate of 200 °C/h.

Crystalline phases of the sintered specimens were identified with X-ray powder diffraction patterns

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(Rigaku D/Max-3C, Japan). The density was obtained using ASTM C373-72. Microstructures of the specimens were studied by scanning electron microscopy (SEM, Jeol, JSM 820, Japan). Dielectric constant, unloaded Q value and TCF at microwave frequencies were measured by the post resonant method[11] using the TE_{011} mode in the temperature range from 20 °C to 80 °C at 5 GHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ specimens sintered at 1200 and 1250 °C for 3 h with the content of B_2O_3–Li_2O. For all the specimens, the complete solid solutions were formed in the orthorhombic perovskite structure and no secondary phase was detected. The superstructure reflection lines were observed at about $2\theta = 49°$ due to the ordering of Li^+ and Sm^{3+} ions and A-site vacancies along the c axis.[12]

Fig. 2 shows the relative densities of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ specimens with various B_2O_3–Li_2O contents. From previous studies,[4] pure $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ specimens sintered at 1300 °C for 3 h exhibited about 98% theoretical density. With an addition of B_2O_3–Li_2O, however, the specimens sintered at 1250 °C for 3h showed 97–99% of relative density through the entire composition range. For the specimens with the same B_2O_3–Li_2O content, the specimens sintered at 1250 °C showed a slightly higher density than those sintered at 1200 °C. With an increase of the B_2O_3–Li_2O contents up to 0.5 wt.%, the density of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ systems increased and then remarkably decreased. It has been reported[13] that during the sintering process, the sintering aids containing boron oxide promoted densification by liquid phase sintering and then evaporate. The use of up to 0.5 wt.%, B_2O_3–Li_2O formed a liquid phase which helped to increase the density of the sintered body. However, the addition of B_2O_3–Li_2O above 0.5 wt.% induced excess pores due to evaporation of the sintering aid, which in turn, reduced the density of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ systems.

SEM micrographs of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ sintered at 1200 and 1250 °C for 3 h with B_2O_3–Li_2O content are shown in Fig. 3. No secondary phase was observed in any specimen and complete solid solution of the complex perovskite phase was confirmed. Pure $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ showed uniform microstructures with pores in the grain boundaries [Fig. 3(a) and (d)]. However, the grain size of the specimen sintered at 1250 °C was larger than that of the specimen sintered at 1200 °C. The addition of 0.5 wt.% B_2O_3–Li_2O reduced the porosity, and dense microstructures with maximum relative densities were obtained. However, further addition of B_2O_3–Li_2O increased the porosity due to the evaporation of liquid

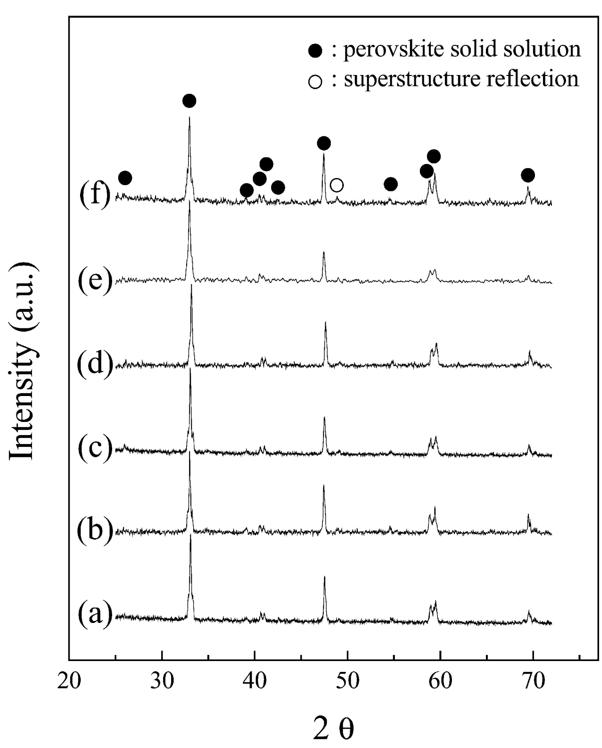

Fig. 1. X-ray diffraction patterns of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system sintered for 3 h at 1200 °C with B_2O_3–Li_2O content; (a) 0.0, (b) 0.5, (c) 2.0 wt.%, and sintered at 1250 °C with B_2O_3–Li_2O content; (d) 0.0, (e) 0.5, and (f) 2.0 wt.%, respectively.

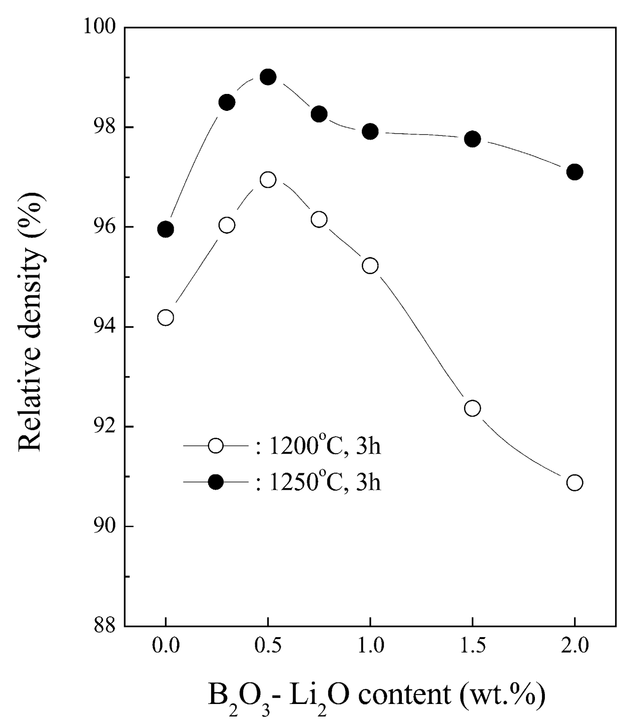

Fig. 2. Relative density of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system sintered at 1200 and 1250 °C for 3 h with the B_2O_3-Li_2O content.

phase as shown in Fig. 3(c) and (f). To assess the evaporation of liquid phase formed from B_2O_3–Li_2O addition, the weight loss of the specimens sintered at 1200 °C for 3 h was investigated (Fig. 4). With an increase of B_2O_3–Li_2O content, the weight loss of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ after the sintering processes increased drastically. This increase of weight loss resulted in an increase of porosity and the decrease of density of the sintered body.[13]

Fig. 5 shows the microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ systems sintered at 1200 and 1250 °C for 3 h with B_2O_3–Li_2O content. Dielectric constant and Q_f value increased with B_2O_3–Li_2O content up to 0.5 wt.% and then decreased remarkably, which agreed well with the change of relative density. The increase of dielectric constant and Q_f value could be attributed to the decrease of pores and grain size, which were confirmed by microstructure analysis in Fig. 3. The specimens sintered at 1250 °C exhibited larger grains than the specimen sintered at 1200 °C, and the reduction of grain boundaries improved the microwave dielectric properties. These results agreed well with the correlation between dielectric properties and density reported in $(Zr_{0.8}Sn_{0.2})TiO_4$[14] and complex perovskites.[15] For the addition of 0.5 wt.% B_2O_3–Li_2O, the dielectric constant and Q_f value of $(Ca_{0.275}Sm_{0.4}Li_{0.25})$-$TiO_3$ sintered at 1200 and 1250 °C were as high as those

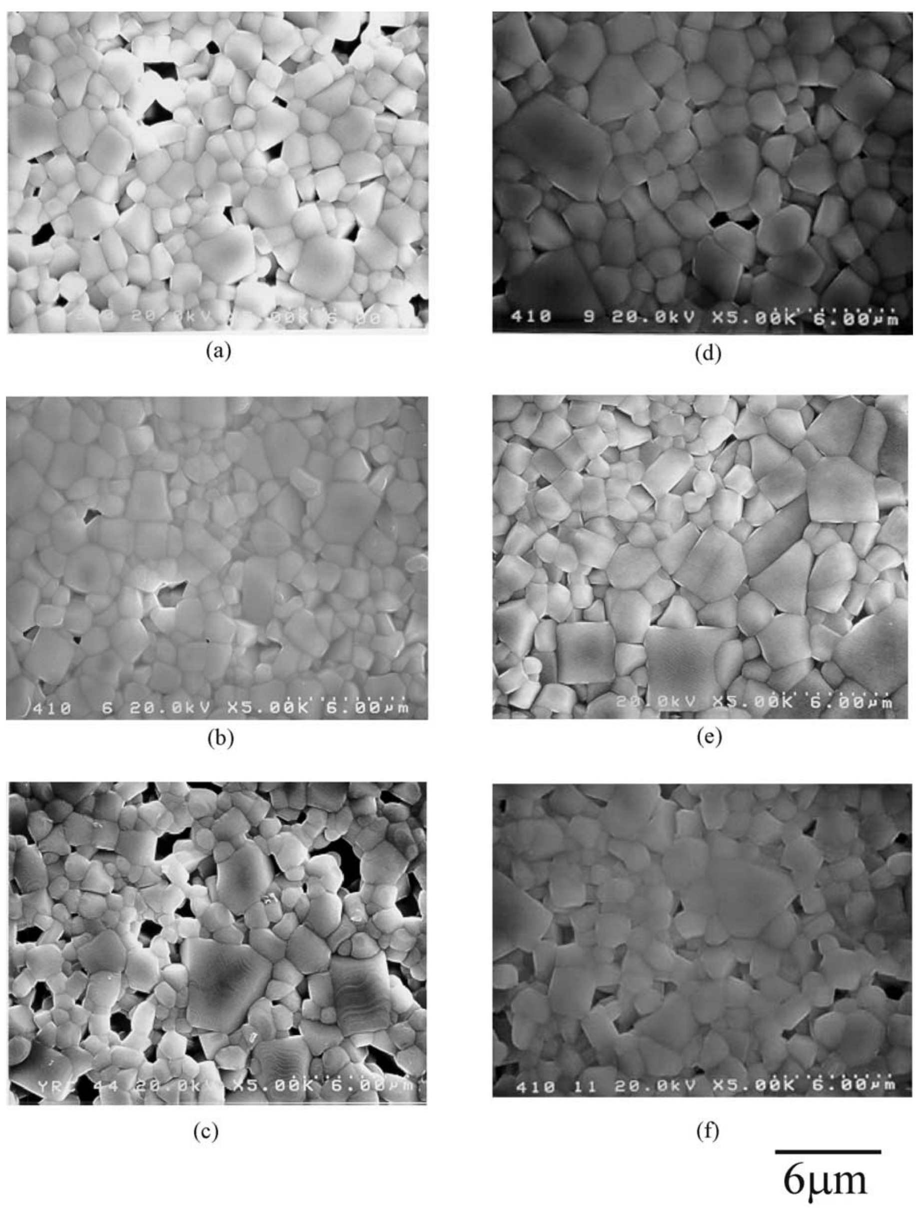

Fig. 3. Scanning electron micrographs of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system sintered for 3 h at 1200 °C with content of B_2O_3–Li_2O; (a) 0.0, (b) 0.5, (c) 2.0 wt.%, and 1250 °C with content of B_2O_3–Li_2O; (d) 0.0, (e) 0.5, and (f) 2.0 wt.%, respectively.

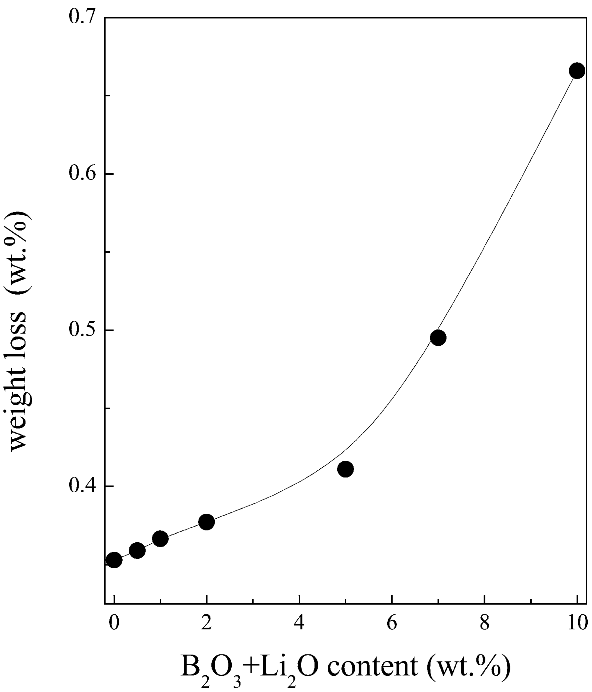

Fig. 4. Weight loss of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system sintered at 1200 °C for 3 h with B_2O_3–Li_2O content.

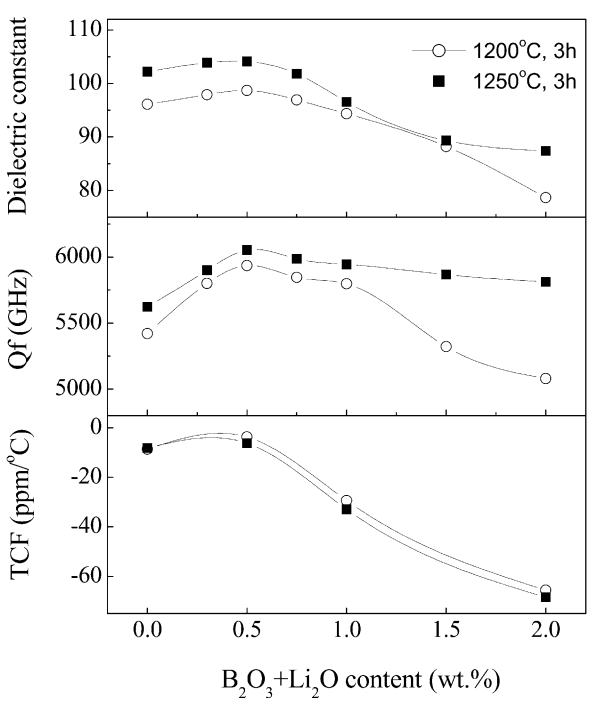

Fig. 5. Microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system sintered for 3 h at 1200 and 1250 °C with content of B_2O_3–Li_2O.

of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$[4] sintered at 1300 °C without any sintering aids. Therefore, the sintering temperature of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system was effectively lowered without any degradation of microwave dielectric properties by an addition of B_2O_3–Li_2O in this study.

4. Conclusion

The density of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ ceramics was increased up to nearly 99% of theoretical density by an addition of B_2O_3–Li_2O up to 0.5 wt.% without formation of any secondary phase. With greater addition of B_2O_3–Li_2O, the density reduced by formation of large pores due to the evaporation of the liquid phase. This increased porosity degraded the microwave dielectric properties. The $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system with 0.5 wt.% B_2O_3–Li_2O sintered at 1200 °C for 3 h showed good microwave dielectric properties as high as those of pure $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ sintered at 1300 °C. B_2O_3–Li_2O could be an effective sintering aid that improves densification and microwave dielectric properties of the specimens.

Acknowledgements

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