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Journal of the European Ceramic Society 23 (2003) 2455–2459

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Microwave dielectric properties in the $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramic system

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Abstract

Microwave dielectric properties have been investigated in the ceramic system $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$. In this system, $(Na_{1/2}La_{1/2})TiO_3$ (NLT) exhibits relative permittivity (εr) of 122, dielectric Q value (Q) of 3260 and a positive temperature coefficient of resonant frequency (τ_r) of 480 ppm/°C at 3 GHz. On the other hand, $(Li_{1/2}Sm_{1/2})TiO_3$ (LST) shows $\varepsilon_r=52$, $Q=760$ and $\tau_f=-260$ ppm/°C at 3 GHz. Therefore, an appropriate mixing of these two components yields material with both high permittivity and temperature-stable resonant frequency. From X-ray diffraction analyses, it was found that the ceramics are single phase perovskites. We have found that ceramics at the composition $x=0.7$ in this system (sintered at 1300 °C) have high ε_r of 117, Qf products of 2281 and temperature coefficient of resonant frequency $\tau_f=-$l9 ppm/°C at 3 GHz.

Keywords: $(Na_{1/2}La_{1/2})TiO_3$; $(Li_{1/2}Sm_{1/2})TiO_3$; Dielectric properties; Microwave properties; Resonator materials

1. Introduction

Recently, high quality microwave dielectric ceramics, which enable miniaturization of the dimensions of resonators, have received much attention due to the rapid progress in microwave telecommunications, for example, in car telephone systems, portable telephones and satellite broadcasting receivers. The dielectric characteristics required for microwave resonator materials are as follows. The first one is high dielectric constant (ε_r) for reducing the size of resonators, because the wave length (λ) in a dielectric is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_o) in vacuum ($\lambda = \lambda_o\sqrt{\varepsilon_r}$). Secondly, the inverse of the dielectric loss (Q = l/tanδ) is required to be high for achieving significant frequency selectivity and stability in transmitter components. The third characteristic, the temperature coefficient of resonant frequency (τ_f) is required to be as close to 0 ppm/°C as possible.

In general, dielectric materials with high dielectric constant have large positive temperature coefficient for the resonant frequency (τ_f).[1] So far, many microwave dielectrics, such as (Pb,Ba)O–Nd_2O_3–TiO_2,[2] $(Pb,Ca)ZrO_3$[3] and BaO–Sm_2O_3–TiO_2[4] have been developed. However the dielectric constant is not sufficient to miniaturize the filter. Hence we studied a system in which a material with large negative τ_f is combined with a material with a large positive τ_f in order to obtain a high dielectric constant material with good temperature stability at resonant frequency.

It has been reported that the Li_2O–Sm_2O_3–TiO_2 system with a perovskite (ABO_3) structure, has a high ε_r and a large negative τ_f. It has also been reported that the Na_2O–La_2O_3–TiO_2 system has a high ε_r and a high Q and a large positive τ_f.[5] Therefore, the system $(Na_{1/2}La_{1/2})TiO_3$–$(Li_{1/2}Sm_{1/2})TiO_3$ may be useful for obtaining material with the desired τ_f. In this study, the microwave dielectric properties of the system $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ were studied by changing the amount of x.

2. Experimental

Fig. 1 shows the flowchart of sample preparation. Regent-grade Na_2CO_3, Li_2CO_3, TiO_2, Sm_2O_3 and La_2O_3 with 99.9% purity were used as raw materials. The examined system is nominally expressed as $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ $(1.0\geqslant x\geqslant 0)$. The two mixtures NLT and LST were ground for 24 h in a ball mill with ethanol, dried and calcined for 2 h in air at 950 and 1050 °C respectively. The calcined powder, was reground in an alumina mortar, mixed with an organic binder of 3 wt.% PVA, passed through a 50

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0955-2219/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0955-2219(03)00342-X

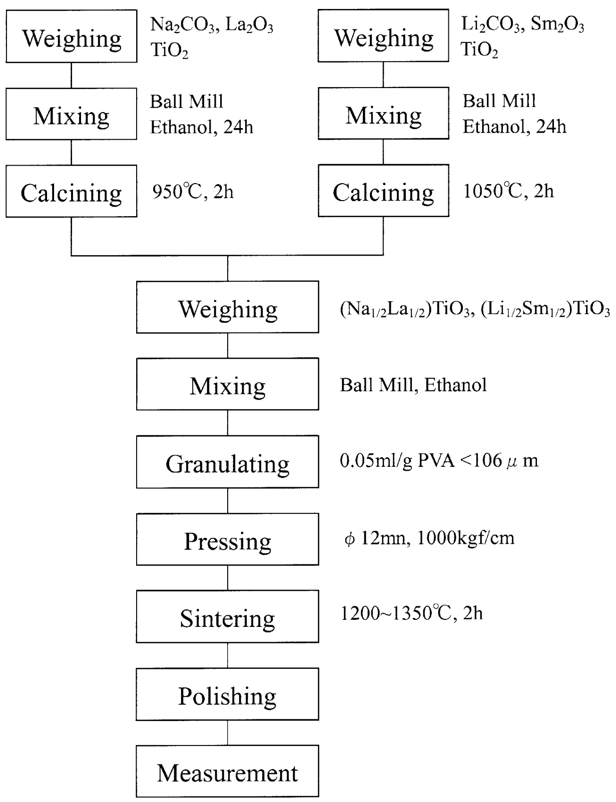

Fig. 1. Flowchart of sample preparation.

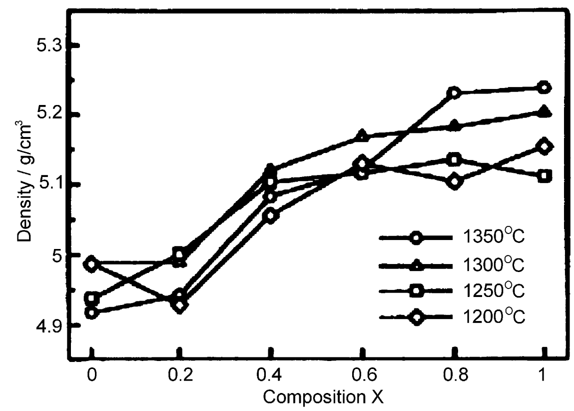

Fig. 2. Densities of $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramics sintered at various temperature.

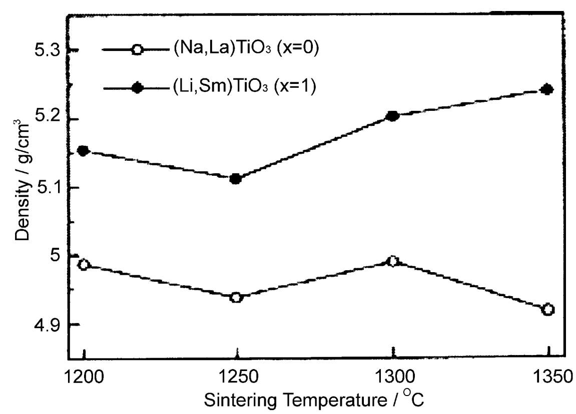

Fig. 3. Densities of $(Na_{1/2}La_{1/2})TiO_3$ and $(Li_{1/2}Sm_{1/2})TiO_3$ ceramic sintered at various temperatures.

mesh screen to produce a granular powder, and pressed into a disk at a pressure of 1 t/cm^2. The disks were sintered at 1200–1350 °C in air for 2 h. The apparent densities of the sintered samples were measured by Archimedes's method.

The relative densities were obtained from the apparent densities and the calculated values. The crystalline phases of the sintered samples were identified by X-ray powder diffraction patterns, using CuK_α radiation. The dielectric constants at microwave frequencies (3 GHz) were calculated using the size of the fired disk and the Hakki and Coleman method.[6] The temperature coefficient of the resonant frequency, τ_f was measured between 25 and 85 °C.

3. Results and discussion

The sintering temperatures were determined on the basis of the apparent densities of the solid solutions; the latter are shown as a function of sintering temperature in Fig. 1. The densities of specimens sintered at various temperatures as a function of x are presented in Fig. 2. The densities of specimen for $x=0$ and $x=1$ are shown in Fig. 3. All specimens have high relative densities over 95%, independent of sintering temperature. Bulk densities are increased with increase of x because of the higher density of LST.

Fig. 4 shows X-ray powder diffraction patterns for this system, as a function of sintering temperature. They are mostly identified to be of the perovskite type structure. It is reported that NLT has a cubic structure in which $a=3.873$ Å, whilst LST has an orthorhombic structure with $a=5.363$ Å, $b=5.502$ Å, $c=7.657$ Å.[7] The crystal structure change from cubic to orthorhombic in this system is found at $x=0.5$, by the splitting of higher angle peaks (Fig. 4).

Dielectric properties, i.e. relative permittivity (ε_r), $Q{\cdot}f$ values and temperature coefficient (τ_f) are shown as a function of composition (x) for various sintering temperature in Figs. 5–7. As previously reported, NLT has a positive τ_f of 480 ppm/°C and LST has a negative value of −260 ppm/°C. According to the amount of x in the system $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$, the τ_f changes linearly from negative to positive, as shown in Fig. 7.

A range of dielectric properties were obtained for different x values: most notably, when $x=0.7$, a relatively high quality resonator material with dielectric properties of $\varepsilon_r=117$, $Q{\cdot}f=2281$ and $\tau_f=-19$ ppm/°C at 3 GHz were obtained at a sintering temperature of 1300 °C.

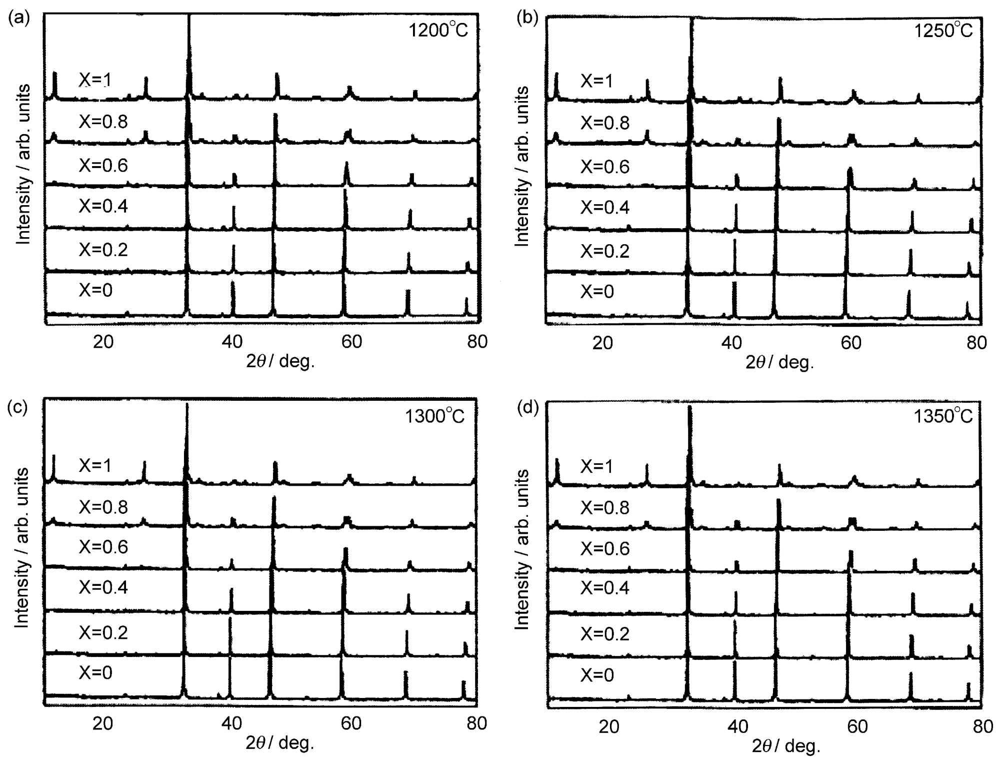

Fig. 4. X-ray diffraction patterns of $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramics sintered at various temperatures.

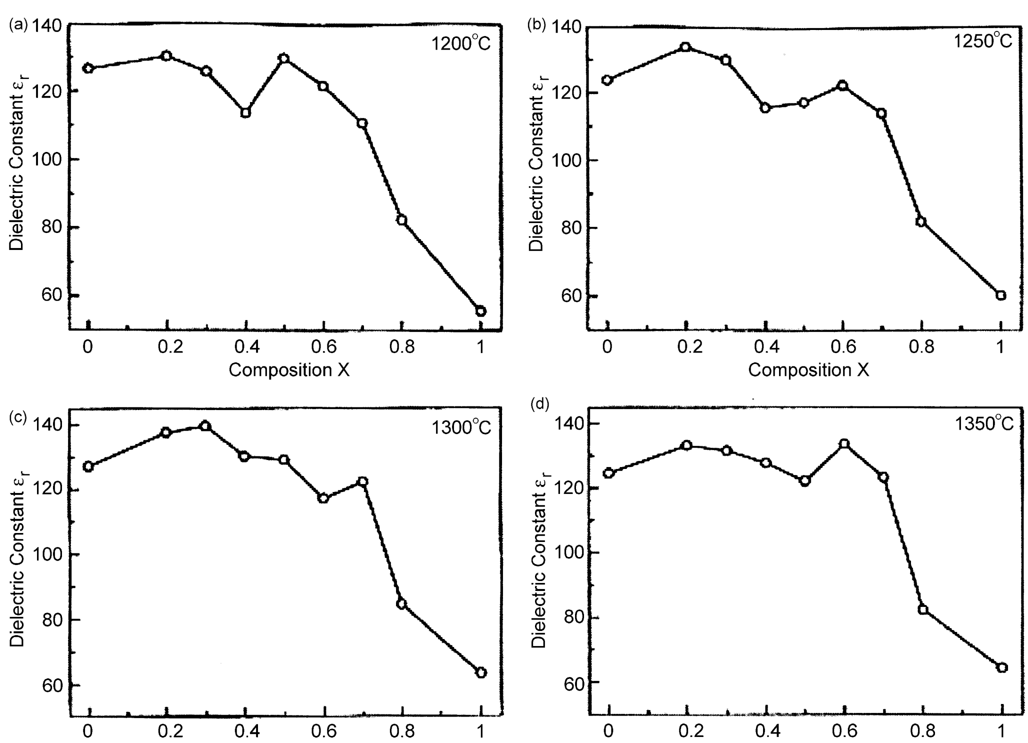

Fig. 5. Dielectric constant ε_r for $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramics sintered at various temperatures.

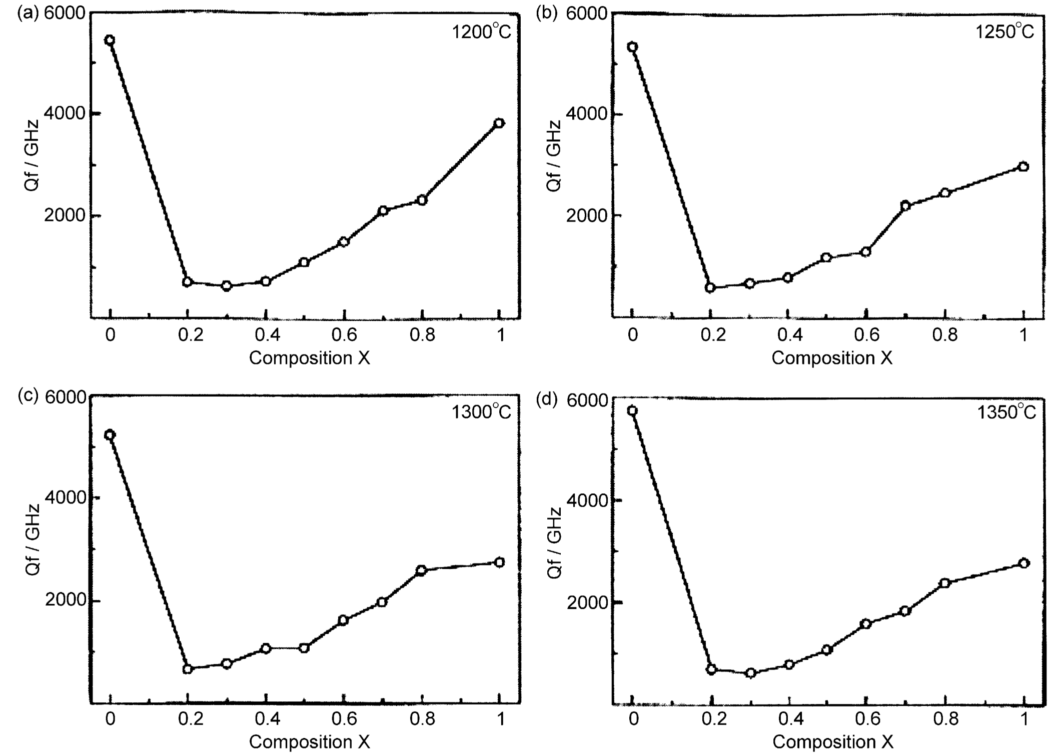

Fig. 6. *Qf* value for $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramic sintered at various temperatures.

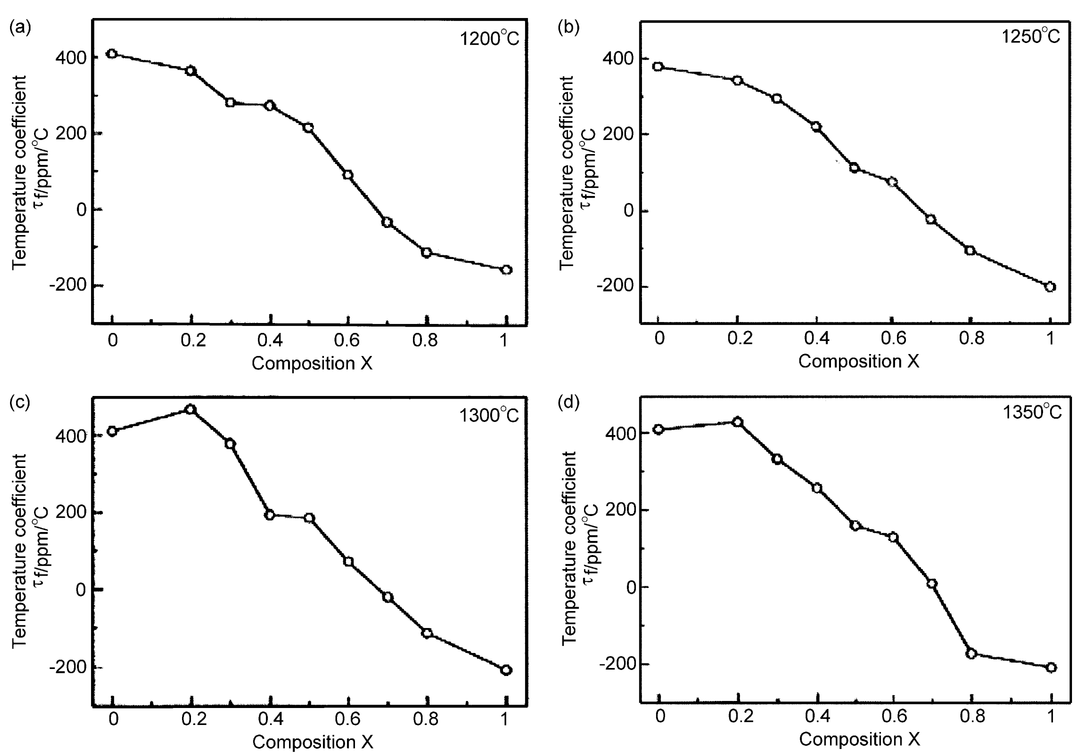

Fig. 7. Temperature coefficient τ_f for $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramic sintered at various temperatures.

4. Conclusions

For the $(1-x)(Na_{1/2}La_{1/2})TiO_3-x(Li_{1/2}Sm_{1/2})TiO_3$ ceramic system, perovskite type phases are formed for most of the composition range examined. The crystal structure changes from cubic to orthorhombic at around $x=0.5$.

At the composition of $x=0.7$, materials sintered at 1300 °C exhibited high value of $\varepsilon_r=117$ and $Q{\cdot}f=2281$ GHz at 3 GHz with $\tau_r=-19$ ppm/°C.

References

1. Nishigaki, S., Microwave dielectrics, FC Rep., 1987, 5, 413–422 (Translation: FC Annu., Rep. Overseas Readers, 1988, 32–39).
2. Wakino, K., Minai, K. and Tamura, H., Microwave characteristics of (Zr, Sn)TiO_4 and BaO–PbO–Nd_2O_3–TiO_2 dielectric resonators. *J. Am. Ceram. Soc.*, 1984, **67**, 278–281.
3. Kagata, H., Kato, J., Nashimoto, K. and Inoue, T., Dielectric properties of Pb-based perovskite substituted by Ti for B-site at Microwave frequencies. *Jpn. J. Appl. Phys.*, 1993, **32**, 4332.
4. Nishigaki, S., Kato, H., Yano, S. and Kamimura, R., Microwave dielectric properties of (Ba, Sr)O–Sm_2O_3–TiO_2 ceramics. *Ceram. Bull.*, 1987, **66**, 1405–1410.
5. Takahashi, H., Baba, Y., Ezaki, K., Okamoto, Y., Shibata, K., Kuroki, K. and Nakano, S., Dielectric characteristics of $(A^{1+}_{1/2}{\cdot}A^{3+}_{1/2})TiO_3$. *Jpn. J. Appl. Phys.*, 1991, **30 No9B**, 2339.
6. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans. Microwave Theory Technol.*, 1960, **8**, 402.
7. Takahashi, H., Baba, Y., Ezaki, K. and Ito, A., High dielectric microwave materials and its application. *Sanyo Tech. Rev.*, 1996, **28**, 104 (in Japanese).