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Microwave dielectric properties of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ $[0.1 \le x \le 1]$ ceramics

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Abstract

The microwave dielectric properties of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3(0.1 \le x \le 1.0)$ have been investigated. The system forms a solid solution throughout the entire compositional range. The dielectric constant decreases from 86 to 25 as x varies from 0.1 to 1.0. The Qxf varies non-linearly and increases for composition with $x \ge 0.6$. The nonmonotonic variation with composition x is more pronounced in τ_f than in ε_r. The microwave dielectric properties indicate the possibility of a phase transformation for x between 0.4 and 0.5. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dielectrics; Dielectric resonators; Microwave ceramics; Perovskites; Titanates; Solid solutions

1. Introduction

The complex perovskites with general formula $A(B_{1/2}' B_{1/2}'')O_3$ have been recently reported [1–3] as useful microwave dielectric materials. Miniaturization of microwave communication components such as band pass filters, duplexers and oscillators can be achieved with high dielectric constant materials. At the same time, both a near to zero τ_f and low dielectric loss ($\tan\delta$) are required for microwave ceramics [4] for stability and frequency selectivity. But it is difficult to find materials that satisfy all the three required characteristics.

Recently, $Ln(Mg_{1/2}Ti_{1/2})O_3$ has been reported [5–7] as low loss dielectric material suitable for YBCO substrate applications. Among these perovskite compounds $La(Mg_{1/2}Ti_{1/2})O_3$ and $Sm(Mg_{1/2}Ti_{1/2})O_3$ (SMT) exhibited relatively low dielectric loss. Although SMT has a relatively high dielectric constant ($\varepsilon_r = 25$) and quality factor, it has a high negative temperature coefficient of resonant frequency (τ_f) of -26 ppm/°C [7]. The perovskite $CaTiO_3$ has a high dielectric constant ($\varepsilon_r = 170$), high quality factor and a high positive τ_f value of 800 ppm/°C. Hence, it may be possible to make a nearly zero τ_f material by adding different stoichiometric amounts of $CaTiO_3$ to SMT. The objective of the present study is to develop a new dielectric material which has high dielectric constant, high quality factor and near to zero τ_f by incorporating $CaTiO_3$ into SMT and to study the variation of microwave dielectric properties of the solid solution system $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ as a function of composition (x).

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2. Experimental

The starting materials were high purity Sm_2O_3, $MgCO_3$, TiO_2 and $CaCO_3$. They were weighed in the appropriate molar ratio and ground in an agate mortar and then dried and calcined at 1350–1400 °C for 4–6 h in air. The calcined powder was ground again with 3 wt.% polyvinyl alcohol that acts as a binder, and disks of 11 mm diameter and 5–7 mm in thickness were made by pressing at a pressure of 150 MPa. The disks were sintered at different temperatures between 1450 and 1600 °C for 4 h in air to optimize the sintering conditions. A cooling rate of 2.7 °C/min is given for all the materials.

The dielectric properties were measured in the C band (4–8 GHz). The $TE_{011}/TE_{01\delta}$ mode is used for all microwave measurements. The dielectric constant ε_r was measured using the TE_{011} mode using the Hakki–Coleman dielectric resonator method. The temperature coefficient of resonant frequency was measured by noting the variation of resonant frequency with temperature in the range 25–80 °C. The quality factor was measured using a cavity method [8].

3. Results and discussion

The $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ ceramics were sintered to dense materials. The sintering temperature increased from 1450 to 1600 °C for 4 h with increase in x. Fig. 1 shows the X-ray diffraction pattern recorded from $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ for various values of x in the range 0 to 1. $CaTiO_3$ is orthorhombic and has a $GdFeO_3$-type perovskite structure with lattice dimensions $a=5.442$ Å, $b=7.6417$ Å and $c=5.3807$ Å and with space group *Pnma* (JCPDS: 42–423). $Sm(Mg_{1/2}Ti_{1/2})O_3$ is also orthorhombic ($Z=4$) with space group *Pnm*1 and the lattice dimensions are $a=5.595$ Å, $b=7.719$ Å and $c=5.411$ Å [9]. The XRD patterns of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ show significant change with increasing x. The symmetry changes when x is between 0.4 and 0.5 and is supported by the sudden change in the sign of τ_f values, dielectric properties and densities (see Figs. 2–5). In Fig. 1, The dotted line between $x=0.4$ and 0.48 broadly separates the regions having different symmetries. The ceramic

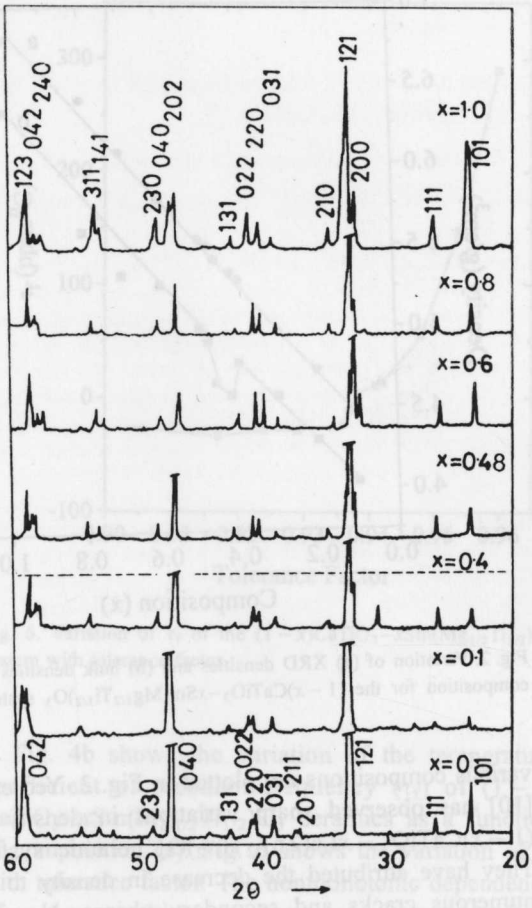

Fig. 1. X-ray diffraction patterns of the $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ system.

system is orthorhombic for all values of x. The lattice parameters were calculated for different values of x from the X-ray diffraction patterns and the theoretical densities obtained using the lattice parameters are plotted in Fig. 2a. Fig. 2b shows the observed variation of the bulk densities with composition. It is expected that the density should increase with increasing x because of the larger molecular weight of SMT. But the bulk density varies non-linearly in the region between $0.4<x<0.5$. The abrupt variation in the bulk density for the compositions with x between 0.4 and 0.5 is due to phase transformation as indicated by the microwave dielectric properties. In fact the samples are difficult to sinter or densify for x between 0.4 and 0.5. The percentage densities of the

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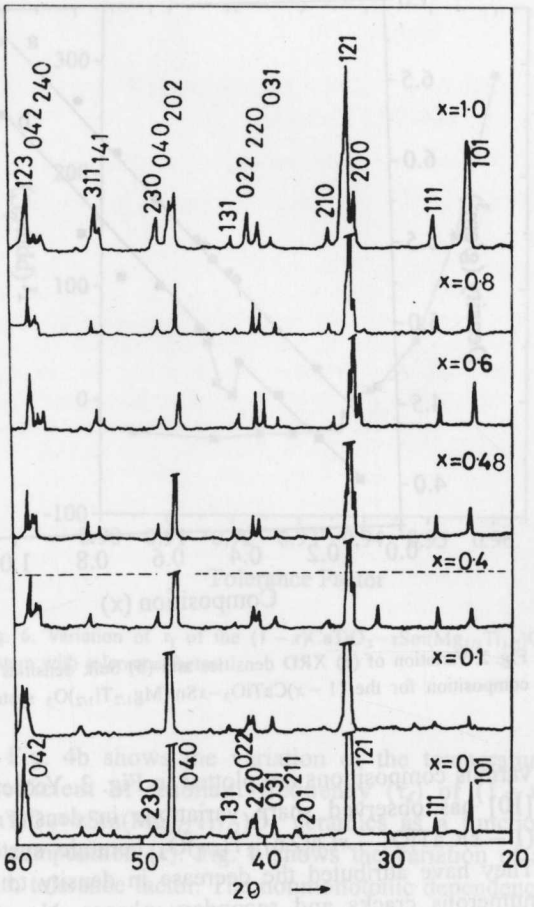

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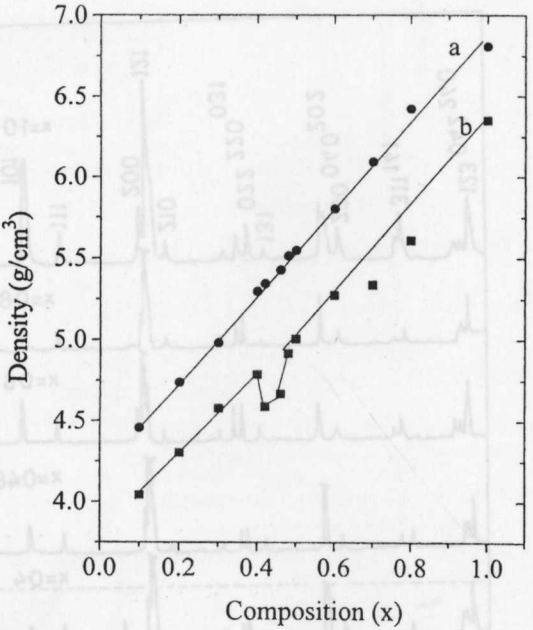

Fig. 2. Variation of (a) XRD densities and (b) bulk densities with composition for the $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ system.

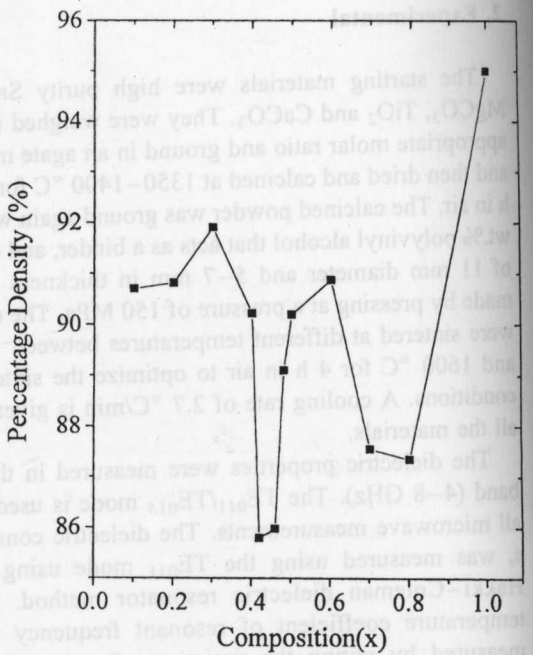

Fig. 3. Percentage density of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ sintered at 1550 °C for 4 h as a function of x.

various compositions are plotted in Fig. 3. Yeo et al. [10] has observed sharp variations in density for $(1-x)CaTiO_3-xLa(Zn_{1/2}Ti_{1/2})O_3$ ceramic system. They have attributed the decrease in density to the numerous cracks and secondary phases. No such cracks or secondary phases were observed in the present system. Fig. 4a shows the variation of the tolerance factor with the composition (x). The tolerance factor [11] was calculated using the crystal radius data of Shannon [12]. The tolerance factor decreased with the increase in the value of x.

The microwave dielectric properties of several perovskite-type solid solutions reported in the literature are divided into three groups according to their dielectric behaviour [13].

1. Solid solution between complex perovskites in which the dielectric properties increase or decrease to outside the range exhibited by the end members, e.g. $Ba(Zn_{1/3}Nb_{2/3})O_3-Sr(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3}O_3)-Sr(Mg_{1/3}Ta_{2/3})O_3$ [14–16].
2. Solid solution between simple perovskite like $BaZrO_3-SrZrO_3$, $CaZrO_3-CaTiO_3$ and $SrZrO_3-SrTiO_3$ [17] in which the microwave dielectric properties vary linearly with compositions.

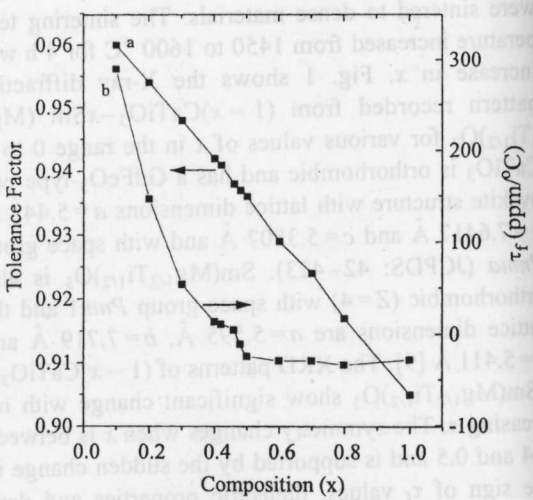

Fig. 4. Variation of (a) tolerance factor and (b) temperature coefficient of resonant frequency with composition for the $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ system a function of x.

3. Nonmonotonic mixture-like behavior as in $(1-x)La(Zn_{1/2}Ti_{1/2})O_3-xSrTiO_3$ [18] where the solid solution is between $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ and the dielectric mixture rule $1/\varepsilon_{total}=v_1/\varepsilon_1+v_2/\varepsilon_1$ is applicable.

The dielectric constant for $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1550 °C for 4 h are plotted in Fig. 5a. The measured dielectric constant was corrected for porosity [19]. The dielectric constant of $CaTiO_3$ and SMT are 170 and 25, respectively. The dielectric constant decreases rapidly as x varies from 0.0 to 0.4. The plot of dielectric constant versus composition shows a dip at x between 0.4 and 0.5, indicating a phase transformation. Fig. 5b shows that the dielectric constant of the system under study follows a mixture-like behaviour as in $(1-x)La(Zn_{1/2}Ti_{1/2})O_3-xSrTiO_3$ [18] and $(1-x)LaAlO_3-xSrTiO_3$ [13]. Sareni et al. [20] have also reported a similar variation of dielectric constant with composition in the finite element calculations of the two-component dense composites.

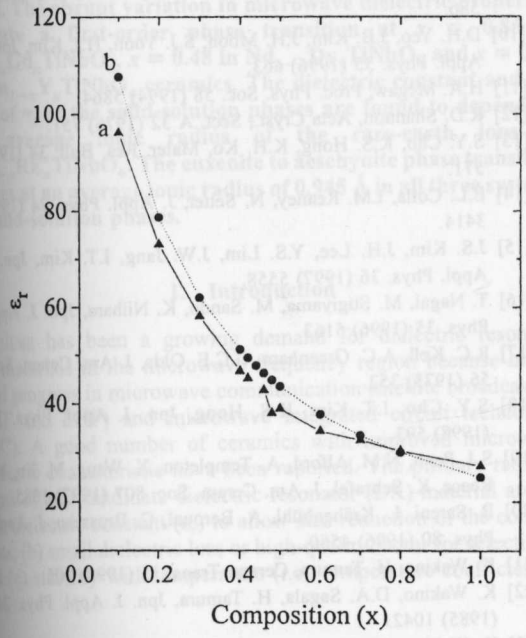

Fig. 5. Dielectric constant (a) corrected for porosity (b) according to the rule of mixtures for the $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ system as a function of x.

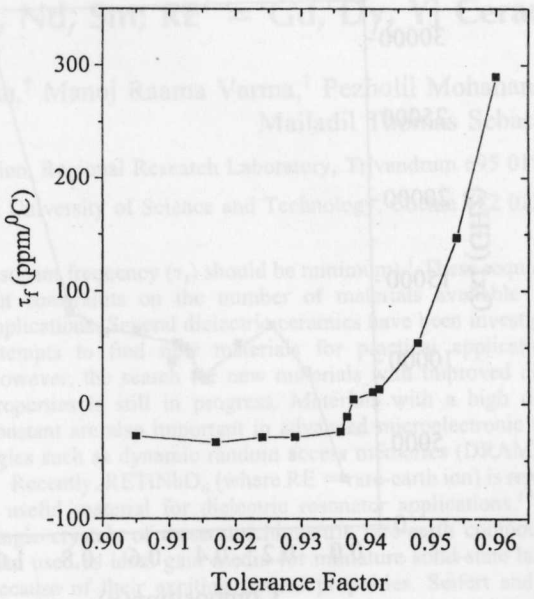

Fig. 6. Variation of τ_f of the $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ system with tolerance factor.

Fig. 4b shows the variation of the temperature coefficient of resonant frequency (τ_f) of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ ceramics as a function of composition (x). Fig. 6 shows the variation of τ_f with tolerance factor. The nonmonotonic dependency of τ_f on composition (x) is more pronounced than in ε_r. The τ_f value changes from 800 ppm/°C to 290 ppm/°C as x varies from 0 to 0.1. There is an abrupt variation in τ_f for compositions with $0.4 \le x \le 0.5$ similar to that as for dielectric constant. But the variation is minimal in the range $0.5 \le x \le 1$. The observed deviation in τ_f for x between 0.4 and 0.5 is attributed to phase transformation.

Intrinsic dielectric loss ($=1/Q$ for low loss ceramics) in the microwave region is directly proportional to the frequency, and hence Qxf is a constant in this range [21–23]. In Fig. 7 the quality factor (Qxf) of the system $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ is plotted as a function of x. The quality factor of $Sm(Mg_{1/2}Ti_{1/2})O_3$ is much higher than that of $CaTiO_3$ and hence it is expected that the Qxf should increase as the amount of $Sm(Mg_{1/2}Ti_{1/2})O_3$ increases from 0 to 1. Fig. 7 shows that the quality factor of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ increases with the composition (x) as expected. However, the Qxf versus (x)

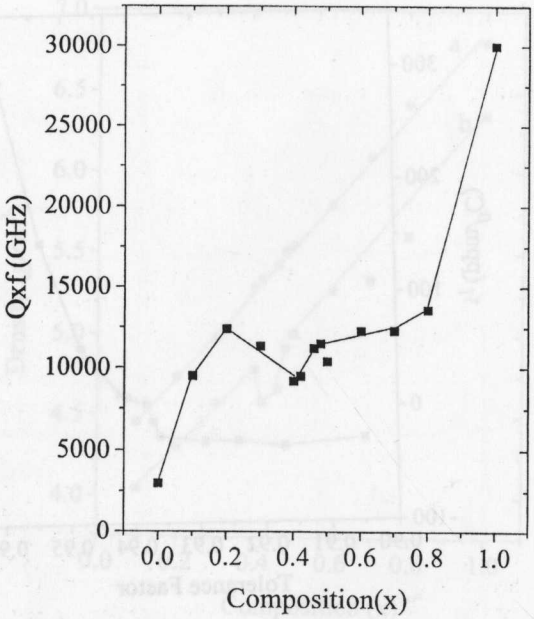

Fig. 7. Qxf value of $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ sintered at 1550 °C for 4 h as a function of x.

plot shows a decrease in Q for composition in the range x between 0.4 and 0.5. This is attributed to the fact that the material undergoes a phase transition from *Pnma* space group to *Pnm*1 space group where the atoms are in a state of re-orientation to form the new structure. This is supported by the variation of density, τ_f, ε_r, quality factor and X-ray diffraction patterns as a function of composition. Careful work is needed to find out the exact composition of phase transition and the associated changes in physical properties that do not come under the scope of the present work.

4. Conclusion

The microwave dielectric properties of the solid solution system $(1-x)CaTiO_3-xSm(Mg_{1/2}Ti_{1/2})O_3$ have been studied. The dielectric constant, temperature coefficient of resonant frequency and Qxf vary non-linearly with composition. The microwave dielectric properties and density variation indicate a phase transformation for x between 0.4 and 0.5.

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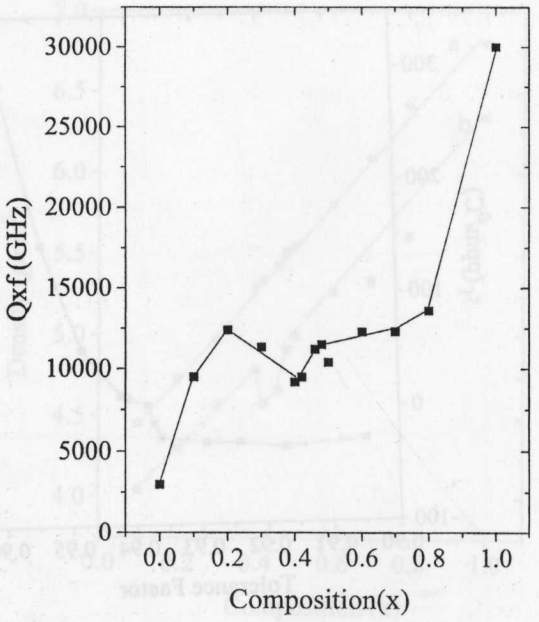

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