

Microwave dielectric properties of $\text{Mg}_{1+x}(\text{Ca}_y\text{Ti}_{x+y})\text{Al}_{2-2x-2y}\text{O}_4$ system

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In one of our previous research, we have analyzed a ceramic dielectric material with the following composition $\text{Mg}_{1+x}\text{Ti}_x\text{Al}_{2-2x}\text{O}_4$ (MTA). It has been revealed that the last one represents a single phase spinel with the following dielectric properties: $\varepsilon_r = 6-12$, $\tan \delta = (1.5-3.5) \times 10^{-4}$, $Q_f = 33000 - 85000$ and $\tau_f = -50$ to -70 ppm/deg. In the present work we have introduced very small quantities of Ca^{2+} ($y = 0.02 - 0.08$) in our ceramic compounds in order to achieve thermal compensation ($\tau_f \rightarrow 0$). As a result, the following dielectric material with general formula $\text{Mg}_{1+x}(\text{Ca}_y\text{Ti}_{x+y})\text{Al}_{2-2x-2y}\text{O}_4$ was synthesized. For $x=0.2$ and $y=0.05-0.06$ the material achieves full thermal compensation as it has the following properties: $\tau_f \rightarrow 0$, $\varepsilon_r = 12-13$ and $\tan \delta = (1-3) \times 10^{-4}$.

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1. Introduction

In one of our previous work we have declared that materials with $\varepsilon_r \approx 40$ are practically unsuitable when used at frequencies above 30-40 GHz due to the small size of the resonator discs, therefore it is difficult to press and polish them. In this case it is convenient to use materials with smaller values of the dielectric permittivity ($\varepsilon_r = 10-15$). Such materials are spinels $(1-x)\text{MgAl}_2\text{O}_4 \cdot x\text{TiO}_2$ and $(1-x)\text{ZnAl}_2\text{O}_4 \cdot x\text{TiO}_2$ that have $\varepsilon_r = 9-14$, $Q_f = 80\,000 - 90\,000$ and $\tau_f = -27$ to -6.2 ppm/deg [1-5]. Nevertheless it is necessary to notice that these compounds are not electron equilibrated and the Ti^{4+} cations could cause defects in the structure. For that reason we have analysed the material $\text{Mg}_{1+x}\text{Ti}_x\text{Al}_{2-2x}\text{O}_4$ (MTA), in which part of Al^{3+} cations are partially replaced with constitutive cation of $(\text{Mg}^{2+}-\text{Ti}^{4+})$ with the same valence as Al^{3+} . The synthesized dielectric material represents a single phase spinel with good microwave properties, but with relatively high $\tau_f = -70$ to -50 ppm/deg. In order to achieve temperature compensation, in the material's composition are added $y(\text{Ca}^{2+}-\text{Ti}^{4+})$, ($y = 0.02 - 0.08$) so it could be formed a minimum quantity of CaTiO_3 phase. We supposed that the basic structure would not change, as we counted on the high tolerance factor of spinels and perovskites.

The investigation of the effect of $\text{Ca}^{2+}-\text{Ti}^{4+}$ additions on the microwave properties of the material, and the compensation of τ_f represent a scientific and practical interest in the field of telecommunications.

2. Experimental procedures

As starting materials, we used MgO Fluka, TiO_2 Kronos, Al_2O_3 Fluka and CaCO_3 Fluka with purity 98-99 %. The synthesis is made by the conventional mixed oxide route. The ball milling and homogenization are done in planetary ball mill Retsch in agate milling pots and balls, using deionized water as a wetting agent, during one hour. The dried mixture is calcined in alumoxide pots at 1100°C for three hours. Before the second milling and homogenization 0.3% Bi_2O_3 is added to ease the sintering process, and thereafter a secondary milling is made. From the dried material, it is made press-powder with binder PVA (10% solution). For pressing we use a powder fraction of 0.25-0.5 grain size at a pressure of 1.5 t/cm^2 . The sintering process is proceeded in superkanthal furnace Linn, at different temperatures for three hours with isothermal maintaining at each sintering temperature. For XRD analysis we use a powder from the sintered samples.

The measurements of ε_r , $\tan \delta$, and τ_f are made by Hakki and Kolemman [6] method modified by Courtney [6].

3. Results and discussions

On Fig.1 is shown the XRD pattern of the material $\text{Mg}_{1+x}(\text{Ca}_y\text{Ti}_{x+y})\text{Al}_{2-2x-2y}\text{O}_4$ for the compositions $x=0.2$ and $y=0.02, 0.04, 0.06, 0.08$. The figure demonstrates that the main present phase is a spinel one and small quantities of CaTiO_3 and MgO appear also.

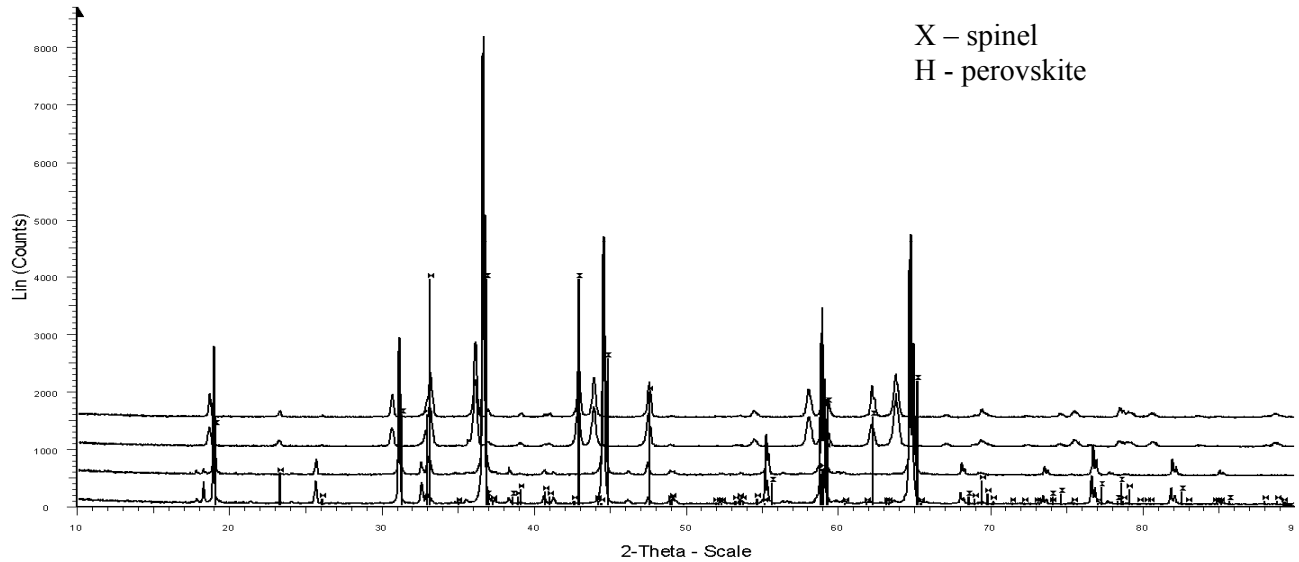


Fig. 1. XRD pattern of $Mg_{1+x}(Ca_yTi_{1-x-y})Al_{2-2x-2y}O_4$ composition sintered at 1480 °C.

Fig. 2 reflects the dependence of dielectric permittivity ϵ_r with the composition (y) in the above mentioned formula. As expected ϵ_r increases with the composition (y) which is due to higher $CaTiO_3$ concentration ($\epsilon_r = 150$). Even in small quantity (0.02 $CaTiO_3$ -0.08 $CaTiO_3$), the last one increase ϵ_r with about 50%.

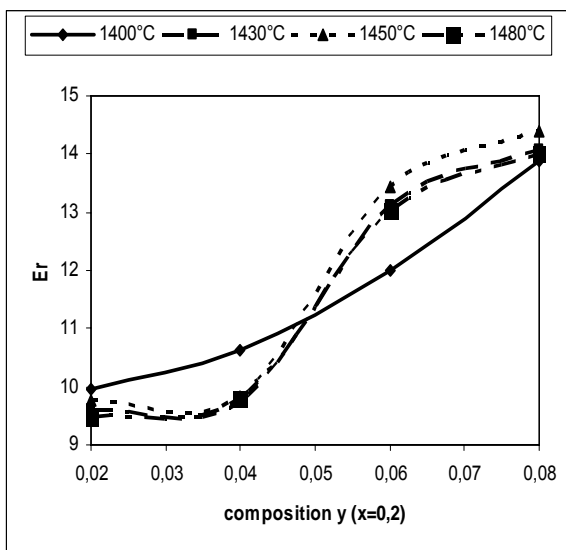


Fig. 2. Evolution of ϵ_r with the composition (x).

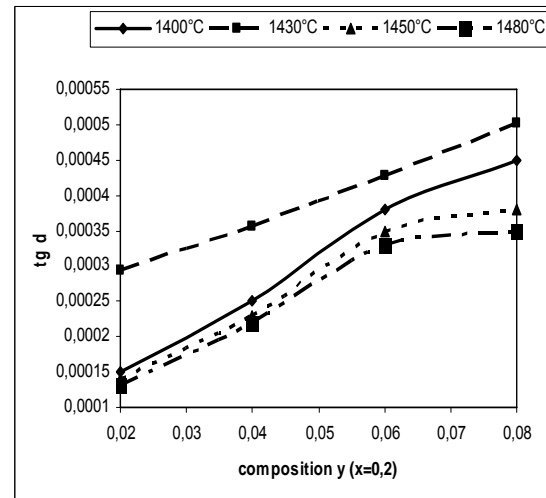


Fig. 3. Dielectric losses as a function of the composition (x).

Fig. 3 shows that dielectric losses also increase with composition (y) as the perovskite phase $CaTiO_3$ has higher losses than the spinel phase. This variation of losses is significant, from $(1-1.5) \times 10^{-4}$ (respectively $Q_f = 100\,000 - 66\,000$) to 4.5×10^{-4} ($Q_f = 22\,000$).

Fig. 4 represents the relation between τ_f and the composition (y). The figure shows that the perovskite phase $CaTiO_3$ compensates τ_f ($\tau_f \rightarrow 0$) for $y = 0.05$ at a sintering temperature of 1450°C, and for $y = 0.07$ at sintering temperatures 1400°C, 1430°C and 1480°C.

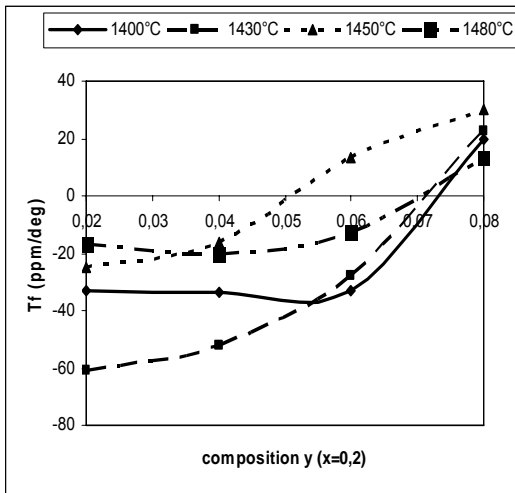


Fig. 4. Evolution of τ_f with the composition (x).

The figures reveal that the dielectric permittivity and losses have a low impact on the sintering temperature. The optimal sintering temperature in our case appears to be 1480°C.

4. Conclusions

The dielectric material with general formula $Mg_{1+x}(Ca_yTi_{x+y})Al_{2-2x-2y}O_4$, $x = 0.2$ and $y = 0.02-0.08$ was synthesized and has the following dielectric properties:

$\epsilon_r = 10-15$ and $\tan \delta = (1-1.5) \times 10^{-4}$ at 10 GHz, respectively $Q_f = 100\,000 - 66\,000$. The last one presents a main spinel phase and contains a very small quantity of $y(CaTiO_3)$ phase ($y = 0.02 - 0.08$) that reveals to be sufficient for achieving a complete compensation of $\tau_f \rightarrow 0$ for $y = 0.05-0.06$, as both above mentioned phases have opposite signs of temperature coefficient.

The produced material could be used as a resonator for frequencies above 30 GHz, and for dielectric substrate material for microwave circuits.

References

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