SYNTHESIS AND MICROWAVE PROPERTIES OF THE SUBSTITUTED MgTiO$_3$ CERAMICS

V. Parvanova

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: vparvanova@hotmail.com

ABSTRACT

A low-temperature microwave ceramic with the following composition was synthesized: Mg$_x$Li$_{1-x}$La$_{0.1}$TiO$_3$ and MgTi$_{1-x}$Cr$_x$TiO$_3$, where $x = 0.4 \%$ B$_2$O$_3$. The optimum conditions of obtaining were determined. The most important microwave properties were studied, such as: dielectric permittivity, quality factor, temperature coefficient of frequency, density at $T_{\text{calc}} = 1250, 1300, 1350, 1400^\circ$ C and frequency $8-10$ GHz. By increasing the (Li$_{1-x}$La$_{0.1}$) concentration the materials density and permittivity also increase ($\varepsilon_r = 26$, $T_{\text{calc}} = 1250^\circ$ C), the quality factor reduces, and the temperature stability of resonators is improved ($\tau_f = 0$ ppm °C$^{-1}$ with $x = 0.18$ mol for $T_{\text{calc}} = 1250-1350^\circ$ C). The substitution of Ti$^{4+}$ for (Cr$_{0.5}$ Ta$_{0.5}$) results a temperature compensation of material as with $x = 0.10$ mol $\tau_f = -11.3$ ppm °C$^{-1}$ Q = 5000.

Keywords: synthesis, microwave materials, substituted MgTiO$_3$, microwave characteristics.

INTRODUCTION

The materials used for dielectric resonators are required to have dielectric properties as follows: permittivity ($\varepsilon_r$) greater than 20, high Q value greater than 3000 (at 10 GHz) and very small temperature coefficient ($\tau_r$) [1]. The polycomponent microwave materials based on MgTiO$_3$ have the properties mentioned above. And besides they are obtained by a relatively simple technology, have a good repeatability of parameters, they are widely used, they are economical and also are environmentally appropriate dielectrics. MgTiO$_3$, however, has a low permittivity ($\varepsilon_r = 17$ and temperature coefficient of frequency $\tau_r = 45$ ppm °C$^{-1}$ [2]. Reasonable efforts were made in a number of publications to eliminate these defects of MgTiO$_3$. For example, in [1] the system $x$MgTiO$_3$-(Na$_{0.5}$, La$_{0.5}$)TiO$_3$ was obtained (where Ln = La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$) and the following parameters were measured: $\varepsilon_r = 22-25$, $Qxf = 5500 - 2800$ GHz and $\tau_r \rightarrow 0$. Through introducing La, Cr, CaTiO$_3$, etc. in [3-6] a compromise of properties was achieved. [7-9] may be of interest, where the MgTiO$_3$- ceramic, MgTiO$_3$-CaTiO$_3$ was synthesized with additions of ZnO, SnO$_2$, SiO$_2$ and B$_2$O$_3$ by the so-called technology of low-temperature co-fired ceramic (LTCC).

This study is aimed at synthesizing by the peroxo method a low-temperature microwave ceramic based on MgTiO$_3$. The addition of B$_2$O$_3$ will contribute for the reducing of the calcination temperature. It is well known that a MgTiO$_3$-ceramic is obtained at $T=1450 - 1500^\circ$C. By introducing substitutions from (Li$_{1-x}$La$_{0.1}$)$^{3+}$ and (Cr$_{0.5}$ Ta$_{0.5}$)$^{4+}$ it is expected to control the temperature coefficient of frequency in order to obtain temperature stable resonators ($\tau_f \rightarrow 0$). In this sense the tasks set are of particular scientific and practical interest.

EXPERIMENTAL

The MgTiO$_3$ were synthesized by the peroxo method [10]. The essence of the method can be illustrated with the following chemical reaction:

$$\text{TiCl}_4 + \text{Mg(CH}_2\text{COO)}_2 + \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{Mg}_x[\text{Ti}_y\text{O}_z\text{(OH)}_{1-x}]_{4\text{H}_2\text{O}} \xrightarrow{t_{30}} \text{MgTi}_x\text{O}_z + \text{O}_2 + \text{H}_2\text{O}$$

A 20 % solution of Mg(CH$_2$COO)$_2$ and a 30 % solution of H$_2$O$_2$ in a mol ratio of 2:2:10 were added to a 30 % solution of TiCl$_4$ in HCl. It was alkalized to pH
= 10·11 with a 12% solution of NH₄OH. A temperature of 10·15°C was maintained during the synthesis. Amorphous sediment of Mg-peroxotitanate was obtained. The latter was used as a precursor for obtaining MgTiO₃. For this purpose the dried sediment (in an aerol environment at T=20°C) with composition Mg₃[Ti₂(O₃)₄(OH)₄]·4H₂O was subjected to a thermal decomposition at T= 600°C from 4 h or at 700°C from 2 h as a result of which MgTiO₃ crystallizes. The final product was characterized by X-ray diffraction analysis. The stoichiometrically calculated qualities of Li₃CO₃, La₂O₃, Cr₂O₃, Ta₂O₅ with frequency 99·95% were introduced to the so MgTiO₃ thus obtained. The materials Mgₓ(Li₀·₅La₀·₅)₁₋ₓTiO₂ were obtained where x = 0.05, 0.10, 0.15, 0.20 mol and Mg₀·₅(Ti₀·₅Ta₀·₅)₀·₅O₂ + 0.4% B₂O₃ (x = 0.025, 0.050, 0.075, 0.100 mol). The addition of small quantities of B₂O₃ is aimed at reducing the calcination temperature, and the substations (Li₁₋ₓLaₓ)²⁺ and (Cr₁₋ₓTaₓ)³⁺ at improving the temperature stability. A temperature compensation is achieved in references [11, 12] by the substitution of Ba²⁺ with Sr²⁺ and Ca²⁺, and Ti⁴⁺ with Zr⁴⁺.

Grinding and homogenization of raw materials was performed in a planetary ball mill for 35 minutes in a water environment. The presintering was performed at T = 1000°C for 2 h 0.4% B₂O₃ were added to the Mg₀·₅(Ti₀·₅Ta₀·₅)₀·₅O₂ system. A subsequent grinding was performed in the same mill for 55 minutes. The powders were pressed at P = 200 MPa. 10% polyvinyl alcohol was used as a plastificator. As a result, tablets with diameter of 10 mm and height 3 mm were obtained for the Mg₀·₅(Li₀·₅La₀·₅)ₓTiO₂ material. They were calcinated at 1250, 1300 and 1350°C in an air environment. While the tablets for the Mg₀·₅(Ti₀·₅Ta₀·₅)₀·₅O₂ + 0.4% B₂O₃ system have a diameter of 10 mm and height 9 - 10 mm calcinated at 1300, 1350 and 1400°C. The heating continued 3 h as a half an hour break was made at 350 and 400°C in order to obtain a gradual evaporation of the plastificator. In order to avoid the partial reduction of Ti⁴⁺ to Ti³⁺ which would cause weakening of the permittivity as a result of the electron exchange [13], the thermal processing was performed in an oxygen environment.

The microwave parameters were measured by the resonance method [14] in a test structure using a sweep generator and a scalar network analyzer manufactured by Hewlett-Packard within the range 8 - 10 GHz. An X-ray diffraction study was carried out with a TURM-M62 diffractometer of the manufacturer Zeiß (Jena) using the CuKα radiation. Due to the low concentration of substitutions just one phase was registered – the phase of MgTiO₃ without patterns displacements.

**RESULTS AND DISCUSSION**

The dependences of the permittivity (εᵣ) on the composition of systems (x) and the calcination temperatures are shown on Figs. 1 and 2. It is evident from the figures that εᵣ is strongly dependent on the composition of materials and considerably less dependent on the studied calcination temperatures. For the Mgₓ(Li₀·₅La₀·₅)ₓTiO₂ system (Fig.1) εᵣ increases with increasing the concentration of substitution (Li₁₋ₓLaₓ)²⁺, while for the Mg₀·₅(Ti₀·₅Ta₀·₅)₀·₅O₂ + 0.4% B₂O₃ (Fig. 2) system the opposite case was observed. These dependencies were registered at all calcination temperatures.

The dₑ_max density relation is shown in % on Figs. 3 and 4 as a function of the composition of systems and the

---

**Fig. 1.** Dependence of the permittivity on the composition and the calcination temperature for the Mgₓ(Li₀·₅La₀·₅)ₓTiO₂ material.

**Fig. 2.** Dependence of the permittivity on the composition and the calcination temperature for the Mg₀·₅(Ti₀·₅Ta₀·₅)₀·₅O₂ + 0.4% B₂O₃ material.
calcination temperature. It is evident from the figures that the density of both materials increases with increasing the concentration of substitutions. For the Mg$_{1-x}$(Li$_{0.5}$La$_{0.5}$)$_x$TiO$_3$ system (Fig. 3) d reduces as calcination temperature increases. $d_{\text{max}} = 99.4$ % is obtained at $T_{\text{calc}} = 1250^\circ$C. Probably at high temperature calcination partial evaporation of Li$^+$ appears because at $T_{\text{calc}} = 1350^\circ$C d = 95.5 %.

For the MgTi$_{1-x}$(Cr$_{0.5}$Ta$_{0.5}$)$_x$O$_3$ system + 0.4 % B$_2$O$_3$ it is assumed that B$_2$O$_3$ improves calcination and d increases with the increase of the calcination temperature (Fig. 4).

The dependences of Qxf ($Q = 1/\tan\delta$) on the composition of systems and the calcination temperatures are shown on Figs. 5 and 6. It is known that the losses depend on the materials permittivity and density. In both systems Q weakens as the concentration of substitution increases. It could be assumed that in this case (Li$_{0.5}$La$_{0.5}$)$_2^+$ and (Cr$_{0.5}$Ta$_{0.5}$)$_{2x}^{2+}$ increase the permittivity of ceramic materials. It is evident, from Fig. 6, that Q increases with the increase of calcination temperature, respectively with the increase of density, while this dependence for the Mg$_{1-x}$(Li$_{0.5}$La$_{0.5}$)$_x$TiO$_3$ system (Fig. 5) is not clearly displayed.

The temperature coefficient of frequency (τ) is shown on Figs. 7 and 8 as a function of the composition and calcination temperature. It is evident from the figures that τ depends mainly in the composition and calcination temperature. By increasing the concentration of substitutions the temperature stability of resonators is improved. For the Mg$_{1-x}$(Li$_{0.5}$La$_{0.5}$)$_x$TiO$_3$ system the τ values vary from $-13.25$ to $+3.05$ ppm °C$^{-1}$ as with x = 0.18 mol (Li$_{0.5}$La$_{0.5}$)$_{2x}^{2+}$ τ = 0 ppm °C$^{-1}$ for all calcination temperatures. It is evident, from Fig. 8, that the substitution (Cr$_{0.5}$Ta$_{0.5}$)$_{2x}^{2+}$ results in τ reduction to appropriate values τ = $-11.3$ ppm °C$^{-1}$ with x = 0.10 mol, which is also one
A low-temperature microwave ceramics with the following composition were synthesized: Mg(1-x)(Li$_x$La$_{0.5}$)$_3$TiO$_4$ and MgTi$_{1-x}$(Cr$_{1/2}$Ta$_{1/2}$)$_3$O$_4 + 0.4$ % B$_2$O$_3$. The optimum conditions of obtaining were determined.

The most important microwave properties were studied, such as: dielectric permittivity, quality factor, temperature coefficient of frequency, density at $T_{cal} = 1250$, 1300, 1350, 1400°C and frequency $8 \times 10^{11}$ GHz.

The effect of substitutions of Mg$^{2+}$ with (Li$_{1-x}$La$_{0.5}$)$_3^{2+}$ and Ti$^{4+}$ with (Cr$_{1/2}$Ta$_{1/2}$)$_3^{4+}$ in MgTiO$_3$ was studied.

By increasing the concentration of (Li$_{1-x}$La$_{0.5}$)$_3^{2+}$ the materials density and permittivity also increase ($\varepsilon_r = 26$, $T_{cal} = 1250^\circ$C), the quality factor reduces, and the temperature stability of resonators is improved ($\tau_f = 0$ ppm °C$^{-1}$ with $x = 0.18$ mol for $T_{cal} = 1250-1350^\circ$C).

The substitution of Ti$^{4+}$ for (Cr$_{1/2}$Ta$_{1/2}$)$_3^{4+}$ results in reducing the $\tau_f$ and temperature compensation of material as with $x = 0.10$ mol $\tau_f = -11.3$ ppm °C$^{-1}$, $Q = 5000$.

REFERENCES