Journal of the University of Chemical Technology and Metallurgy, 41, 2, 2006, 221-224

SYNTHESIS AND MICROWAVE PROPERTIES OF THE SUBSTITUTED $MgTiO_3$ CERAMICS

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Received 20 March 2006
Accepted 23 April 2006

ABSTRACT

A low-temperature microwave ceramic with the following composition was synthesized: $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ *and* $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3 + 0.4\ \%\ B_2O_3$. *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* $T_{cal} = 1250, 1300, 1350, 1400^\circ C$ *and frequency 8 – 10 GHz. By increasing the* $(Li_{0.5}La_{0.5})^{2+}$ *concentration 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* $T_{cal.} = 1250\text{-}1350^\circ C$*.). The substitution of* Ti^{4+} *for* $(Cr_{0.5}Ta_{0.5})^{4+}$ *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 (ε_r) greated than 20, high Q value greater than 3000 (at 10 GHz) and very small temperature coefficient (τ_f) [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 $\tau_f = -45$ 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 $xMgTiO_3\text{-}(Na_{1/2}Ln_{1/2})TiO_3$ 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 $\tau_f \rightarrow 0$. 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, $MgTiO_3\text{-}CaTiO_3$ was synthesized with additions of ZnO, SnO_2, SiO_2 and B_2O_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_2O_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°C. By introducing substitutions from $(Li_{0.5}La_{0.5})^{2+}$ 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:

$$TiCl_4 + Mg(CH_3COO)_2 + H_2O_2 + OH^- \rightarrow Mg_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O \xrightarrow{t^\circ} MgTiO_3 + O_2 + H_2O$$

A 20 % solution of $Mg(CH_3COO)_2$ and a 30 % solution of H_2O_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 NH_3. 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 $MgTiO_3$. For this purpose the dried sediment (in an aerial environment at T=20°C) with composition $Mg_2[Ti_2(O_2)_4(OH)_4]{\cdot}4H_2O$ 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 $MgTiO_3$ crystallizes.The final product, was characterized by X-ray diffraction analysis. The stoihiometrically calculated qualities of Li_2CO_3, La_2O_3, Cr_2O_3, Ta_2O_5 with frequency 99-99,5 % were introduced to the so $MgTiO_3$ thus obtained. The materials $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ were obtained where x= 0.05, 0.10, 0.15, 0.20 mol and $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3. (x= 0.025, 0.050, 0.075, 0.100 mol). The addition of small quantities of B_2O_3 is aimed at reducing the calcination temperature, and the substations $(Li_{0.5}La_{0.5})^{2+}$ and $(Cr_{0.5}Ta_{0.5})^{4+}$ at improving the temperature stability. A temperature compensation is achieved in references [11, 12] by the substitution of Ba^{2+} with Sr^{2+} and Ca^{2+}, and Ti^{4+} with Zr^{4+}.

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 % B_2O_3 were added to the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ 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 $Mg_{1-x}(Li_{0.5}La_{0.5})xTiO_3$ material. They were calcinated at 1250, 1300 and 1350°C in an air environment. While the tablets for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3 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 plasticizer. In order to avoid the partial reduction of Ti^{4+} to Ti^{3+} 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 TUR-M62 diffractometer of the manufacturer Zeiβ (Jena) using the CuK_α radiation. Due to the low concentration of substitutions just one phase was registered – the phase of $MgTiO_3$ without patterns displacements.

RESULTS AND DISCUSSION

The dependences of the permittivity (ε_r) on the composition of systems (x) and the calcination temperatures are shown on Figs. 1 and 2. It is evident from the figures that ε_r is strongly dependent on the composition of materials and considerably less dependent on the studied calcination temperatures. For the $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ system (Fig.1) ε_r increases with increasing the concentration of substitution $(Li_{0.5}La_{0.5})^{+2}$, while for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3 (Fig. 2) system the opposite case was observed. These dependencies were registered at all calcination temperatures.

The d_{exp}/d_{theor} density relation is shown in % on Figs. 3 and 4 as a function of the composition of systems and the

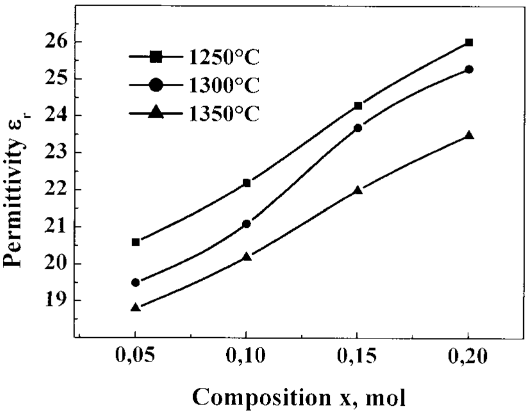

Fig. 1. Dependence of the permittivity on the composition and the calcination temperature for the $Mg_{1-x}(Li_{0.5}La_{0.5})xTiO_3$ material.

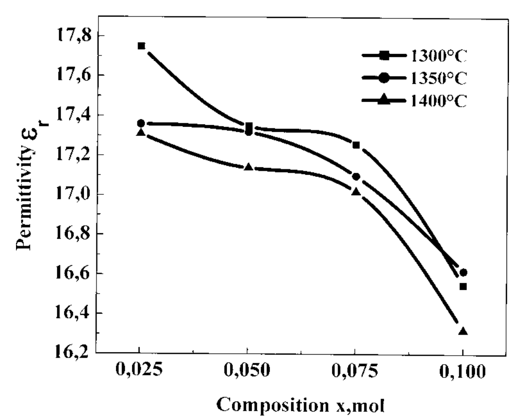

Fig. 2. Dependence of the permittivity on the composition and the calcination temperature for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3 material.

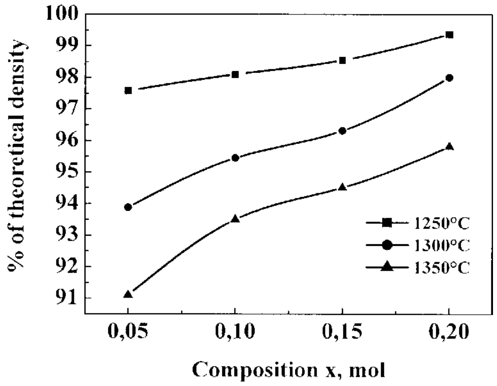

Fig. 3. $d_{exp.}/d_{teor.}$ Ratio in % as function on the composition and the calcination temperature for the $Mg_{1-x}(Li_{0.5}La_{0.5})xTiO_3$ material.

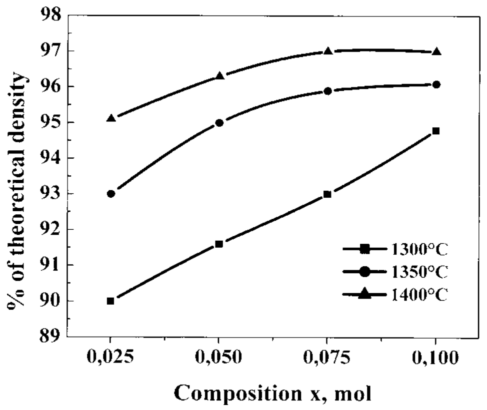

Fig. 4. $d_{exp.}/d_{teor.}$ ratio in % as function on the composition and the calcination temperature for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % material.

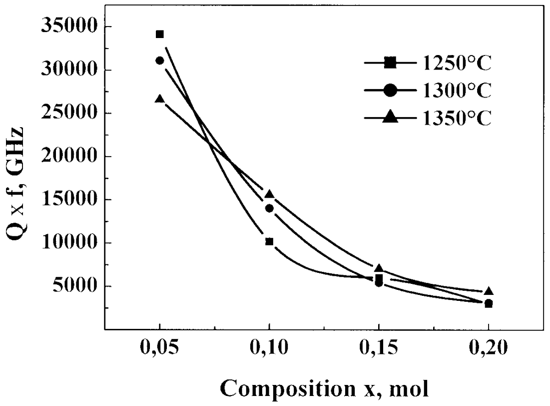

Fig. 5. Dependence of the Qxf on the composition and the calcination temperature for the $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ material.

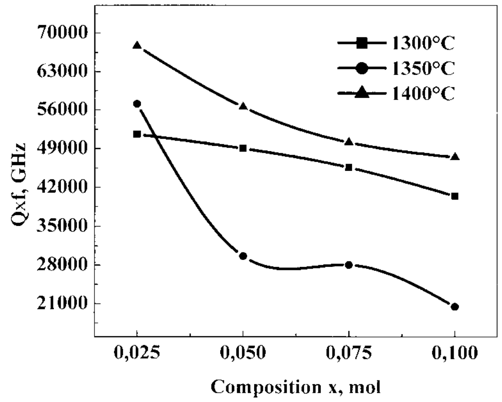

Fig. 6. Dependence of the Qxf on the composition and the calcination temperature for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3 material.

calcination temperature. It is evident from the figures that the density of both materials increases with increasing the concentration of substitutions. For the $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ system (Fig. 3) d reduces as calcination temperature increases. d_{max} = 99.4 % is obtained at $T_{cal.}$ = 1250°C. Probably at high temperature calcination partial evaporation of Li^+ appear because at $T_{cal.}$ = 1350°C d = 95.5 %.

For the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ system + 0.4 % B_2O_3 it is assumed that B_2O_3 improves calcination and d increases with the increase of the calcination temperature (Fig. 4).

The dependences of Qxf (Q = 1/tan δ) 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 $(Cr_{0.5}Ta_{0.5})^{4+}$ 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 $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ system (Fig. 5) is not clearly displayed.

The temperature coefficient of frequency (τ_f) is shown on Figs. 7 and 8 as a function of the composition and calcination temperature. It is evident from the figures that τ_f depends mainly in the composition as for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ system + 0.4 % B_2O_3 (Fig. 7) it also depends to some extent on the calcination temperature. By increasing the concentration of substitutions the temperature stability of resonators is improved. For the $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ system the τ_f values vary from -13.25 to + 3.05 ppm °C^{-1} as with x = 0.18 mol $(Li_{0.5}La_{0.5})^{2+}$ τ_f = 0 ppm°C^{-1} for al calcination temperatures. It is evident, from Fig. 8, that the substitution $(Cr_{0.5}Ta_{0.5})^{4+}$ results in τ_f reduction to appropriate values τ_f = -11,3 ppm °C^{-1} with x = 0.10 mol, which is also one

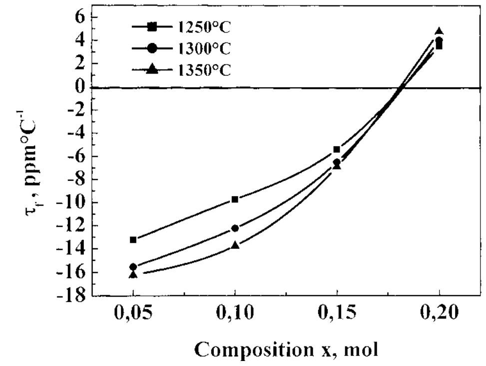

Fig. 7. Dependence of the temperature coefficient of the resonance frequency on the composition and the calcination temperature for the $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ material.

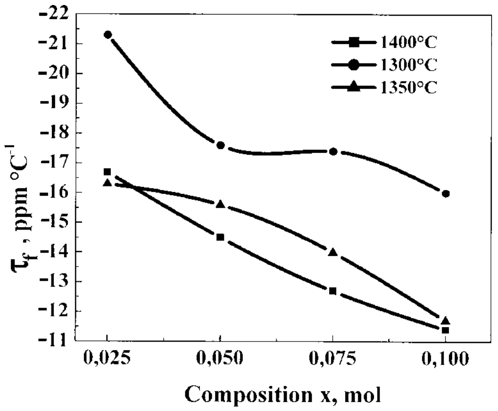

Fig. 8. Dependence of the temperature coefficient of the resonance frequency on the composition and the calcination temperature for the $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_3 material.

of the basic aims of this study since it is known that the temperature coefficient of frequency of $MgTiO_3$ is τ_f = -45 ppm °C^{-1} [1].

CONCLUSIONS

A low-temperature microwave ceramics with the following composition were synthesized: $Mg_{1-x}(Li_{0.5}La_{0.5})_xTiO_3$ and $MgTi_{1-x}(Cr_{0.5}Ta_{0.5})_xO_3$ + 0.4 % B_2O_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 – 10 GHz.

The effect of substitutions of Mg^{2+} with $(Li_{0.5}La_{0.5})^{2+}$ and Ti^{4+} with $(Cr_{0.5}Ta_{0.5})^{4+}$ in $MgTiO_3$ was studied.

By increasing the concentration of $(Li_{0.5}La_{0.5})^{2+}$ the materials density and permittivity also increase (ε_r = 26, $T_{cal.}$ = 1250°C), the quality factor reduces, and the temperature stability of resonators is improved (τ_f = 0 ppm °C^{-1} with x= 0.18 mol for $T_{cal.}$ = 1250- 1350°C.).

The substitution of Ti^{4+} for $(Cr_{0.5}Ta_{0.5})^{4+}$ results in reducing the τ_f and temperature compensation of material as with x= 0.10 mol τ_f = -11.3 ppm °C^{-1}, Q =5000.

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