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Microwave dielectric properties of the spinel composition $Mg_{1+x}Ti_xAl_{2-2x}O_4$

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The objects of our research is magnesium aluminates (spinel), in which the electric charge of Al^{3+} cation is partially substituted with constitutive trivalent cation of Mg^{2+} and Ti^{4+} in the system with the following composition: $Mg_{1+x}Ti_xAl_{2-2x}O_4$ with (x) varying from 0,1 to 0,6. X-ray diffraction data shows that within the above values of (x) the composition is a single phase spinel. The microwave basic parameters were measured as ε_r, tan δ and τ_f, respectively with the following values: $\boldsymbol{\varepsilon_r}$ = 6-12, tanδ = (1.5-3.5) x 10^{-4} at 10 GHz and Q_f = 70 000 – 90 000, and τ_f from -50 to -70 ppm/deg.

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1. Introduction

It is known that for microwave dielectric materials with relatively high $\boldsymbol{\varepsilon_r}$ in the range of 40, experimental difficulties exist at frequencies above 30 GHz, as the size of the resonator disks becomes very small, and therefore it is difficult to press and polish them. The size of the disks become acceptable when materials like spinels with ε_r = 9-14 are used. Monospinels of Zn and Mg have ε_r = 8.5 – 8.7, Q_f = 56000 to 69000 at 12 GHz (respectively tanδ = 2×10^{-4} – 1.7×10^{-4}). Unfortunately they have relatively high temperature coefficient of frequency τ_f = -75 to- 79 ppm/deg. Compensation of τ_f could be achieved upon additives with opposite sign, like TiO_2. For example, systems like (1-x) $MgAl_2O_4$. x TiO_2 or (1-x) $ZnAl_2O_4$. x TiO_2 for x = 0.12 to 0.5 have ε_r = 9 – 14 and τ_f = -27 to 6.2 ppm/deg [1- 5]. It is necessary to notice that these compositions are not electron equilibrated. Such materials have a sintering temperature of 1400-1450 °C, at which a spinel solid solution is formed and contains a cation (Ti^{4+}) with different valence than M^{2+} and Al^{3+} that could cause oxygen defects, and it therefore worsens dielectric losses.

The object of the present work is the study of $MgAl_2O_4$, in which Al^{3+} cations are partially substituted with constitutive trivalent cation Mg^{2+} - Ti^{4+} for the composition $Mg_{1+x}Ti_xAl_{2-2x}O_4$ to be electron balanced , which represents a scientific and practical interest. We suppose that this substitution will lead to an increase of ε_r and a probable decrease of τ_f, keeping dielectric losses at10^{-4} rate.

2. Experimental procedure

As starting materials, MgO Fluka, TiO_2 Kronos, Al_2O_3 Fluka and $CaCO_3$ Fluka with purity 98-99 % were used. The synthesis is made by the conventional mixed oxide route. The ball milling and homogenization are made in agate milling pots and balls in deionized water in planetary ball mill Retsch during one hour. The dried mixture is calcined at 1100°C for three hours in corundum pots. After drying, 0.3 % B_2O_3 is added to ease the sintering process, and thereafter a secondary milling is made. Press-powder is made from the dried mixture, using PVA (10% solution) as a binder agent. For the pressing process, we use a powder fraction of 0.25-0.5 mm grain size at a pressure of 1.5 t/cm^2. The sintering is proceeded in super kantal furnace Linn, at different temperatures with isothermal maintaining during three hours. X-ray analysis is made from the powder material using CuKα radiation in CIRIMAT-Toulouse.

The measurements of $\boldsymbol{\varepsilon_r}$, tanδ, and τ_f are made according Hakki and Koleman' s method [6] modified by Courtney [7].

3. Results and discussions

3.1 X-Ray analysis

According to the ternary diagram of the MgO-Al_2O_3-TiO_2 system at sintering temperatures between 1400-1450°C, a solid solution which consists of $MgAl_2O_4$ and $TiMg_2O_4$ phases with a spinel structure is formed.

Fig. 1 presents the dependence between the lattice parameter calculated for different values of (x) by Végard law and the real measured one.

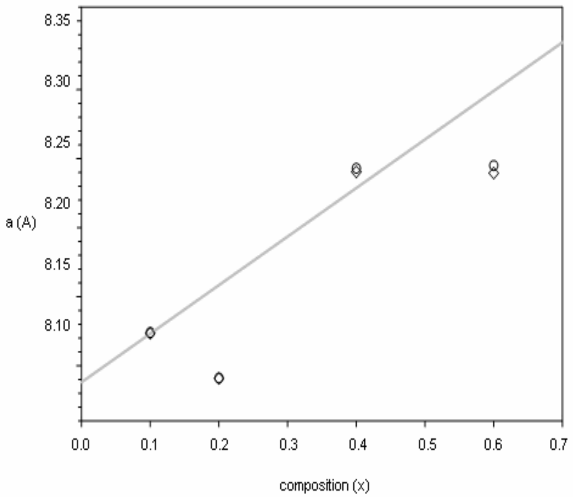
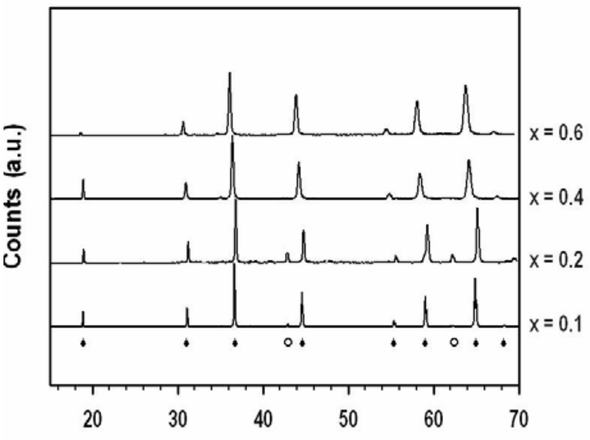


Fig. 1. Evolution of unit cell parameter as a function of the composition (x)



Spinel phase $Mg_{1+x}Ti_xAl_{2-2x}O_4$ (.)
Periclase phase (o)

Fig. 2. XRD pattern of $Mg_{1+x}Ti_xAl_{2-2x}O_4$ *system sintered at 1480°C.*

Fig.1 shows, that for all (x) values a spinel phase with lattice parameter varying from 8.1 to 8.25 is formed. Fig.2 confirms the appearance of the single phase spinel, as only for x=0.1 a very small quantity of MgO did not react.

3.2 Microwave properties

On Fig. 3 is shown the relation between ε_r and the composition (x) in the formula $Mg_{1+x}Ti_xAl_{2-2x}O_4$. The figure shows that ε_r increases with (x) from 6 – 12, which is probably due to the increase of Ti^{4+} acting as a polarizing agent. Fig. 4 below shows that with increasing (x),dielectric losses move from 1.5×10^{-4} to 3.5×10^{-4}

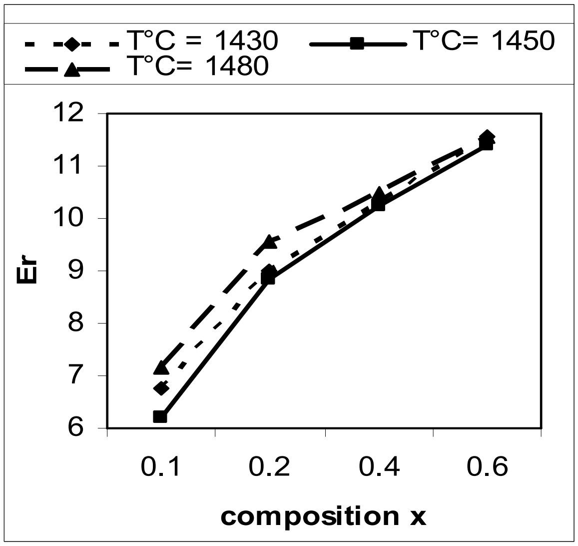


Fig. 3. Evolution of ε_r *with the composition (x).*

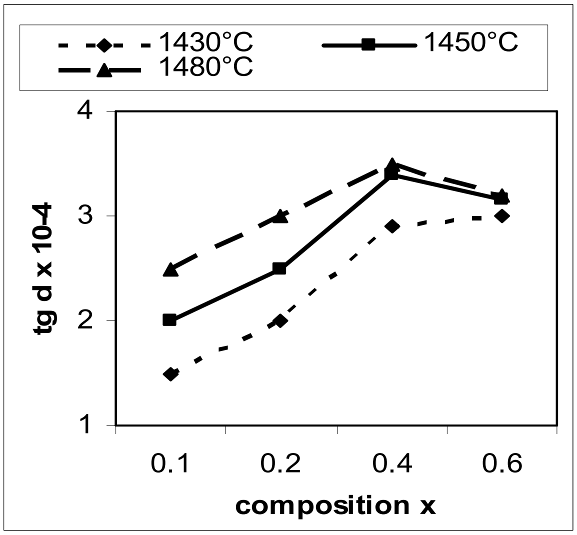


Fig. 4. Dielectric losses as a function of the composition (x).

Likely for all dielectric materials losses increase with ε_r which is due to conductivity phenomenon and electron exchange betweenTi^{4+} and Ti^{3+}. Therefore the quality factor which is related to dielectric losses, decreases with (x) content (from 90 000 to 33-40 000).

Fig 5. shows that the temperature coefficient of frequency τ_f linearly decreases (from -70 to -50 ppm/deg) with composition (x).

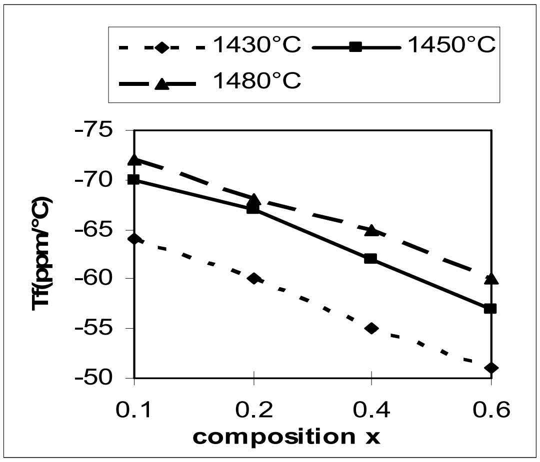


Fig. 5. Evolution of τ_f *with the composition (x)*

This is due to a certain compensation of the temperature coefficient by the presence of Ti^{4+} cations. This compensation is lightly shown due to the presence of Mg^{2+} whose oxides have a τ_f with an opposite sign than that of Ti^{4+} (respectively TiO_2). The sintering temperature has a low impact on ε_r but reflects on the losses and τ_f. It is directly related to the microstructure (size of grains and porosity) and therefore affects losses tan δ. The optimal sintering temperature for our compositions appears to be 1430°C where losses and τ_f are minimal.

4. Conclusions

The following system $Mg_{1+x}Ti_xAl_{2-2x}O_4$ (MTA) is studied, in which Al^{3+} cations are partially replaced with constitutive trivalent cation Mg^{2+} - Ti^{4+} to preserve the stochiometry and electronic balance between the positive and negative ions.

The synthesized obtained material is a single phase spinel.

The materials from the MTA system, especially those with x=0,1-0,2 have very good microwave properties as $\boldsymbol{\varepsilon_r}$ = 9-10, tan δ = $(1.5\text{-}3)_x10^{-4}$ and Q_f = 70 000 – 90 000 at 10 GHz, but unfortunately relatively high τ_f = -50 to -60 ppm/deg within the same range as Al_2O_3 and $MgAl_2O_4$. Therefore they are not suitable for microwave resonators, but they can be used as thin films for electronic circuits. One of our additional research showed that the MTA composition could be thermally compensated (50-60 ppm/°C) with substitutions of Ca^{2+}, which we will report in another paper.

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