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Microwave properties of hollandite type $Ba_xMg_xTi_{8-2x}O_{16}$ ceramic material

A. BADEV[a,b*], I. ILIEV[a], J-P. CAMBRONNE[b]
[a]*Department of non ferrous materials and semiconductors, UCTM, Sofia, Bulgaria*
[b]*Laboratory of plasma and conversion of energy, LAPLACE, 31062 Toulouse cedex 9, France*

The microwave dielectric properties of hollandite type $Ba_xMg_xTi_{8-2x}O_{16}$ ceramic material were investigated, as such compounds have not been studied yet. It has been revealed that the dielectric permittivity depends on the material's composition and varies from 21 to 24. Dielectric losses for x = 0.6-0.7 are very low, tan δ = $(6.7 – 8)x10^{-5}$, but unfortunately the temperature coefficient is too high τ_f = 200 – 300 ppm/deg. The last one anneals ($\tau_f \rightarrow 0$) at x = 1 – 1.1 where losses are tan δ = $1.4x10^{-4}$, respectively Q = 7100 at 9.5 – 10 GHz. These losses are in the same range as alumina ($1x10^{-4}$) and some spinel compositions ($2x10^{-4}$).

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1. Introduction

In the reference [1] and on the internet, there are practically no data about the microwave properties of hollandite type ceramic materials such as $Ba_xMg_xTi_{8-2x}O_{16}$. There are known compounds with compositions according to the above mentioned formula, which for x = 0.6 - 1.14 have a hollandite structure, but their applications are not mentioned [2,3]. In [4], it is shown that these materials could be used as ionic conductors with unidirectional conductivity due to the existing tunnels in their structure. Considering all of the above said, these type of materials represent a scientific and practical interest.

2. Experimental procedures

As starting materials the following components are used: $BaCO_3$ and MgO Fluka with purity > 99 % and TiO_2 Kronos with purity also > 99 %. The weights of the initial oxides are calculated according the component's formula. The synthesis is done by the conventional mixed oxide route. The ball milling and homogenization are done in planetary ball mill in agate milling pots and balls, using deionized water as a wetting agent, during one hour. The dried mixture is calcined in alum oxide pots at 1100°C for three hours. A secondary milling and homogenization is then made likely the first one. From the dried material it is made press-powder with PVA (6% solution as a binder).

For pressing we use a powder fraction of 0.25-0.5 mm grain size at a pressure of 1.5 t/cm^2. The sintering process is proceeded in superkhantal Linn furnace with isothermal maintaining for three hours at 1380°C. The samples are thereafter polished.

The measurements of the microwave parameters (ε_r, tan δ, and τ_f) are done by Hakki and Coleman's method [5] modified by Courtney [6].

XRD analysis is carried out to conclude on the structure of the material and to prove that it belongs to the hollandite group.

3. Results and discussion

Fig. 1 is shows the XRD pattern of $Ba_xMg_xTi_{8-2x}O_{16}$ (x=0.6-1.1); it proves that the compound belongs to the hollandite group of materials.

As seen from the diagram above for x=1.1 the predominant phase is hollandite. The rutile phase is present for lower values of (x) and decreases with the composition.

Fig. 2 illustrates the dependence of ε_r on the composition (x). The values of the permittivity decrease with (x) content (from 24 to 21) which is the consequence of the concentration drop of the polarizing cation Ti^{4+}.

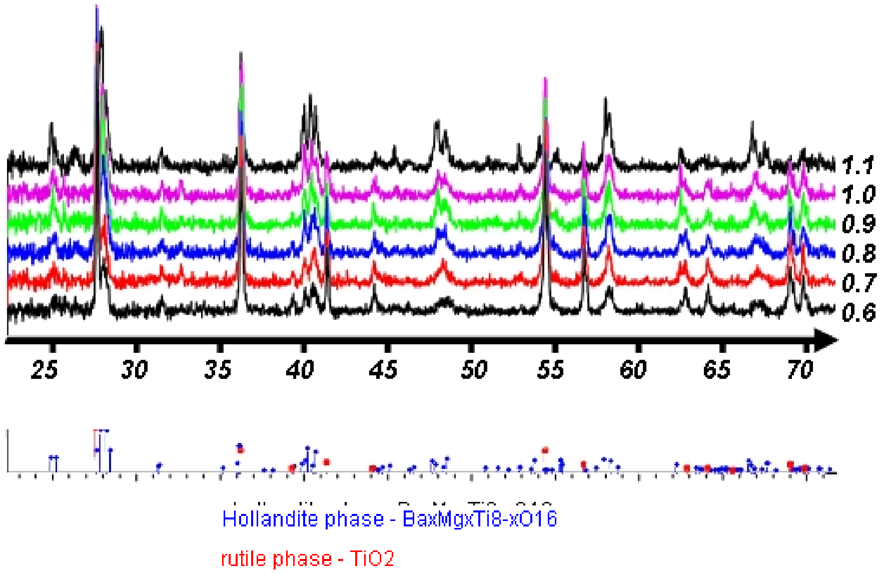

Fig 1. XRD pattern of $Ba_xMg_xTi_{8-2x}O_{16}$ sintered at 1380°C.

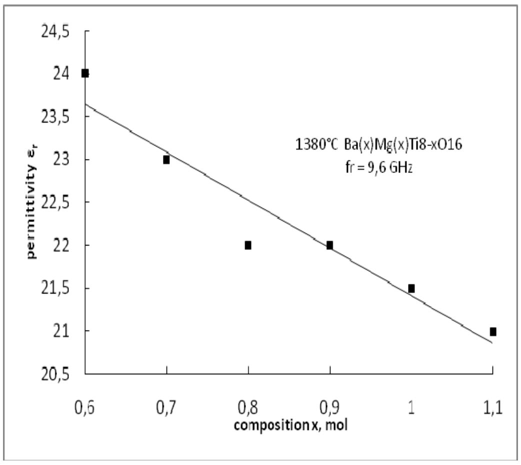

Fig . 2. Evolution of permittivity as a function of the composition in $Ba_xMg_xTi_{8-2x}O_{16}$.

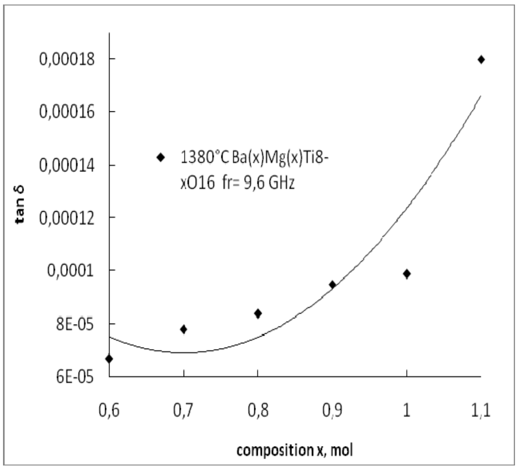

Fig. 3. Dielectric losses as a function of the composition in $Ba_xMg_xTi_{8-2x}O_{16}$.

In Fig. 3 above is shown the dependence of the dielectric losses on the composition (x). From there it can be seen that losses increase with (x) content in the formula (from 6.7×10^{-5} for x=0.6 to 1.4×10^{-4} for x=1.0) but they remain very low at the working frequency (9.6 GHz). The correspondent quality factor decreases from 14925 to 10101 (Qxf = 149250 to 101010) as shown in Fig. 5 below. This increase of the losses is due to the presence of a secondary phase of TiO_2.

The quality factor is also related to the density and microstructure of the material. As seen on the SEM pictures below the density decreases with the composition (x) (from the highest density at x=0.6 ≈ 98.9 % of theoretical density (Fig. 4a) to the lowest density at x=1.1 ≈ 79.5 % of theoretical density). There (Fig. 4c) are two distinguished colors on the pictures; the dark sides correspond to the reduction of Ti (Ti^{4+}/Ti^{3+} - TiO_2 phase) and the brighter ones to the formation of $BaMgTi_7O_{16}$ hollandite phase. As Ba^{2+} content increases in the formula the quantity of the hollandite phase increases, responsible for the increase in dielectric losses.

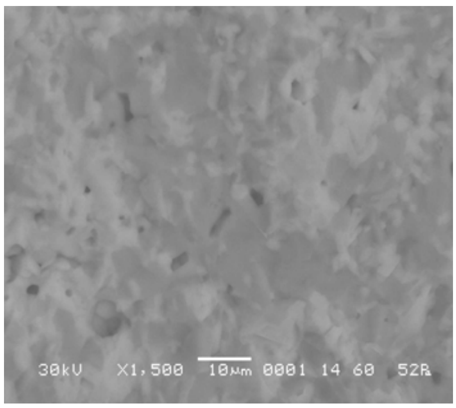

Fig. 4a. $Ba_xMg_xTi_{8-2x}O_{16}$ (x=0.6) sintered at 1380 °C.

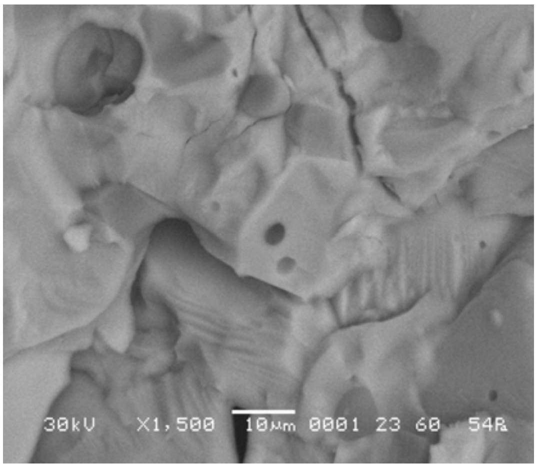

Fig 4b. $Ba_xMg_xTi_{8-2x}O_{16}$ (x=1.1) sintered at 1380°C.

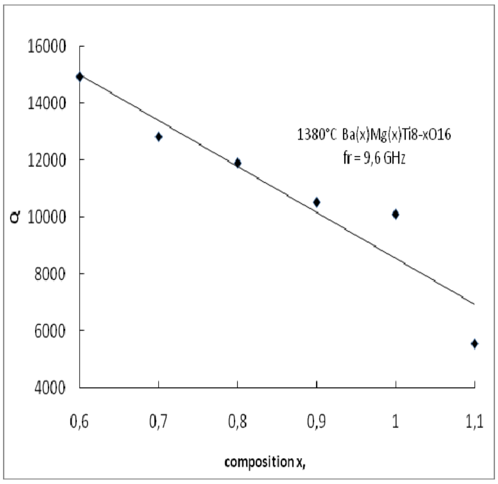

Fig. 5. Evolution of the quality factor with the composition (x).

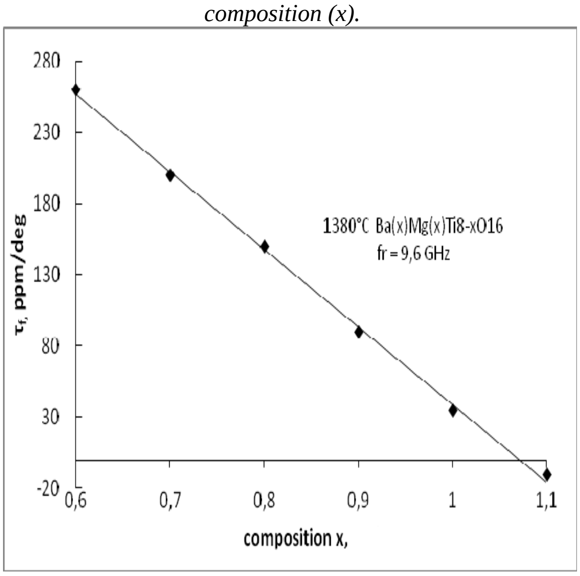

Fig 6. Evolution of the temperature coefficient with composition (x).

Fig. 6 demonstrates the variation of the temperature coefficient of resonant frequency τ_f with (x). τ_f linearly decreases with the composition; it anneals at $x \approx 1.08 - 1.1$. This is done to the equilibrium of phases with opposite signs of τ_f. The correspondent microwave properties are: $\varepsilon_r = 18$, $\tan\delta = 1.5\times10^{-4}$. If we compare these values with those of alumina and some spinel compositions, we can see that our compound has two times higher permittivity than alumina and is temperature compensated – table 1 below.

Material	ε_r	$\tan\delta$	τ_f
$BaMgTi_7O_{16}$	20	1.4×10^{-4}	0
alumina	9.5	1×10^{-4}	-60
spinel	8	2×10^{-4}	-50

As it can be seen, $BaMgTi_7O_{16}$ is therefore one of the best candidate components for microwave applications.

4. Conclusions

X-ray analysis has confirmed that in the $Ba_xMg_xTi_{8-2x}O_{16}$ system a $Ba_{1.1}Mg_{1.1}Ti_{6.9}O_{16}$ (hollandite) solid solution is formed as well as small quantity of TiO_2 secondary phase. The material has excellent microwave properties for all values of (x) and is temperature stable at $x \approx 1.1$. The optimal microwave properties were obtained for x= 0.6 where $\varepsilon_r = 23.6$, $\tan\delta = 6.5\times10^{-5}$ respectively Q = 15 000. The temperature annealing is done at $x \approx 1.08$.

Since this low loss ceramic have the desired characteristics for microwave resonators, it is a good candidate to be used in base station filtering and as DR antennas for wireless communication devices.

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*Corresponding author: alex_badev@yahoo.com