

Microwave properties of $ZrTiO_4$ with partial substitution of Zr^{4+} and Ti^{4+} for Ce^{4+}

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The $ZrTiO_4$ system is one of the classic materials used for microwave devices such as microwave dielectric resonators, but unfortunately it has $\tau_f = 58$ ppm/deg. A technological disadvantage of this material is its high sintering temperature (1600 °C). For the synthesis of $ZrTiO_4$ (ZT) with zero τ_f , there have often been made substitutions of Zr^{4+} for Sn^{4+} - the material ZST, and for lowering the sintering temperature, different sintering aids such as ZnO, CuO, V_2O_5 have been used. As Cerium is of fourth valence and will not disrupt the electro neutrality of the mixed oxide, it is interesting to investigate the microwave properties of ZT at a partial substitution of Zr^{4+} or Ti^{4+} for Ce^{4+} . It has been revealed that for small concentrations of CeO_2 the microwave properties of ZT do not worsen, the temperature compensation is achieved for $\tau_f \rightarrow 0$, and the sintering temperature lowers to 1300 °C.

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1. Introduction

The $ZrTiO_4$ solid solution is one of the most adapted ones for materials used as dielectric resonators. The following ceramic has ϵ_r of (40-42) and Q_f (28000-31000 GHz) at 7 GHz, respectively $\tan\delta = 2.3 \times 10^{-4}$ [1,2]. Unfortunately the compound has a relatively high $\tau_f = 58$ ppm/deg. By means of partial substitution of Zr^{4+} for Sn^{4+} respectively SnO_2 , the material ZST ($Zr_{0.8}Sn_{0.2}TiO_4$) has been successfully synthesized with a zero temperature coefficient of resonant frequency, ϵ_r (37-40) and losses from 1.9×10^{-4} to 1.4×10^{-4} respectively Q_f from 53 000 GHz (at 10 GHz) to 61 000 GHz (at 7 GHz) [3-6].

There have also been made substitutions with Hf such as $Zr_{0.8}Hf_{0.2}TiO_4$ and $Zr_{0.75}Hf_{0.25}TiO_4$ [7,8], where the following parameters were obtained : ϵ_r (38-43), Q_f (62 000 at 4 GHz, 20 000 at 8.5 GHz) and a near zero τ_f .

Jacob and co-authors [9] have analyzed ZST composition doped with small quantities of CuO and ZnO for lowering the sintering temperature. It has the following parameters ϵ_r (35-38), $\tan\delta$ $(1-3) \times 10^{-4}$ and $\tau_f \rightarrow 0$. Wang and co-authors [10] have investigated ZST ceramic material with glass additives (10%). The synthesized ceramic has a low sintering temperature (1150°C), $\epsilon_r = 30$, $Q_f = 30$ 000 GHz and $\tau_f = -4$ ppm/deg.

Wang and co-authors [11] diminished the sintering temperature of ZST material to 1300 °C by adding 2% V_2O_5 . The compound has $\epsilon_r = 37$, $\tan\delta = 1.35 \times 10^{-4}$ and $\tau_f = -2.1$ ppm/deg [12].

In a previous paper [13] we investigated the effect of Ca^{2+} - Ti^{4+} additions on the microwave properties of the Mg-(Ca,Ti)-Al-O spinel and the compensation of τ_f .

The purpose of this work is to evaluate the effect of substitutions of Zr^{4+} and Ti^{4+} for Ce^{4+} , which is of same valence and therefore will not affect the electro-neutrality of the system.

We have analyzed the microwave properties in the conditions of a partial substitution of Zr^{4+} for Ce^{4+}

($Zr_{1-x}Ce_xTiO_4$), and Ti^{4+} for Ce^{4+} ($ZrCe_xTi_{1-x}O_4$).

According to Aguila [13] in the system $ZrO_2 - CeO_2 - TiO_2$ a solid solution ($Zr_xCe_yTi_zO_2$) occurs at $x+y+z=1$, much alike $ZrTiO_4$, with possible presence of phases like ZrO_2 , TiO_2 and $Zr_2Ce_2O_7$.

2. Experimental procedures

As starting materials, we used ZrO_2 Fluka, TiO_2 Kronos, CeO_2 Fluka with purity 98-99 %. The weights of the initial oxides are calculated according to the formula $Zr_{1-x}Ce_xTiO_4$ and $ZrCe_xTi_{1-x}O_4$.

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.

A secondary milling is then made with the same conditions as the first one. From the dried material, it is made press-powder with binder PVA (5% solution). For pressing we use a powder fraction of 0.25-0.5 grain size at a pressure of 1.5 t/cm². The sintering process is proceeded in superkanthal furnace Linn, at 1300 °C and 1350 °C 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 method modified by Courtney [15,16].

3. Results and discussion

- *X-ray* results

The XRD Figs. 1 and 1 bis below show that the main phase is $ZrTiO_4$. There is a small quantity of CeO_2 or

$Zr_2Ce_2O_7$ phase (their characteristic lines are too close, to be clearly separated).

According to Aguilla [14] in the system ZrO_2 - CeO_2 - TiO_2 a liquid phase at high temperature is possible to appear. This phase forms at room temperature an inter-crystalline phase rich in CeO_2 and TiO_2 .

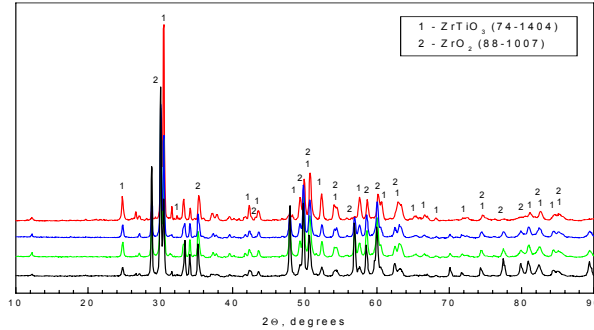


Fig. 1. XRD pattern of $ZrCe_xTi_{1-x}O_4$ composition sintered at 1350°C.

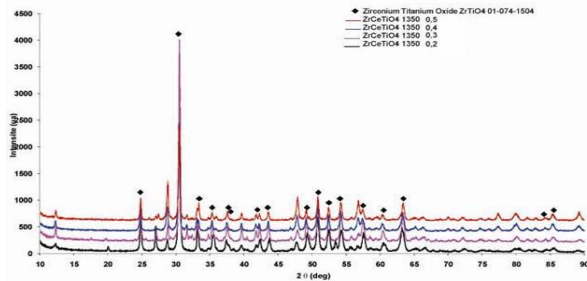


Fig.1 bis. XRD pattern of $Zr_{1-x}Ce_xTiO_4$ composition sintered at 1350°C.

- *Microwave parameters*

Fig. 2 below shows that ϵ_r increases with Ce^{4+} content. The function $\epsilon_r = f(x)$ for $Zr_{1-x}Ce_xTiO_4$ is well expressed within Fig. 3 and has a linear shape. This proves that a solid solution is formed within the above mentioned composition. ϵ_r probably increases with Ce^{4+} content as the value of ϵ_r of CeO_2 (20) is higher than the one of ZrO_2 (8-9). The dielectric permittivity of $ZrCe_xTi_{1-x}O_4$ poorly depends on the composition (x). This may be due to the presence of an inter crystalline phase rich in CeO_2 and TiO_2 . In such cases the influence of additions is poorly expressed. It is likely for dielectric losses (see Fig. 3).

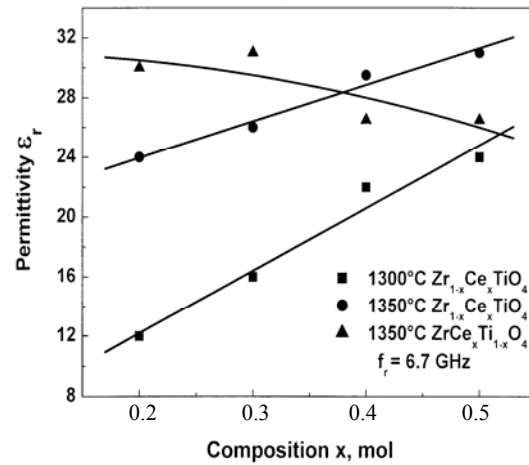


Fig. 2. Evolution of ϵ_r as a function of the composition (x) in $Zr_{1-x}Ce_xTiO_4$ and $ZrCe_xTi_{1-x}O_4$ system.

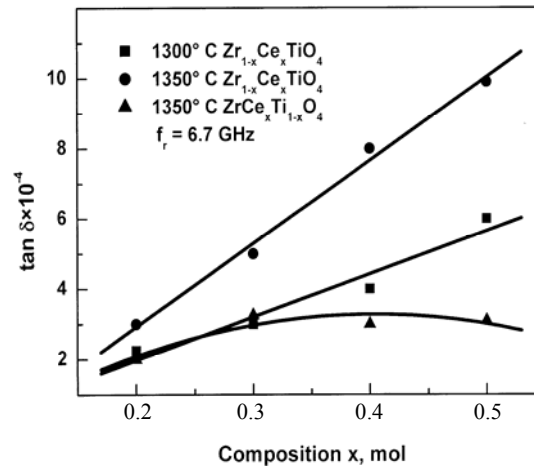


Fig. 3. $\tan \delta$ as a function of (x) in $Zr_{1-x}Ce_xTiO_4$ and $ZrCe_xTi_{1-x}O_4$ system.

As seen on Fig. 3, for $ZrCe_xTi_{1-x}O_4$ $\tan \delta$ stays low $(2-3) \times 10^{-4}$ and do not depend on the composition (x). As for the quality factor Q_f - Fig. 4, it can be seen that the compositions with high Q_f value are the ones that possess small quantity of CeO_2 ($x < 0.25$). Furthermore the increase in dielectric losses can be related to the presence of a cation with variable valence (Ce^{4+} , Ce^{3+}).

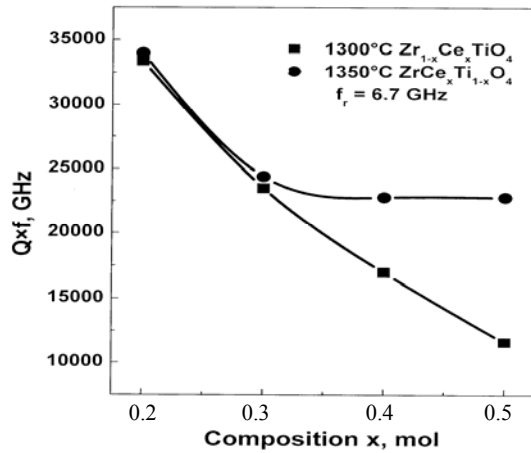


Fig. 4. Evolution of Q_f with the composition (x).

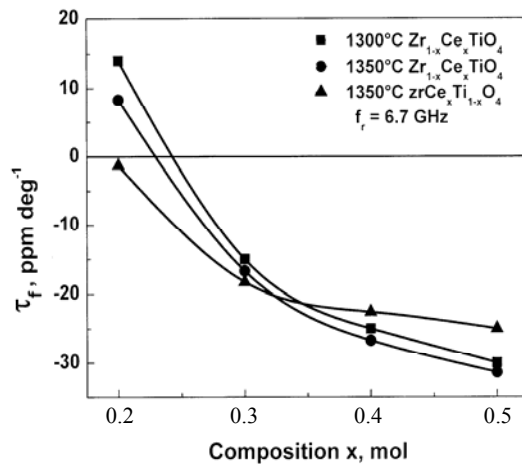


Fig. 5. Evolution of τ_f with the composition (x).

Fig. 5 shows that for both compositions, the temperature coefficient tends to zero for x (0.20-0.25) due to the compensation of the present phases with opposite signs.

4. Conclusions

The X-ray analysis show that in the ZrO₂-CeO₂-TiO₂ system, a Zr_xCe_yTi_zO₄ solid solution is formed as well as small quantities of secondary phases (CeO₂ or Zr₂Ce₂O₇-Ti₂Ce₂O₇). Their characteristic lines are too close to be distinguished.

The partial substitution of Zr⁴⁺ for Ce⁴⁺ or Ti⁴⁺ for Ce⁴⁺ lower the sintering temperatures (from 1600 °C for ZrTiO₄ to 1300 - 1350 °C) without a significant deterioration of the microwave parameters.

The temperature annealing of τ_f ($\tau_f \rightarrow 0$) is done at $x = 0.24-0.25$ for both substitutions.

The optimal parameters for both compositions are achieved at sintering temperature 1350 °C/3hrs, where $\epsilon_r = 30$, $\tan\delta = 2-3 \times 10^{-4}$ and $\tau_f \rightarrow 0$.

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