

Microwave properties of ZrTiO₄ with partial substitution of Zr⁴⁺ and Ti⁴⁺ for Ce⁴⁺

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The ZrTiO₄ 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 ZrTiO₄ (ZT) with zero τ_f , there have often been made substitutions of Zr⁴⁺ for Sn⁴⁺ - the material ZST, and for lowering the sintering temperature, different sintering aids such as ZnO, CuO, V₂O₅ 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 Zr⁴⁺ or Ti⁴⁺ for Ce⁴⁺. It has been revealed that for small concentrations of CeO₂ 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 ZrTiO₄ 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 Zr⁴⁺ for Sn⁴⁺ respectively SnO₂, the material ZST (Zr_{0.8}Sn_{0.2}TiO₄) 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}TiO₄ and Zr_{0.75}Hf_{0.25}TiO₄ [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% V₂O₅. 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 Ca²⁺-Ti⁴⁺ 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 Zr⁴⁺ and Ti⁴⁺ for Ce⁴⁺, 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 Zr⁴⁺ for Ce⁴⁺

(Zr_{1-x}Ce_xTiO₄), and Ti⁴⁺ for Ce⁴⁺ (ZrCe_xTi_{1-x}O₄).

According to Aguila [13] in the system ZrO₂ – CeO₂ – TiO₂ a solid solution (Zr_xCe_yTi_zO₂) occurs at x+y+z=1, much alike ZrTiO₄, with possible presence of phases like ZrO₂, TiO₂ and Zr₂Ce₂O₇.

2. Experimental procedures

As starting materials, we used ZrO₂ Fluka, TiO₂ Kronos, CeO₂ Fluka with purity 98-99 %. The weights of the initial oxides are calculated according to the formula Zr_{1-x}Ce_xTiO₄ and ZrCe_xTi_{1-x}O₄.

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 Kolemann 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 ZrTiO₄. There is a small quantity of CeO₂ or

$\text{Zr}_2\text{Ce}_2\text{O}_7$ phase (their characteristic lines are too close, to be clearly separated).

According to Aguilla [14] in the system $\text{ZrO}_2\text{-CeO}_2\text{-TiO}_2$ 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 .

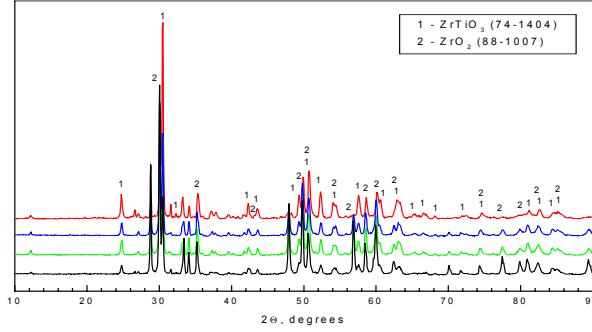


Fig. 1. XRD pattern of $\text{ZrCe}_x\text{Ti}_{1-x}\text{O}_4$ composition sintered at 1350°C .

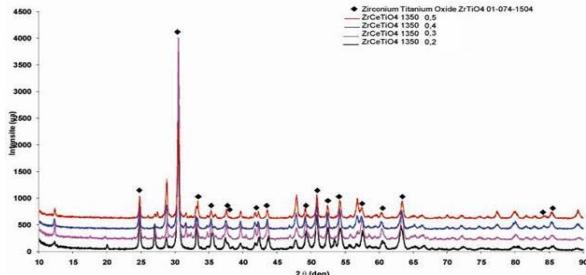


Fig. 1 bis. XRD pattern of $\text{Zr}_{1-x}\text{Ce}_x\text{TiO}_4$ composition sintered at 1350°C .

- *Microwave parameters*

Fig. 2 below shows that ϵ_r increases with Ce^{4+} content. The function $\epsilon_r = f(x)$ for $\text{Zr}_{1-x}\text{Ce}_x\text{TiO}_4$ 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 $\text{ZrCe}_x\text{Ti}_{1-x}\text{O}_4$ 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).

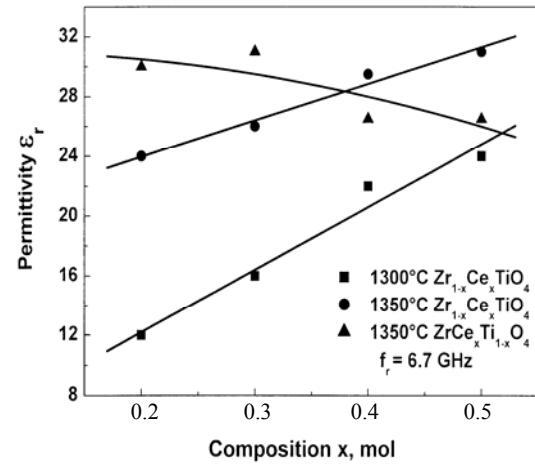


Fig. 2. Evolution of ϵ_r as a function of the composition (x) in $\text{Zr}_{1-x}\text{Ce}_x\text{TiO}_4$ and $\text{ZrCe}_x\text{Ti}_{1-x}\text{O}_4$ system.

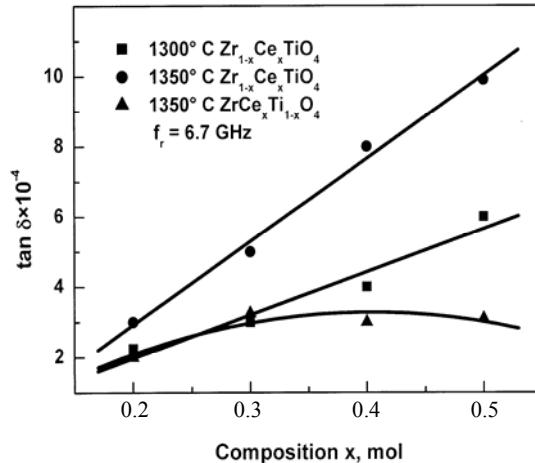


Fig. 3. $\tan\delta$ as a function of (x) in $\text{Zr}_{1-x}\text{Ce}_x\text{TiO}_4$ and $\text{ZrCe}_x\text{Ti}_{1-x}\text{O}_4$ system.

As seen on Fig. 3, for $\text{ZrCe}_x\text{Ti}_{1-x}\text{O}_4$ $\tan\delta$ 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 ($\text{Ce}^{4+}, \text{Ce}^{3+}$).

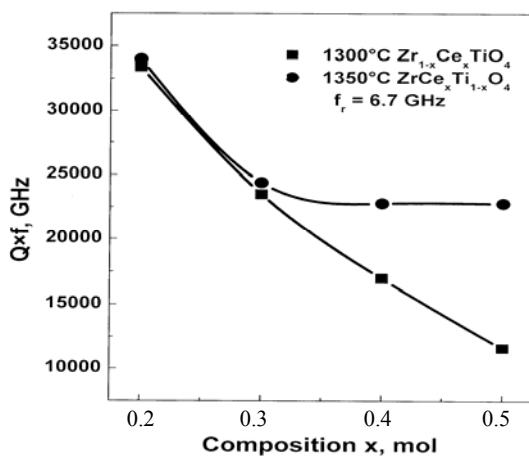


Fig. 4. Evolution of Q_f with the composition (x).

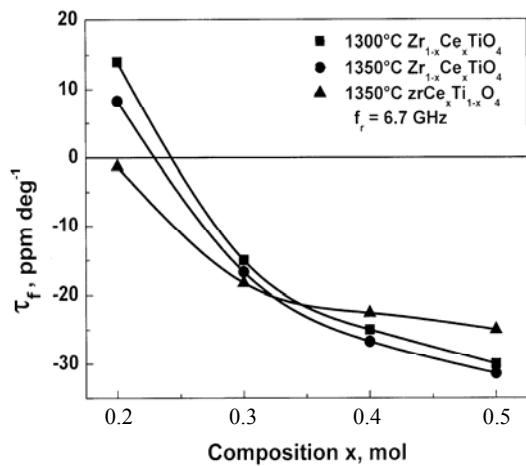


Fig. 5. Evolution of τ_f with the composition (x).

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 ZrO_2 - CeO_2 - TiO_2 system, a $Zr_xCe_yTi_zO_4$ solid solution is formed as well as small quantities of secondary phases (CeO_2 or $Zr_2Ce_2O_7$ - $Ti_2Ce_2O_7$). Their characteristic lines are too close to be distinguished.

The partial substitution of Zr^{4+} for Ce^{4+} or Ti^{4+} for Ce^{4+} lower the sintering temperatures (from 1600 °C for $ZrTiO_4$ 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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