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Temperature-stable dielectric ceramics with nominal composition of $Ca_6Ti_2Ta_8O_{30}$

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Abstract

The dielectric ceramics with nominal composition of $Ca_6Ti_2Ta_8O_{30}$ were synthesized and characterized. The cubic $CaTa_2O_6$ major phase combined with minor amount of $CaTiO_3$ were formed in the present ceramics, and this differed from the similar compositions of $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$, which had the filled tungsten bronze structure. The present ceramics indicated a high dielectric constant of 85–86 with a small temperature coefficient of dielectric constant of +24–29 ppm/°C together with a dielectric loss of 0.0056–0.0060 (at 1 MHz). The dielectric constant was almost a constant, while the dielectric loss and temperature coefficient of dielectric constant were sensitive to the sintering conditions. The present ceramics might be promising in temperature compensated capacitor applications.

Keywords: Dielectric ceramics; Dielectric properties

1. Introduction

The dielectric ceramics with high dielectric constant, low dielectric loss, and small temperature coefficient of dielectric constant are very important, due to the applications in microelectronics and microwave communication systems.[1–8] Recently, a number of dielectrics with filled tungsten bronze structure have indicated promising characteristics fitting these needs.[5–8]

In the previous work,[9] we have synthesized $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$ with filled tungsten bronze structure, which revealed high dielectric constant (170–180), low dielectric loss (in the order of 10^{-4} at 1 MHz) and relatively low temperature coefficient of dielectric constant. So, it is an interesting issue to investigate the structure and dielectric characteristics for the similar nominal composition of $Ca_6Ti_2Ta_8O_{30}$ (exactly, $6CaO\cdot 2TiO_2\cdot 4Ta_2O_5$).

In the present work, preparation of the $Ca_6Ti_2Ta_8O_{30}$ ceramics is attempted using solid state reaction approach, and their dielectric properties and microstructure are investigated. To this new composition, the tungsten bonze structure is unstable and a complex phase structure is detected.

2. Experimental procedures

$6CaO\cdot 2TiO_2\cdot 4Ta_2O_5$ ceramics were prepared from reagent-grade $CaCO_3$ (99%), Ta_2O_5 (99.99%), and TiO_2 (99.5%) raw powders using a solid state reaction approach. The raw powders were fully mixed through ball milling with zirconia media in distilled water for 24 h, then calcined in a high-purity alumina crucible at 1325 °C in air for 3 h after drying. A second attrition grinding was performed to reach a homogeneous granulometric distribution after calcination. Added with PVA, the re-milled powders were pressed into the cylindrical compacts of 12 mm in diameter and 2–5 mm in height under 98 MPa. These disks were sintered at 1400–1475 °C in air for 3 h to create dense $6CaO\cdot 2TiO_2\cdot 4Ta_2O_5$ polycrystalline samples. The samples were cooled at a rate of 2 °C/min from sintering temperature to 1100 °C, and then cooled with the furnace.

The crystal structure was identified by powder X-ray diffraction (XRD) analysis with Cu Kα radiation, and the microstructures were evaluated by scanning electron microscopy (SEM) on the polished and thermal-etched surfaces. For dielectric characterization, the silver paste was used as electrodes. It was blushed on each side of the ceramic discs and fired at 500 °C in air for 30 min. Dielectric properties at room temperature of the present ceramics were measured with an LCR meter (HP4284A). Microwave dielectric properties were measured by Hakki and Coleman's dielectric resonator method.[10]

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3. Results and discussion

Wakiya et al.[11] have used tolerance factor indicating stability of the compositions with tungsten bronze structure. The general formula are:

$$t_{A1} = \frac{r_{A1} + r_O}{\sqrt{2}(r_B + r_O)},$$

$$t_{A2} = \frac{r_{A2} + r_O}{\sqrt{23 - 12\sqrt{3}}(r_B + r_O)}, \qquad t = \frac{t_{A1} + 2t_{A2}}{3}$$

The more the tolerance factor is near to 1, the more stable the tungsten bronze structure is. Generally, the compositions become unstable when the tolerance factor is smaller than 0.95. According to calculation, the tolerance factor of hypothetical $Ca_6Ti_2Ta_8O_{30}$ is 0.92, which make the tungsten bronze structure unstable.

Fig. 1 shows the XRD patterns for $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ ceramics. Apparently, the present ceramics are significantly different from the similar compositions of $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$, which form the tetragonal tungsten bronze structure. While most peaks in the XRD patterns for the present ceramics can be assigned to the cubic $CaTa_2O_6$ (JCPDS card no. 74-1835), and some minor peaks ($2\theta = 25.8°$, $38.5°$ and $48.3°$) belong to the secondary phase of $CaTiO_3$. The $CaTa_2O_6$ structure consists of eight TaO_6 octahedral sharing corners. The center of the eight TaO_6 octahedral is Ca^{2+}, i.e. the number of the O^{2-} nearest to the Ca^{2+} is 12.[12]

The SEM micrographs of the polished and thermal etched surfaces of the present ceramics confirmed that the dense ceramics can be obtained by sintering at 1400–1475 °C in air (Fig. 2). The fine isometric grain morphology is observed in the present ceramics, and the grain size increases with increasing sintering temperature. From the SEM micrograph of the ceramics sintered at 1475 °C, we can see small pores between the large grains.

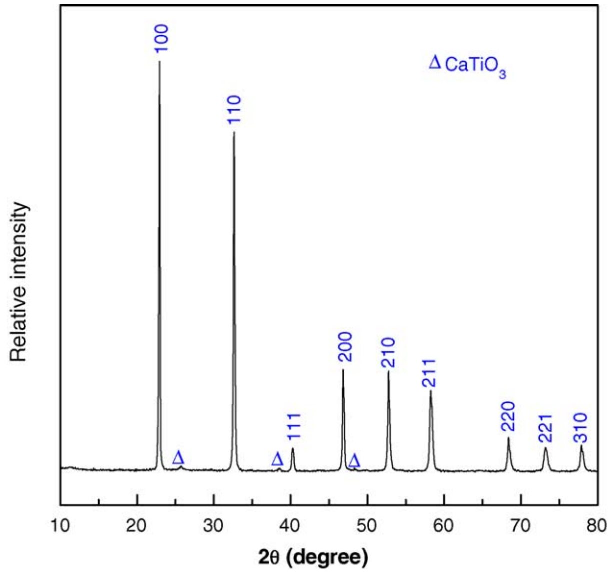

Fig. 1. XRD patterns of $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ ceramics indicating $CaTa_2O_6$ major phase combined with minor amount of $CaTiO_3$.

The room-temperature dielectric properties of the present ceramics compared with those of the similar composition of $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$ are shown in Table 1. Generally, the present ceramics indicate high dielectric constant and low dielectric loss together with a small temperature coefficient of dielectric constant. The dielectric constant is almost a constant, and the dielectric loss and temperature coefficient of dielectric constant are sensitive to the sintering conditions. Compared with the tungsten bronze ceramics, the present ceramics has a small dielectric constant (~85) than those of $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$ ceramics, which are 174 and 180, respectively. The dielectric loss of the present ceramics is in order of 10^{-3} at 1 MHz, while those of $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$

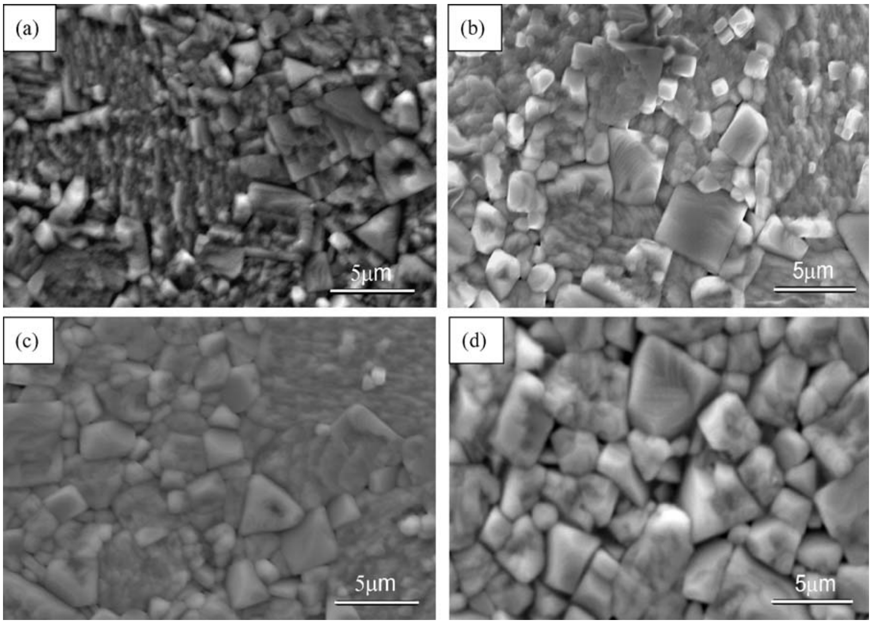

Fig. 2. SEM micrographs of polycrystalline $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ sintered at (a) 400 °C, (b) 1425 °C, (c) 1450 °C and (d) 1475 °C.

Table 1
Room temperature dielectric properties (at 1 MHz) of polycrystalline $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$, $Ba_6Ti_2Ta_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$

Composition	Sintering conditions (°C/3 h)	ε	$\tan\delta$	τ_ε (ppm/°C)
$6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$	1400	84	0.0059	29
$6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$	1425	86	0.0056	24
$6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$	1450	85	0.0061	27
$6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$	1475	86	0.0057	22
$Ba_6Ti_2Ta_8O_{30}$	1400	172	0.000417	−1646
$Ba_6Ti_2Ta_8O_{30}$	1425	173	0.000235	−1639
$Ba_6Ti_2Ta_8O_{30}$	1450	174	0.000271	−1634
$Sr_6Ti_2Ta_8O_{30}$	1400	174.5	0.000393	−1535
$Sr_6Ti_2Ta_8O_{30}$	1425	180	0.000105	−1551
$Sr_6Ti_2Ta_8O_{30}$	1450	178	0.00022	−1547

are in order of 10^{-4} at 1 MHz. With the decreasing of ionic radii from Ba to Ca, the tolerance factor of the similar compositions of $Ba_6Ti_2Ta_8O_{30}$, $Sr_6Ti_2Ta_8O_{30}$ and hypothetical $Ca_6Ti_2Ta_8O_{30}$ decreases from 1.01 to 0.92, which leads to the unstable tungsten bronze structure in $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ ceramics, and therefore the $CaTa_2O_6$ major phase combined with minor amount of $CaTiO_3$ is observed.

Fig. 3 shows the dielectric properties as function of frequency, for the present ceramics sintered at the optimal sintering temperature. The dielectric constant is nearly frequency-independent, except the frequencies below 100 kHz, and the dielectric loss has the same tendency with dielectric constant. As shown in Fig. 4, there is no significant peak and the dielectric constant of present ceramics is almost temperature-stable. The variation of dielectric loss with temperature is also small. These suggest an apparent paraelectric nature for the present ceramics at the temperature above −60 °C.

The microwave dielectric properties of the present ceramics at 4.4 GHz are obtained as: $\varepsilon = 83.1$, $\tan\delta = 0.0105$ and $Q \times f = 421$ GHz. Dielectric loss at microwave frequency is too large due to the frequency dispersion, and the present ceram-

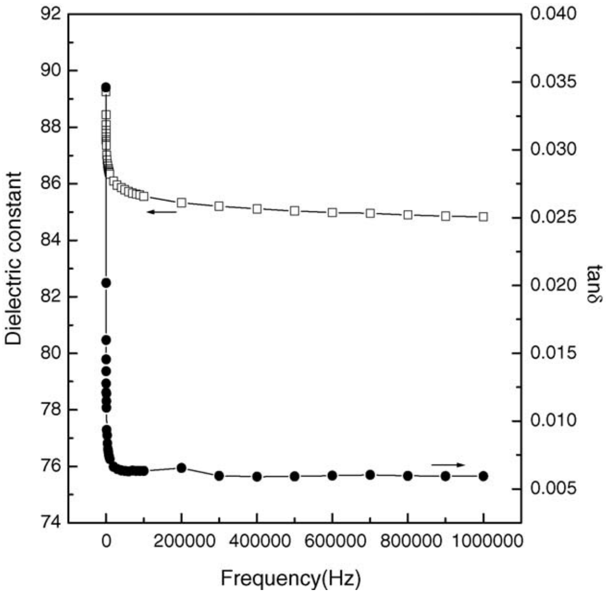

Fig. 3. Room temperature dielectric properties of polycrystalline $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ (sintered at 1400 °C) as function of frequency.

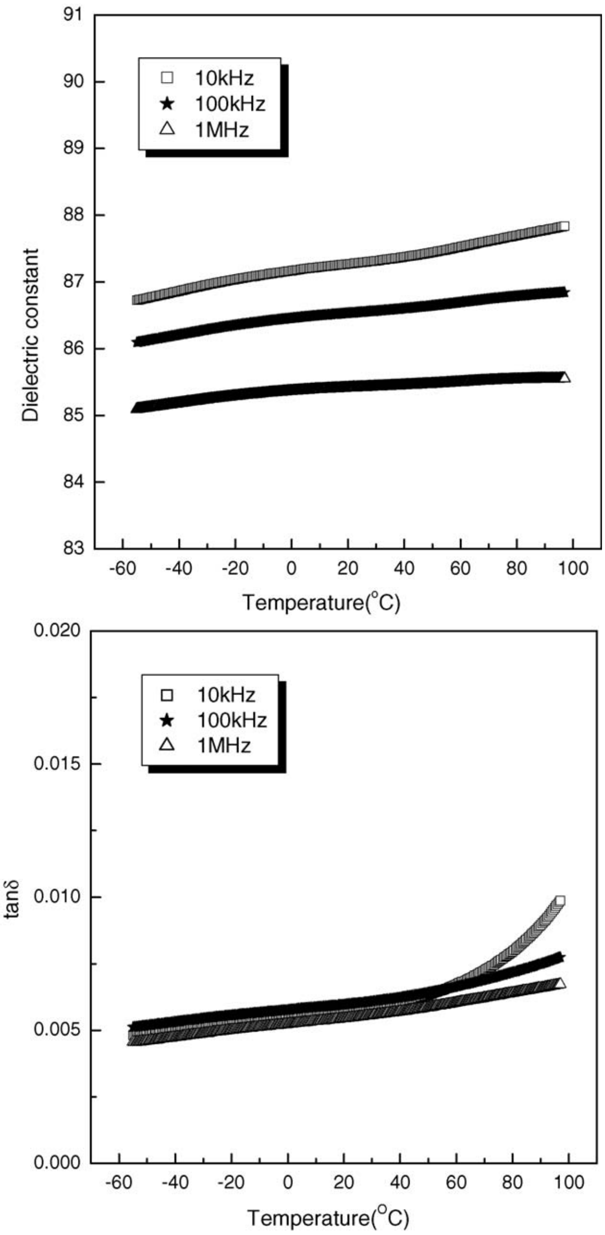

Fig. 4. Dielectric properties of polycrystalline $6CaO{\cdot}2TiO_2{\cdot}4Ta_2O_5$ (sintered at 1400 °C) as function of temperature.

ics are not suitable for microwave applications unless the $Q \times f$ can be significantly improved. Even though, considering the near-zero temperature coefficient of dielectric constant together with the high dielectric constant and low dielectric loss at 1 MHz, the present dielectrics would be promising in the temperature compensated capacitors and high frequency applications.

4. Conclusion

The temperature-stable dielectric ceramics with nominal composition of $Ca_6Ti_2Ta_8O_{30}$ were prepared and characterized. The tungsten bronze structure is unstable for the present composition, and the cubic $CaTa_2O_6$ major phase combined with minor amount of $CaTiO_3$ are observed. The present ceramics indicate a high dielectric constant of 85–86 with a small temperature coefficient of dielectric constant of +24–29 ppm/°C together with a dielectric loss of 0.0056–0.0060 (at 1 MHz). The present materials would be expected in the temperature compensated capacitors and high frequency applications.

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