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Ca_3WO_6: a novel microwave dielectric ceramic with complex perovskite structure

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Abstract Present work introduces a novel Ca_3WO_6 microwave dielectric ceramic with a complex perovskite structure. The Ca_3WO_6 ceramic was prepared by solid state reaction method and can be well densified at above 1,260 °C for 2 h in air. All the XRD patterns can be fully indexed as a single-phase monoclinic structure (space group $P2_1/n$). The sharp Raman vibration mode at 810 cm^{-1} suggests the long range order in the Ca_3WO_6 structure. The best microwave dielectric properties can be obtained in ceramic sample sintered at 1,275 °C for 2 h with a permittivity ~15.3, a Qf value ~29,200 GHz and a TCF value about −30 ppm/°C. Applying the oxide additivity rule, the calculated permittivity agrees well with the measured value. This kind of ceramic might have some potential value for microwave application for its good microwave dielectric behavior. The $(Ca_{1/2}W_{1/2})$ complex cations holding the site of Ti^{4+} in perovskite structure would introduce many new systems in complex perovskite compounds in the future.

1 Introduction

Owing to the simplicity of the crystal structure, the compounds with ordered perovskite structure are particularly suitable as model compounds for fundamental studies of certain physical properties [1–3]. Studies for the compounds A_2BWO_6, in which A and B are bivalent ions, are only a little. The A^{2+} ions are in 12-coordination (Ca^{2+}-site in perovskite, $CaTiO_3$). The B^{2+} and W^{6+} ions are in 6-coordination (Ti^{4+}-site in perovskite). The B^{2+} and W^{6+} ions are ordered in such a way that every WO_6 octahedron has only BO_6 octahedra as nearest neighbor [4, 5]. With the development of microwave communication, many kinds of microwave dielectric ceramics have been investigated [6–11]. The search for new microwave materials is still continuing and a hot topic. Recently, the crystalline structure and microwave dielectric properties of complex perovskite $A(B_1B_2)O_3$ with $(Li_{2/5}W_{3/5})$ and $(Mg_{1/2}W_{1/2})$ substituting for B site Ti^{4+} have been studied in many works [12–15]. The substitution of $(Li_{2/5}W_{3/5})$ and $(Mg_{1/2}W_{1/2})$ can modify the temperature coefficient of resonant frequency to near zero for microwave applications.

The present work is focused on the sintering behavior, microstructure and microwave dielectric properties of Ca_3WO_6 composition with ordered perovskite structure, which can also be written as $Ca(Ca_{1/2}W_{1/2})O_3$, and their relationship. The Clausius-Mossotti relation and influence of porosity were also considered to calculate the microwave dielectric constant of Ca_3WO_6 ceramic.

2 Experimental procedure

Proportionate amounts of reagent-grade starting materials of $CaCO_3$ (>99%, Guo-Yao Co. Ltd., Shanghai, China) and WO_3 (>99%, Tianjin, China) were prepared according to Ca_3WO_6 composition. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, China) with the Zirconia balls (2 mm in diameter) as milling media. The mixed oxides were calcined at 1,000 °C

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for 4 h. After being crushed and re-milled for 5 h using ZrO_2 balls and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2 with PVA binder addition. Green samples were sintered at temperature range from 1,200 to 1,315 °C for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2,400 X-ray diffractometry, Japan). Microstructures of sintered ceramic were observed on the as-fired surface and fractured surface respectively with scanning electron microscopy (SEM) (JEOL JSM-6460, Japan) coupling with energy-dispersive X-ray spectroscopy (EDS). The apparent densities of sintered ceramics were measured by Archimedes' method. Raman spectrum was obtained using a Raman spectrometer (ALMEGA 1110, Nicolet, Wisconsin, Madison, USA). The microscope attachment was an Olympus BX50 system and the excitation wavelength used was 532 nm from a Nd:YVO_4 laser source. Dielectric behaviors at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated by the following formula:

$$\mathrm{TCF} = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

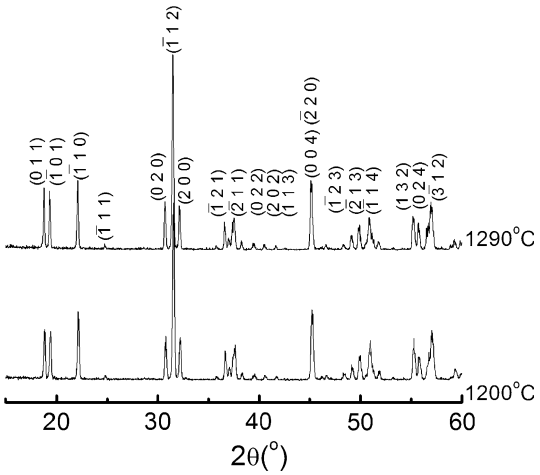

Fig. 1 XRD patterns of Ca_3WO_6 ceramics sintered at 1,200 and 1,290 °C for 2 h

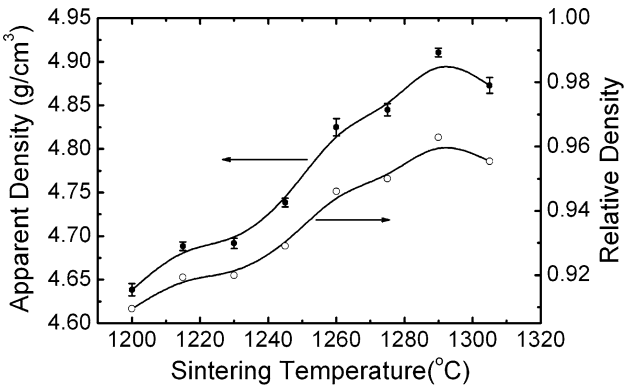

Fig. 2 Apparent density and relative density of Ca_3WO_6 ceramics sintered at different temperatures

3 Results and discussion

Figure 1 shows the XRD patterns of Ca_3WO_6 ceramics sintered at 1,200 and 1,290 °C for 2 h. All the patterns can be fully indexed as a single-phase monoclinic structure (space group $P2_1/n$), suggesting the complete reaction between $CaCO_3$ and WO_3. The lattice parameters were calculated as $a = 5.5498$ Å, $b = 5.8078$ Å, $c = 8.0092$ Å. These values are in close agreement with those reported in PDF card 22-0541. The theoretical density of Ca_3WO_6 calculated from the XRD results was about 5.11 g/cm^3. The apparent density of Ca_3WO_6 ceramics as a function of sintering temperature is shown in Fig. 2. After being sintered at above 1,260 °C for 2 h, the Ca_3WO_6 ceramics get a density larger than 4.84 g/cm^3, which is equivalent to a relative density above 95%. The bulk density gets a maximum value of 4.91 g/cm^3 at 1,290 °C and the relative density is about 96%. The SEM micrographs of the as-fired surface and fractured surface of Ca_3WO_6 ceramics are shown in Fig. 3. The dense microstructure with little pores can be observed from the SEM result. Grain sizes scatter in a very broad range between 5–30 μm, which might be caused by secondary growth of grains. The EDS measurement shows that all the grains possess similar composition. The atom ratio of Ca to W is near to 3:1, as shown in Fig. 3(c). It confirms that the real composition of the samples is Ca_3WO_6, which is the same with the designed composition.

Figure 4 shows the Raman spectrum in the range of 110–1,100 cm^{-1} for Ca_3WO_6 ceramic sample. From the viewpoint of the lattice vibration, the structure of Ca_3WO_6 with a space group $P2_1/n$ [16] is of the double perovskite-type $A_2B'B''O_6$ where A = B′ = Ca and B″ = W. It presents a rock salt type B-cation sublattice with alternating CaO_6 and WO_6 octahedra. Thus the predicted vibrational modes correspond to their reducible representations at the zone center:

$$\Gamma = 12A_g(R) + 12B_g(R) + 17A_u(IR) + 16B_u(IR) \quad (2)$$

where $12A_g$ and $12B_g$ are the Raman active modes and $17A_u$ and $16B_u$ are the Infrared (IR) active modes. In the

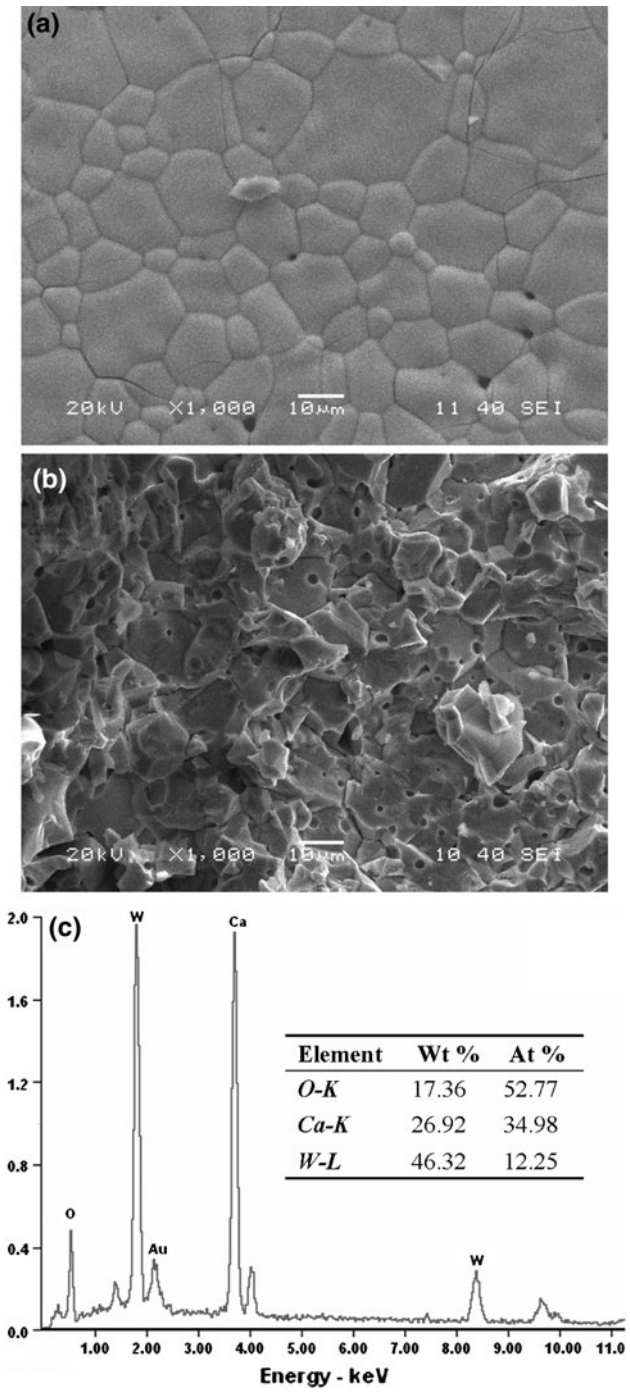

Fig. 3 SEM micrographs of as-fired surface **a**, fractured surface **b** and EDS spectrum **c** of Ca_3WO_6 ceramics sintered at 1,275 °C for 2 h

present work, five strong peaks at 810, 580, 462, 250, and 130 cm^{-1} and several weaker features are observed (as shown in Fig. 4). In particular, the position of the band at 810 cm^{-1} suggest that its nature is similar to the band A_{1g} (825 cm^{-1}) mode observed in other ordered complex perovskites, such as $SrMg_{1/3}Mb_{2/3}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$ [17, 18]. Zheng et al. [17] studied the long-range order

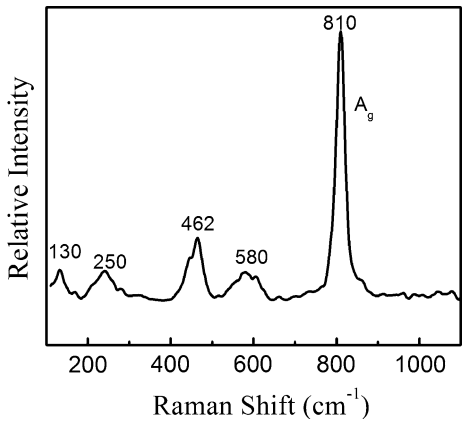

Fig. 4 Raman spectrum of Ca_3WO_6 ceramic sintered at 1,275 °C for 2 h

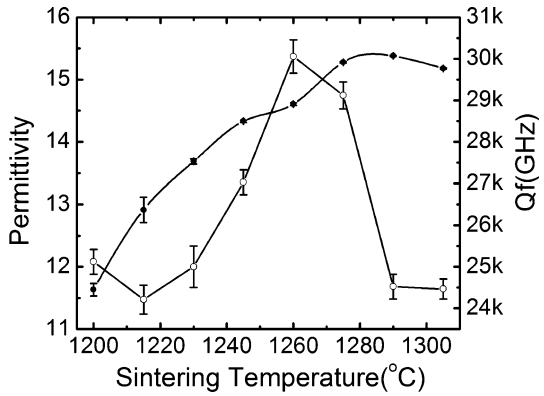

Fig. 5 Microwave dielectric constant and Qf values of Ca_3WO_6 ceramic as a function of sintering temperature

(LOR) and short-range order (SOR) in detail and it was concluded that a sharp A_{1g} mode indicated LRO but that the width of the A_{1g}, once LRO was destroyed, represented the degree of SOR. In this work, the sharp vibration mode at 810 cm^{-1} suggests the LOR in the Ca_3WO_6 structure, and I. Levin et al. [19] related it to the oxygen motion which can be represented as symmetric "breathing" of the BO_6 octahedra resulting from cation ordering on the B sites.

Microwave dielectric permittivity and Qf values of the Ca_3WO_6 ceramic as a function of sintering temperature are shown in Fig. 5. The calculated microwave dielectric properties and measured values are also listed in Table 1. The microwave dielectric permittivity of Ca_3WO_6 ceramic reached a saturated value when sintering temperature increased to about 1,275 °C as shown in Fig. 5, which corresponded well with the trend of density. The Qf values of samples sintered at 1,260 and 1,275 °C got maximum values and it decreased sharply with the further increase of sintering temperature. The best microwave dielectric properties were obtained in ceramic sample sintered at 1,275 °C for 2 h with a dielectric permittivity ~15.3, a Qf value ~29,200 GHz and a TCF value about −30 ppm/°C.

Table 1 Density and microwave dielectric properties of Ca_3WO_6 ceramics

ST (°C)	Density (g/cm^3)	RD	ε_{meas}	ε_{cal}	Qf (GHz)	TCF (ppm/°C)
1,275	4.84	0.95	15.3	12.38	29,200	−30
1,290	4.91	0.96	15.4	12.61	24,700	−32
1,315	4.87	0.96	15.2	12.47	24,500	−32

ST sintering temperature, *RD* relative density

The molecular dielectric polarizability α_x, which contains both ionic and electronic components, could be calculated from the dielectric permittivity and the molar volume, V_x in Å^3, using the Clausius-Mossotti relation.

$$\alpha_x = \frac{V_x \times (\varepsilon_x - 1)}{b \times (\varepsilon_x + 2)} \quad (3)$$

where b is assumed to be $4\pi/3$ for a cubic material and ε_x is the dielectric permittivity. Shannon and Subramanian et al. [20–25] pointed out that while this equation is strictly valid only for compounds where the molecule has cubic symmetries, it can also be used as a good approximation to many non-cubic materials.

The dielectric polarizability for Ca_3WO_6 follows the oxide additivity rule [26]:

$$\alpha(Ca_3WO_6) = 3 \times \alpha_{Ca^{2+}} + \alpha_{W^{6+}} + 6\alpha_{O^{2-}} \quad (4)$$

where $\alpha_{Ca^{2+}}$, $\alpha_{W^{6+}}$ and $\alpha_{O^{2-}}$ are the polarizabilities of Ca^{3+}, W^{6+} and O^{2-} respectively. Using the Clausius-Mossotti relationship, polarizabilities suggested by Shannon [24] and Yoon [27] ($\alpha_{Ca^{2+}} = 3.16$ Å^3, $\alpha_{W^{6+}} = 3.2$ Å^3 and $\alpha_{O^{2-}} = 2.01$ Å^3), and the cell volumes, the dielectric permittivity ε_{cal} of Ca_3WO_6 could be calculated and listed in Table 1 with the measured values. The dielectric permittivities in the Table 1 were corrected by following equation to eliminate the influence of pores in ceramics:

$$\varepsilon_r = \varepsilon^{meas} \times (1 + 1.5P) \quad (5)$$

where p is the porosity [28]. The calculated and measured dielectric permittivities showed agreement with each other with a relative error smaller than 20%. The oxide additivity rule can only give some approximate result and the deviations from the measured results might be attributed to the specific crystalline structure of the compound.

4 Conclusions

A novel Ca_3WO_6 microwave dielectric ceramic with a complex perovskite structure was prepared via the solid state reaction method. The Ca_3WO_6 ceramic can be well densified at 1,260 °C and got a relative density above 95%. The best microwave dielectric properties have been obtained in ceramic sample sintered at 1,275 °C for 2 h with a permittivity ~15.3, a Qf value ~29,200 GHz and a TCF value about −30 ppm/°C. This kind of ceramic can be a candidate for microwave application and $(Ca_{1/2}W_{1/2})$ holding the site of Ti^{4+} in perovskite structure would introduce many new systems in complex perovskite compounds.

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