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Letter

A new $Li_{0.5}Sm_{0.5}WO_4$ low temperature firing microwave dielectric ceramic

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ABSTRACT

Present work introduces a new kind of low temperature sintering microwave dielectric ceramic of $Li_{0.5}Sm_{0.5}WO_4$. $Li_{0.5}Sm_{0.5}WO_4$ ceramic can be prepared by the solid-state reaction method and be well densified in the temperature range from 750 °C to 850 °C for 0.5–6 h in air. The compound crystallizes in the single-phase tetragonal system ($I41/a$) with unit cell parameter $a = 5.22211(9)$ Å, $c = 11.3220(9)$ Å, $V = 308.6(5)$ Å^3 and $Z = 4$. The best microwave dielectric properties can be obtained in ceramic sintered at 800 °C for 2 h with permittivity about 17.0, $Q \times f$ about 5792 GHz and TCF about 86.7 ppm/°C. The additions of $Li_{0.5}Sm_{0.5}WO_4$ not only can reduce the sintering temperature, but also can adjust the TCF values of $ZnWO_4$ to near-zero.

1. Introduction

Rapid development in wireless communication systems has increased demand for the miniaturization of components such as band pass filters and local oscillators. Low temperature co-fired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high density, high RF and fast digital applications requiring hermetical packaging and good thermal management [1,2]. Microwave dielectric materials with low sintering temperature, high dielectric constant ε_r, low dielectric loss and near-zero temperature coefficient of resonant frequency τ_f/TCF are needed to co-fire with low-loss, low-melting-point conductors such as Ag, Cu, Au or Al.

Many materials with good microwave dielectric properties have high sintering temperature (above 1000 °C) such as $ZnO–Nb_2O_5$ system [3,4], $BaO–TiO_2$ system [5–7], $BaO–TiO_2–Nb_2O_5$ system [8,9], $Li_2O–Nb_2O_5–TiO_2$ system [10–13], $(Zr,Sn)TiO_4$ [14,15] and $(A_1A_2)(B_1B_2)O_3$ complex perovskite system [16–18]. To lower the sintering temperature, addition or substitution of some sintering aids, such as V_2O_5, CuO, Bi_2O_3, and B_2O_3, is an often used method. Another approach has been devoted to the use of glass-ceramic composites. However, most glasses are known to exhibit low permittivity, which makes them parasitic phases in high-permittivity systems. Recently, much attention has been attracted by the third method, which is based on many low temperature firing ceramic compounds such as the $Bi_2O_3–TeO_2$, $TiO_2–TeO_2$, $CaO–TeO_2$, $BaO–TeO_2$ binary systems, $BaO–TiO_2–TeO_2$ ternary system and $Bi_2W_2O_9$ systems [19–23]. However, they would react with Ag electrode. This problem was recently overcome for $BaTe_4O_9$ through the use of Al electrodes. However, cost of TeO_2 is rather expensive and it is poisonous. With the increasing requirements for the low temperature firing materials, there is always much interest in searching for new material systems.

In the present study, dielectric properties of a new microwave dielectric ceramics of $Li_{0.5}Sm_{0.5}WO_4$ was investigated, and the effect of crystal structure on their microwave dielectric properties were also examined.

2. Experimental procedure

Specimens of the $Li_{0.5}Sm_{0.5}WO_4$ ceramics were prepared by a conventional mixed oxide route from the high-purity oxide powders (≥99%) of Li_2CO_3, Sm_2O_3, and WO_3. Stoichiometric proportions of the above raw materials were mixed in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 650 °C for 4 h. The powders were uniaxially pressed under the pressure of about 200 MPa into disks measuring 12 mm in diameter and 6 mm in thickness. And the ceramic pellets were sintered at 750–850 °C for 0.5–6 h in air.

The crystal structures of the specimens were analyzed by an X-ray diffractometer (Rigaku D/MAX-2400, Japan) with Cu K_α radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructures observation of the samples was performed using scanning electron microscopy (JEOL JSM-6460LV, Japan). Samples were then thermally etched for 1 h at 100 °C lower than the sintering temperature and then Au coated to prevent surface charging in the microscope.

Dielectric behaviors at microwave frequency were measured in the range of 8–9 GHz by the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The specimens were placed on a low-loss quartz spacer inside a copper cavity, whose

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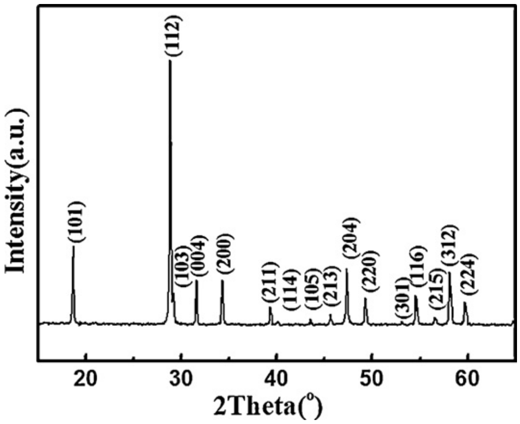

Fig. 1. XRD patterns of $Li_{0.5}Sm_{0.5}WO_4$ ceramics sintered at 800 °C for 2 h.

inner side was silver-plated. The use of low-loss single-crystal quartz spacer reduces the effect of losses due to the surface resistivity of the cavity. The diameter of the cavity was about 4 times larger than that of the sample for better isolation of the excited $TE_{01\delta}$ mode.

3. Results and discussion

Fig. 1 illustrates the room temperature XRD patterns recorded for the ceramic powders sintered at 800 °C of $Li_{0.5}Sm_{0.5}WO_4$ using CuK_α radiation. The pattern is similar and matches with that for $CaWO_4$ (Powder Diffraction File No 41-1431). All peaks can be indexed with the space group $I41/a$ and unit cell parameters $a = 5.2211(9)$ Å, $c = 11.3220(9)$ Å, $V = 308.6(5)$ Å^3 and $Z = 4$, refined by the least-squares method, and confirmed the powder to be pure phase. The SEM micrographs of the surfaces of $Li_{0.5}Sm_{0.5}WO_4$ ceramics are represented in Fig. 2. The dense microstructure of $Li_{0.5}Sm_{0.5}WO_4$ ceramics sintered at 750 °C for 2 h with only a little pores existing can be confirmed by the SEM result. The pores decrease with increasing the sintering temperature. The grain sizes of the samples enlargen with increasing the sintering temperature.

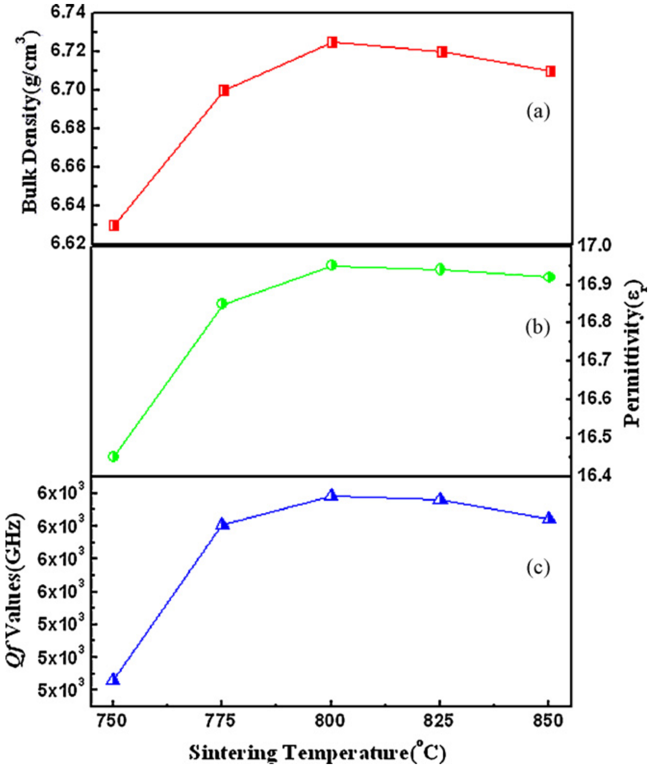

Fig. 3. Bulk density, permittivity and *Qf* values as a function of sintering temperature of $Li_{0.5}Sm_{0.5}WO_4$ ceramics.

Fig. 3 shows the bulk density, permittivity and *Qf* values of the $Li_{0.5}Sm_{0.5}WO_4$ceramics at various temperatures for 2 h. The bulk densities increase, reach the max value when the sintering temperature is 800 °C and decrease slightly with further increasing the sintering temperature. The permittivity and *Qf* values as a function of sintering temperature of $Li_{0.5}Sm_{0.5}WO_4$ ceramics present a trend similar to that between densities and sintering temperatures since a higher density means a lower porosity. The dielectric constant

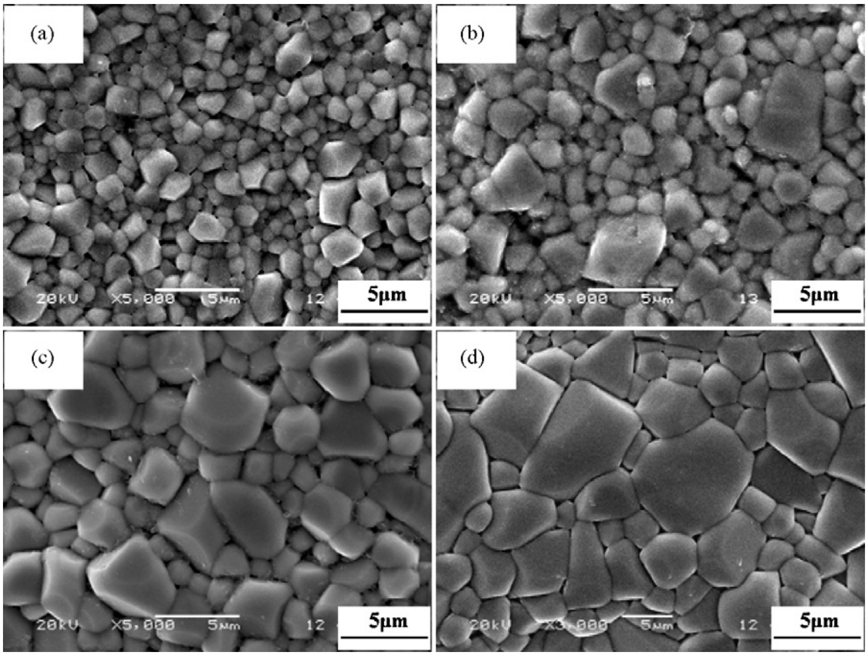

Fig. 2. SEM photographs of $Li_{0.5}Sm_{0.5}WO_4$ samples sintered at different temperature: (a) 750 °C, (b) 775 °C, (c) 800 °C, (d) 825 °C.

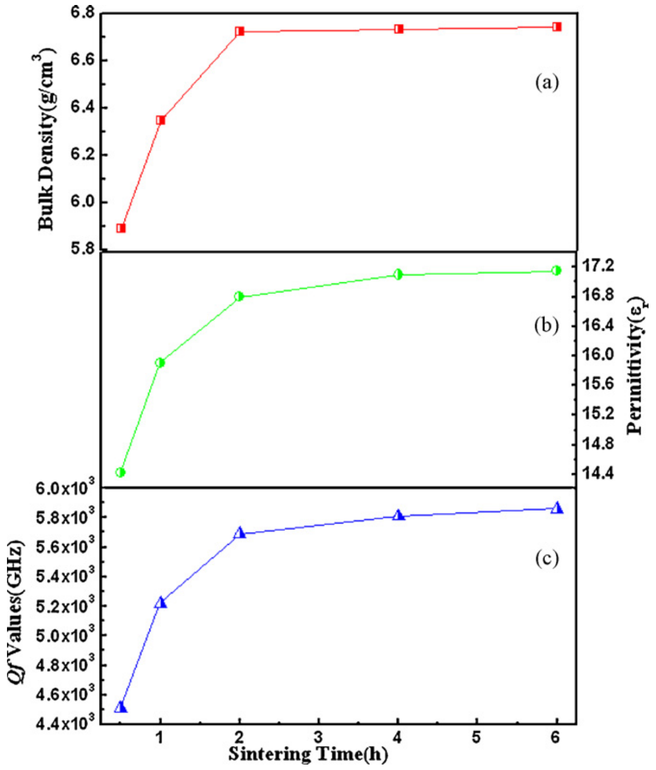

Fig. 4. Bulk density, permittivity and *Qf* values as a function of sintering time of $Li_{0.5}Sm_{0.5}WO_4$ ceramics.

first increases, reaches the peak and then decreases slightly with increasing the sintering temperature. Microwave (MW) losses in $Li_{0.5}Sm_{0.5}WO_4$ ceramics may arise from a combination of extrinsic and intrinsic factors. Intrinsic losses are essentially determined by an harmonic interactions of the electric field with the crystal phonons. The noncentrosymmetric nature of $Li_{0.5}Sm_{0.5}WO_4$ may also have deleterious effects on $Q\times f$; however, this premise needs further investigation. Nevertheless, extrinsic losses associated with microstructural imperfections, such as porosity and secondary phases, might dominate the MW losses in $Li_{0.5}Sm_{0.5}WO_4$ ceramics. Porosity is well known to adversely affect the dielectric losses at MW frequencies, whereas, secondary phases in particular ferroelectric phases are also known to increase the dielectric losses [24]. The sintering time has a great influence on the bulk density, permittivity and *Qf* values of $Li_{0.5}Sm_{0.5}WO_4$ ceramics (as shown in Fig. 4). Their values keep slow when the soak time is below 1 h, increase sharp when the soak time is more than 2 h and change slightly with further increasing the soak time.

Fig. 5 illustrates the variation of resonant frequencies in the $TE_{01\delta}$ mode of $Li_{0.5}Sm_{0.5}WO_4$ ceramic as a function of the temperature. The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \tag{1}$$

where f_T, f_0 were the resonant frequencies at the measuring temperature of T and T_0 (25 °C) respectively. The τ_f of LNT ceramics is 86.7 ppm/°C.

Finally, $Li_{0.5}Sm_{0.5}WO_4$ exhibits a positive temperature coefficient of resonant frequency (∼80 ppm/°C), therefore should be regarded as a potential component for fabrication of ceramic composites with negative TCF ceramics such as $ZnWO_4$ (TCF −60 ppm/°C) in order to design near-zero TCF ceramics. The additions of $Li_{0.5}Sm_{0.5}WO_4$ not only reduce the sintering temperature from 1100 °C to 850 °C, but also adjust the TCF values of $ZnWO_4$ to near-zero. The $0.4Li_{0.5}Sm_{0.5}WO_4$–$0.6ZnWO_4$ sample that sintered at 850 °C for 4 h exhibits good microwave dielectric properties with permittivity about 16.8, $Q\times f$ about 11,000 GHz and TCF about 5.76 ppm/°C.

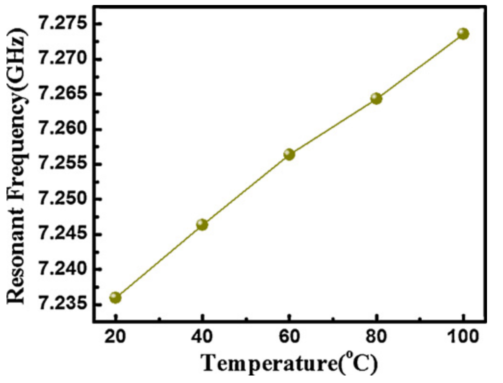

Fig. 5. Resonate frequency as a function of temperature of $Li_{0.5}Sm_{0.5}WO_4$ ceramics sintered at 800 °C for 2 h.

4. Conclusion

The new $Li_{0.5}Sm_{0.5}WO_4$ ceramic can be prepared by solid-state reaction method and be well densified in the temperature range from 750 °C to 850 °C for 0.5–6 h in air. The XRD patterns can be fully indexed as single-phase tetragonal structure ($I41/a$), with lattice parameters $a = 5.2211(9)$ Å, $c = 11.3220(9)$ Å, $V = 308.6(5)$ Å^3 and $Z = 4$. The best microwave dielectric properties can be obtained in ceramic sintered at 800 °C for 2 h with permittivity about 17, $Q\times f$ about 5792 GHz and TCF about 86.7 ppm/°C. The additions of $Li_{0.5}Sm_{0.5}WO_4$ not only reduce the sintering temperature, but also adjust the TCF values of $ZnWO_4$ to near-zero.

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