Microstructure and microwave Dielectric Properties of Sm$_{0.5}$Y$_{0.5}$VO$_4$ Ceramics

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Abstract Sm$_{0.5}$Y$_{0.5}$VO$_4$ ceramics were prepared through the solid-state reaction method. Sintering behavior and microstructure of samples were studied via scanning electron microscopy techniques, X-ray diffraction, and rietveld refinement. A purity phase with tetragonal zircon-type and dense microstructure were obtained in Sm$_{0.5}$Y$_{0.5}$VO$_4$ sintered at 1225 °C-1325 °C for 4 h. The best microwave Dielectric properties of Sm$_{0.5}$Y$_{0.5}$VO$_4$ ceramic with a dielectric constant ~10.98, a $Q\times f$ value ~ 34197 GHz, and a temperature coefficient of resonant frequency ~ -43.6 ppm/°C sintered at 1275 °C for 4 h. Sm$_{0.5}$Y$_{0.5}$VO$_4$ ceramic has excellent microwave properties. If the sintering temperature can be reduced, it may be a potential candidate for microwave devices application.

1. Introduction
A microwave dielectric ceramic whether can be used in commercial device decided by three factors, suitable dielectric constant for different frequency band, high quality factor for better frequency selectivity, a near-zero temperature coefficient of resonant frequency for stability [1-3]. Recently, V-rich compounds have been extensively studies for their intrinsic low sintering temperature and wonderful microwave dielectric properties. such as garnet vanadates NaCa$_2$Mg$_2$V$_3$O$_{12}$, Na$_2$YMg$_2$V$_3$O$_{12}$ with A$_3$B$_2$V$_3$O$_{12}$-type exhibited a dielectric constant 10-13 and excellent $Q\times f$ value in the range 40000-70000 GHz[4-6]. These Mg$_2$V$_2$O$_7$, Ba$_2$V$_2$O$_7$, Mg$_3$V$_2$Os, Ba$_3$V$_2$O$_8$, BaMg$_2$V$_2$O$_8$, MgCo$_2$V$_2$O$_8$ [7-12] ceramics discovered successively with a high performance of dielectric properties and low sintering temperature and might be suitable candidates for LTCC materials.

A$^{3+}$B$^{5+}$O$_4$-type(A=Ln, B = V) compounds have been systematically investigated because of their excellent optical, magnetic properties[13-14]. ReVO$_4$ crystallize in a tetragonal zircon-type structure with space group $I4_{1}/amd$ (Z=4) at ambient, Which composed of [ReO$_8$] dodecahedra and [VO$_4$] tetrahedral[15-17]. Re and V atoms arranged to tetragonal structure along the c axis, [ReO$_8$] Triangle dodecahedron were closely connected with common edge in a axis as shown in Fig. 1. Recently, Wang [18] reported a series of rare-earth vanadates: monoclinic LaVO$_4$ ($\varepsilon_r = 14.2$, $Q\times f = 48197$ GHz, $\tau_f = -37.89$ ppm/°C and S.T. = 850°C) and tetragonal CeVO$_4$ ($\varepsilon_r = 12.3$, $Q\times f = 41460$ GHz, $\tau_f = -34.4$ ppm/°C and S.T. = 950°C). SmVO$_4$ and NdVO$_4$[19] have been extensively investigated and possess permittivity in the range of 11 to 15, the high $Q\times f$ values (> 30000 GHz), and the temperature coefficient of resonant frequency about –40 ppm/°C sintered at 1160°C in our previous work. Compared to the rare-earth element mentioned above, the ion radius of Y$^{3+}$(0.1019 Å) is smaller. To further understand
the influence of the ion radius of rare earth elements and the substitution of A site ions on the sintering behavior and dielectric properties, hence, Sm$_{0.5}$Y$_{0.5}$VO$_4$ was designed synthesized via solid-state reaction method, the sintering behavior and microwave dielectric properties were studied in this work.

2. Experimental Procedure
The Sm$_{0.5}$Y$_{0.5}$VO$_4$ ceramics were synthesized via conventional solid-state reaction method. High-purity powders of Sm$_2$O$_3$ (99.99%), Y$_2$O$_3$ (99.99%) and NH$_4$VO$_3$ (99%) were weighed according stoichiometric amounts, the mixed powder ball-milled in ethanol with zirconia balls for 4 h and calcined at 960 °C for 4 h. Subsequently, the calcined powders were re-milled and pressed into pellets (10 mm in diameter and 6 mm in thickness) in a steel die under a pressure of 200 MPa with polyvinyl alcohol (PVA, 10 vol%) as a binder.

The ground powder were heated to 550 °C for 2 h at 1.5 °C/min heating rate to remove the organic binder and then sintered in air at 1225°C-1325°C for 4 h at a heating rate of 5°C/min.

The phase structure of the calcined and fired ceramic were detected via an X-ray diffractometer (CuK$_\alpha$1, 1.54059 Å, Model X’Pert PRO, PANalytical, Almelo, Holland), The lattice constant, cell volume and atomic site location were analyzed through Rietveld refinement method using FULLPROF software. The surface micrographs of the samples were observed via scanning electron microscopy (FE-SEM, Model S4800, Hitachi, Japan). The bulk density of the sintered samples were determined by the Archimedes method. The microwave dielectric properties were measured using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The values of temperature coefficient of resonant frequency ($\tau_f$) were calculated by the following equation in the temperature range from 25 °C–85 °C.

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$

3. Results and Discussion
Fig. 2 shows the XRD patterns of Sm$_{0.5}$Y$_{0.5}$VO$_4$ ceramics sintered at 1225°C-1325°C for 4 h. Obviously, all the diffraction peaks of Sm$_{0.5}$Y$_{0.5}$VO$_4$ matched well with the SmVO$_4$ (JCPDS 17-0876) or YVO$_4$(JCPDS 16-0250) and no additional peaks were observed, which indicating that the single-phase Sm$_{0.5}$Y$_{0.5}$VO$_4$ with a tetragonal zircon structure (space group I41/amd) were obtained. With the increasing of sintering temperature, the main peak (200) of Sm$_{0.5}$Y$_{0.5}$VO$_4$ shifted toward high diffraction angles and then toward opposite direction after their certain temperature because of the variations of interplanar crystal spacing. Further, the interplanar spacing of crystal was determined with cell parameters, Rietveld refinement method was employed to explain the variation. The refinement results of Sm$_{0.5}$Y$_{0.5}$VO$_4$ shown in Fig. 3. It can be seen that the unit cell volume decreased firstly and then increased, Which kept good consistency with the offset law of diffraction angles of main peak. The reason of cell volume increasing may be attributed by the valence alternation of V atoms, as the V$^{4+}$ has larger ionic radius than V$^{5+}$ will lead to the increment according to the study of G.G.Yao[20]. The lattice parameters of sample sintered at 1275 °C for 4h were a=b=7.262 Å, c=6.274 Å, V=c=330.87 Å$^3$ with Rwp%=15.2%, Rp%=12.6%, $\chi^2$=1.04.
Fig. 2 The XRD patterns of the ReVO₄ ceramics of the Sm₀.₅Y₀.₅VO₄ ceramics sintered at different temperature for 4h.

Fig. 3 The cell volume and lattice parameter of Sm₀.₅Y₀.₅VO₄ ceramics sintered at different temperature for 4h.

Fig. 4 presents the SEM photographs of Sm₀.₅Y₀.₅VO₄ samples sintered at 1275 °C for 4 h. It can be seen that a Homogeneous dense microstructure with grain size ranging from 8μm to 15μm was obtained. The sintering temperature is higher than SmVO₄(1160 °C)[19] may be because the melting point of Y₂O₃(2410 °C) is higher than that of Sm₂O₃(2325 °C). Fig. 5 illustrates the relative density of Sm₀.₅Y₀.₅VO₄ ceramics sintered at various temperatures. As the sintering temperature increases, the bulk densities of Sm₀.₅Y₀.₅VO₄ sample gradually increased initially and saturated at a certain temperature. The maximum bulk density of samples reached 4.56 g/cm³ (about 97% of the theoretical density ~4.71 g/cm³) fired at 1275°C. A slight decreament with further increasing sintering temperature was considered to the unusual grain growth and evaporation of vanadium. The microwave dielectric properties of Sm₀.₅Y₀.₅VO₄ ceramics as a function of the sintering temperature are plotted in Fig. 6. The dielectric constant ε_r gradually increased and achieved maximum value 10.98 with the increasing of sintering temperature and then decreased slightly. It was most probably associated with the relative densities. Meanwhile, Dielectric constant can be seen as basic macro-parameters of dielectric polarization properties, ionic polarizability played a key role of permittivity, the relation between ε_r and ionic polarizability can be described by Clausius – Mossotti equation[21]:

\[ \varepsilon_r = 1 + \frac{2bD^T/V_m}{1 - bD^T/V_m} \]

Where, V_m is the cell volume, \( D^T \) is the sum of all ionic polarizability. The calculated theoretical permittivity were 11.18, the relative error of Sm₀.₅Y₀.₅VO₄ between the measured and theoretical permittivity are among 1.7% to 5.6%. The \( Q\times f \) value of Sm₀.₅Y₀.₅VO₄ exhibiting a similar fluctuation tendency in relative densities and ε_r with the temperature variation. The maximum \( Q\times f \) value achieved
34197 GHz at 1275°C. The \( \tau_f \) value is no significant fluctuation with temperature and stabilize on -43.6 ± 0.6 ppm/°C for Sm\(_{0.5}\)Y\(_{0.5}\)VO\(_4\).

Fig. 5 The relative density of the Sm\(_{0.5}\)Y\(_{0.5}\)VO\(_4\) ceramics sintered at different temperature for 4h.

4. Conclusions
A tetragonal zircon-type Sm\(_{0.5}\)Y\(_{0.5}\)V O\(_4\) ceramic were prepared by the solid-state reaction method. The pure-phase and dense microstructure Sm\(_{0.5}\)Y\(_{0.5}\)VO\(_4\) ceramic obtained with an \( \varepsilon_r \) of 10.98, a \( Q \times f \) value of 34197 GHz, and a \( \tau_f \) value of -43.6 ppm/°C sintered at 1275°C for 4h. If the sintering temperature can be reduced, it may be a potential candidate for microwave devices application.

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