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Investigation of the phase transformation and its effects on the microwave performance in $3ZnO\text{-}Nb_2O_5\text{-}GeO_2$ system

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ABSTRACT

The phase composition, crystal structure and microwave dielectric properties of (1-x) $(3ZnO\text{-}Nb_2O_5)\text{-}xGeO_2$ were investigated systematically. The phase composition and phase transformation of (1-x) $(3ZnO\text{-}Nb_2O_5)\text{-}xGeO_2$ ceramics were confirmed by XRD refinement, SEM micrographs and EDS analysis. All sintered samples were composed of $Zn_3Nb_2O_8$ and $ZnNb_2O_6$ phases. Phase transition between $Zn_3Nb_2O_8$ and $ZnNb_2O_6$ was closely related the introduction of GeO_2. When the doping content was low ($x = 0–0.007$), the phase transformation from $ZnNb_2O_6$ to $Zn_3Nb_2O_8$ occurred, which was discovered for the first time. To clarify the phase transition, the local charge density and band structures were calculated using the CASTEP program. With the substitution of Ge^{4+}, part of the electrons transferred from the oxygen atom to the middle of 'niobium-oxygen' and 'zinc-oxygen'. According, the covalency of 'niobium-oxygen' and 'zinc-oxygen' was enhanced. The shrinkage of ZnO_6 octahedron resulted in a decrease in the coordination number of zinc atoms. At last, the relationships between phase transition, crystal structure and the microwave performance were established. The system of $2.73ZnO\text{-}0.91Nb_2O_5\text{-}0.09GeO_2$ sintered at 1150 °C for 6 h had excellent microwave dielectric properties: $\varepsilon_r = 21.3$, $Qf = 99{,}140$ GHz, $\tau_f = -54$ ppm/°C, which, to our best knowledge, the best performance with relative lower sintering temperature.

1. Instruction

Microwave dielectric ceramic (MWDC) is a kind of information function ceramic material working in the microwave frequency band (300 MHz–300 GHz). Due to the characteristics of light weight, low cost and high dielectric performance, MWDC get a lot of applications in the manufacture of resonator, filter, oscillator, antenna, duplexer, capacitors and other microwave electronic components. Nowadays, 5G communication as a representative for the new generation of communication technology create new and additional challenges to the microwave components [1–7]. Fig. 1 shows the common microwave dielectric ceramic systems with the dielectric constant of 20–25 and its microwave properties [8–14]. It can be clearly seen than the microwave dielectric systems with high quality factor (Qf) normally have a larger resonant frequency temperature coefficient. Complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ systems have excellent microwave properties (high quality factor and small resonant frequency temperature coefficient). However, the sintering temperature of $Ba(Mg_{1/3}Ta_{2/3})O_3$ systems is too high (over 1400 °C) to adapt to the integrated applications. It is necessary to develop new microwave dielectric ceramics with excellent microwave properties and low sintering temperature.

J. Pollard [15] investigated the phase diagram of the $ZnO\text{-}Nb_2O_5$ system and two compounds—$ZnNb_2O_6$ and $Zn_3Nb_2O_8$ were firstly reported. The melting points of $ZnNb_2O_6$ and $Zn_3Nb_2O_8$ were 1308 °C and 1400 °C respectively. R.W. Harrison et al. [16]collected the X-ray diffraction pattern of $Zn_3Nb_2O_8$ powder and determined its structure. After that, Mistsumasa and Ballman et al. prepared the single crystal of $Zn_3Nb_2O_8$ by dropping method and pulling method respectively. Moreover, the chemical structure of the single crystal were studied [17]. $Zn_3Nb_2O_8$ has been studied as luminescent and dielectric host materials in the recent years. M. Birdeanu et al. [18] investigated the optical properties of crystalline $Zn_3Nb_2O_8$ nanomaterials obtained by hydrothermal method and identified it as proper candidates in fluorescence covering of technical devices. X.Z. Xiao et al. [19] investigated photoluminescence of Eu^{3+} or Dy^{3+} doped $Zn_3Nb_2O_8$ microcrystalline phosphor from hybrid precursors. The microwave properties of $Zn_3Nb_2O_8$ was firstly reported by Kim Dong-wan with $\varepsilon_r = 21.6$, $Qf = 83{,}300$ GHz and

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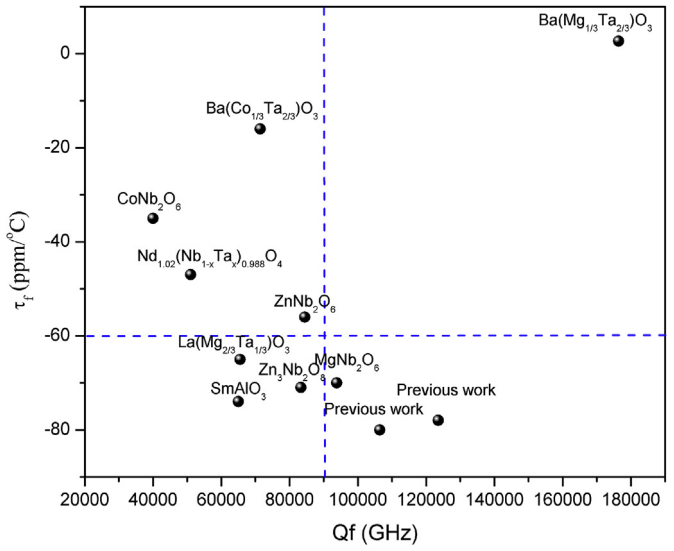

Fig. 1. The common microwave dielectric ceramic systems with the dielectric constant of 20–25 and its microwave properties.

$\tau_f = -71$ ppm/°C. Then, they investigated the sintering behavior and microwave dielectric properties of $(1-x)Cu_3Nb_2O_8$-$xZn_3Nb_2O_8$ and the microwave dielectric properties of $Zn_3Nb_2O_8$ by the doping of TiO_2 [11,20]. After that, M.C.Wu et al. [21] investigated CuO, $0.81MoO_3$-0.19CuO and $0.29BaCO_3$-0.71CuO as sintering aid to lower the sintering temperature of $Zn_3Nb_2O_8$ and their compatibility with silver electrode. O.A. Shlyakhtin et al. [22] investigated the effect of fine powders on the sintering behavior of $Zn_3Nb_2O_8$ ceramics. H. Sun et al. [12] investigated the structure and properties of Ni, Co, Mg and Mn doped substitute the zinc ion.

Here, we intended to study the effect of Ge^{4+} doping on B-site and its influence on the chemical structure and microwave dielectric properties. GeO_2 was firstly used as a dopant by Yutaka et al. [29] in the modification of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$. The introduction of GeO_2 in $Ba_6Sm_8Ti_{18}O_{54}$ ceramic could effectively lower the sintering temperature. The reactions among ZnO, Nb_2O_5 and GeO_2 had been reported by J. J. Brown et al. [23]. The crystal phase of 3ZnO-Nb_2O_5-GeO_2 was affected by the relative content of GeO_2. Moreover, Zn_2GeO_4 had excellent microwave dielectric properties [25]. Therefore, it was hoped that the introduction of GeO_2 can greatly improve the microwave dielectric properties and sintering properties of 3ZnO-Nb_2O_5. In this paper, the novel (1-x) (3ZnO-Nb_2O_5)-xGeO_2 ternary systems were prepared by solid-state method. The phase composition and phase transformation were identified by XRD refinement, SEM micrographs and EDS analysis. The mechanism in phase change was clarified by the density of states. At last, the relationships between the phase composition and the microwave properties were discussed. Undoubtedly, we think this study will provide critical theoretical guidance for materials' design and the optimization of preparation process.

2. Experimental section

2.1. Synthesis of BZNM ceramics

The ternary systems of (1-x) (3ZnO-Nb_2O_5)-xGeO_2 (x = 0, 0.0.003, 0.007, 0.01, 0.03, 0.07, 0.09,0.15, 0.20, 0.25) were synthesized by the mixed solid-state reaction method. Stoichiometric amounts of ZnO, Nb_2O_5, GeO_2 were weighed and mixed in alcohol by ball-milling for 6 h. The slurry was dried in an oven at 100 °C for 6 h. After drying, the mixture was calcined at 1075 °C for 4 h in alumina crucibles. The reacted powders were reground and uniaxially pressed into pellets with 10 mm in diameter and 2–5 mm in thickness with 7% PVA solution as binder. After removing the binder at 600 °C, the pellets were sintered at 1150 °C for 6 h. The heating rate was set to 5 °C/min. The cooling rate were controlled at 2 °C/min until the 1000 °C, and then naturally cooled to room temperature.

2.2. Structural characterization

XRD were recorded with a Bruker AXS GmbH D8-Focus with Cu Kα radiation over a 2theta(2θ) range of 10° to 120°. The crystal models were built by the program CrystalMaker. XRD refinements were performed by the soft-ware of Fullprof_suite to obtain the information on chemical structures (ICSD #36290 for $ZnNb_2O_6$ and ISCD #66147 for $Zn_3Nb_2O_8$, Rwp<14%, Rp<12%). Moreover, the microstructure was observed by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Ltd. Japan). Detailed analysis of element distribution of different areas was carried out using energy dispersive spectroscopy (EDS). Archimedes method was used to calculate the bulk density of the ceramics. The theoretical density was calculated according to the atomic weight and crystal structure.

2.3. Theoretical calculation

The electronic density of states was closely related to the crystal structure. To clarify the effect of the x value to the phase transformation behavior, the electronic density of states and band structures in $ZnNb_{2-x}Ge_xO_{6-x/2}$ were studied. By this way, the phase change process in (1-x) (3ZnO-Nb_2O_5)-xGeO_2 systems was clarified. In this paper, the band structure and partial density of states around each atom were calculated based on the first-principle using the CASTEP program. The density functional theory (DFT) was employed. The energy cutoff of the plane wave basis was set to 600eV and the criterion for self-consistency was eigen-energy convergence within 2×10^{-6} eV/atom. The k-point set was a $2 \times 2 \times 2$ Monkhorst-Pack grid.

2.4. Measurement of the microwave performance

The microwave dielectric properties of samples were measured on a network analyzer (8720 ES, Agilent, Palo Alto, USA) in the frequency range of 7–10 GHz. The dielectric constant was measured by the Hakki-Coleman method, and the unload Q value was measured by the cavity method [20]. The τ_f was calculated by the TE01δ mode resonant frequency of samples at 25 °C and 85 °C, respectively.

3. Results and discussion

3.1. Phase composition and microstructure

Fig. 2 showed the X-ray powder diffraction patterns of the (1-x) (3ZnO-Nb_2O_5)-xGeO_2 ceramics sintered at 1150 °C for 6 h. All data had been smoothed by the adaptive smoothing method and deducted background using Powder-X to reduce noise. $ZnNb_2O_6$ presenting orthorhombic structure with space group of Pnca(60) and $Zn_3Nb_2O_8$ presenting a monoclinic structure with space group of *C*2/*c*(15) were detected in the as-prepared samples. XRD refinement was carried out using the Fullprof_suite program to study the phase composition in (1-x) (3ZnO-Nb_2O_5)-xGeO_2 ceramics. Fig. 3(a) showed the result of XRD refinement for (1-x) (3ZnO-Nb_2O_5)-xGeO_2 (x = 0). Fig. 3(b) showed the phase composition varying with the doping content of GeO_2. For the pristine