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Synthesis, characterization and microwave dielectric properties of Zn_2GeO_4 ceramics

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ABSTRACT

Zn_2GeO_4 ceramic materials were synthesized by solid-state method. Zn_2GeO_4 powders were investigated with X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectrum, Raman spectrum, X-ray photoelectron spectrum (XPS), and high resolution transmission electron microscopy (HRTEM). A dense microstructure of Zn_2GeO_4 ceramics developed when specimens were sintered at above 1150 °C. The Zn_2GeO_4 ceramics sintered at 1300 °C exhibited good microwave dielectric properties: a dielectric constant (ε_r) of 6.87, a quality factor ($Q \times f$) of 102,700 GHz and a temperature coefficient of resonant frequency (τ_f) of -32.4 ppm/°C. The results showed that Zn_2GeO_4 ceramics were promising millimeter-wave ceramic candidate materials.

1. Introduction

Zn_2GeO_4, as a ternary oxide, has many advantages, for example good heat stability, non-toxic and high brightness. It is a self-excited blue phosphor, and considered as the ideal materials for photoluminescent and field emission display [1].

Typical synthesis methods for micrometer-sized particles of Zn_2GeO_4 and $Zn_2GeO_4{:}Mn^{2+}$ are conventional solid state reaction [2–5], hydrothermal synthesis [1,6], surfactant-assisted hydrothermal synthesis [7,8], solvothermal reaction [9] and hydrolysis of alkoxides [10]. One-dimensional Zn_2GeO_4 nanostructures were also prepared by vapor growth techniques [11–13] and aqueous process [14].

Ternary germanates nanowires have been attracted great attention as important nanomaterials for the application of electrochemical sensors, electron devices, optical devices and catalysts. RuO_2-dispersed Zn_2GeO_4 was found to be a stable photocatalyst for decomposition of water [2]. Zn_2GeO_4 nanorods were used as photocatalysts for the decomposition of organic pollutants in water [3]. $Zn_2GeO_4{:}Mn^{2+}$ showed green luminescence, and could be used in the alternating-current thin-film electroluminescence devices [15,16]. It was reported that Zn_2GeO_4 presented white-bluish emission, and its photoluminescence (PL) was brighter than that of ZnO phosphor [3]. Zn_2GeO_4–ethylenediamine membranes exhibit an excellent recyclability, high selectivity, and good thermal stability for highly efficient removal of heavy metal ions from contaminated water [17]. Zn_2GeO_4 could be also used as a candidate as high-capacity anode for lithium batteries [18].

Even though various studies were conducted on Zn_2GeO_4 materials. Microwave dielectric properties of Zn_2GeO_4 ceramics have not been investigated yet. The relation between structures and dielectric properties of Zn_2GeO_4 ceramics has not been revealed. In the present work, the Zn_2GeO_4 ceramic materials were synthesized using solid-state method, and their microwave dielectric properties were investigated.

2. Experimental

2.1. Sample preparations

The Zn_2GeO_4 ceramic materials were synthesized with solid-state method. High purity reagents nano-ZnO particles (50 nm, ⩾99.8%; Aladdin, Shanghai, China) and GeO_2 (⩾99.9%; Aladdin, Shanghai, China) were mixed with the stoichiometric ratio, milled with zirconia balls for 4 h in a planetary milling machine (QM-3SP2, Zhenguang, Nanjing, China) and then dried at 100 °C for 24 h. The powders were partially calcined at various temperatures (600–1300 °C) with a high-temperature electric furnace (SSJ-1600, Shenjia kiln, Luoyang, China) for behavior research of powders. The mixtures were dried and calcined at 1000 °C for 2 h. The calcined powders were re-milled for 4 h, dried, then granulated with 5 wt.% polyvinyl alcohol (PVA) organic binder, and finally pressed into cylindrical disks of 10 mm diameter and 6 mm thickness under about 10 MPa pressure with a manually tableting machine (769YP, TJKQ, Tianjin, China). These pellets were preheated at 580 °C for 2 h to expel the binder and then sintered at 1150–1350 °C for 4 h in air with an above-mentioned electric furnace to obtain bulk ceramic specimens.

2.2. Characterization

The crystalline phases of the calcined Zn_2GeO_4 powders or sintered bulk ceramic specimens were identified by X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) using Cu Kα (λ = 0.15406 nm) radiation with a graphite monochromator

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in the 2θ range of 10–70° operated at 30 kV and 30 mA. The cell parameters were refined with software Jade 6.0. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) pattern were taken by a JEM-2100 electron microscopy (JEM-2100, JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV. Element analysis of microdomain was carried out with an energy dispersive spectrometer (EDS) (EPMA1600, Shimadzu, Japan). FT-IR spectrum was obtained using a Fourier transform infrared spectrometer (Vector 33, Brucker, Germany). Raman spectra of Zn_2GeO_4 powders and the polished and thermally etched ceramic surfaces were obtained with Micro-raman spectrometer (LabRAM Aramis, HJY, France). Composition and chemical states of surface elements of the sample particles were investigated by XPS (Kratos Axis Ultra DLD, Japan) using Al Ka as exciting X-ray source. The spectra were calibrated with respect to the C 1s peak resulted from the adventitious hydrocarbon at the energy of 282.5 eV. Thermal gravimetry (TG) and differential scanning calorimetry (DSC) were performed at a heating rate of 10 K/min in N_2 atmosphere to characterize the thermal behaviors of the milled mixtures containing ZnO and GeO_2 with a molar ratio of 2:1 via thermal analyzer (STA409 C/3/F, Netzsch, Selb, Germany). Thermal mechanical analysis (TMA) of green body, which was made by pressing the milled mixtures of ZnO and GeO_2 (with a molar ratio of 2:1), were carried out at a heating rate of 5 K/min in the air using a thermal mechanical analyzer (402PC, NETZSCH DIL, Germany). The microstructure observations of the polished and thermally etched ceramic surfaces were performed under a scanning electron microscope (SEM) (LEO 1530 VP; Zeiss, Vertrieb Deutschland, Germany). The bulk densities of ceramics were measured by the Archimedes' method. Microwave dielectric constants (ε_r) and the quality factor values ($Q \times f$) at microwave frequencies were measured by Hakki–Coleman [19] dielectric resonator method using a Network Analyzer (N5230 PNA-L, Agilent, Santa Clara, USA). Temperature coefficient of resonant frequency (τ_f) was also measured by the same method with a changing temperature from 25 °C to 75 °C, and was calculated by the following:

$$\tau_f = \frac{f_{75} - f_{25}}{f_{25} \times 50} \times 10^6 \quad \mathrm{ppm/^\circ C} \tag{1}$$

where f_{75} and f_{25} represent the resonant frequency at 75 °C and 25 °C, respectively.

3. Results and discussion

3.1. Synthesis and characterization of Zn_2GeO_4 powders

3.1.1. Phase identification of Zn_2GeO_4 powders

XRD patterns of $2ZnO–GeO_2$ powders (molar ratio = 2:1) calcined at various temperatures for 4 h were shown in 1. When the powders were calcined in the low temperatures of 600–700 °C, the main crystal phases were ZnO (JCPDS No. 65-3411) and GeO_2 (JCPDS No. 36-1463); however, weak diffraction peaks of hexagonal Zn_2GeO_4 phase (JCPDS No. 11-0687) appeared, suggesting that the formation temperature of hexagonal Zn_2GeO_4 phase was at ~600 °C, as exhibited in curve (1) in Fig. 1a. The amounts of Zn_2GeO_4 increased with the increasing calcination temperatures, then, the desired pure Zn_2GeO_4 phase was obtained at 1000 °C. Comparing with the intensity of diffraction peaks, one could analyze relative content of each phase by a semi-quantitative method, and calculate crystalline size by Scherrer equation:

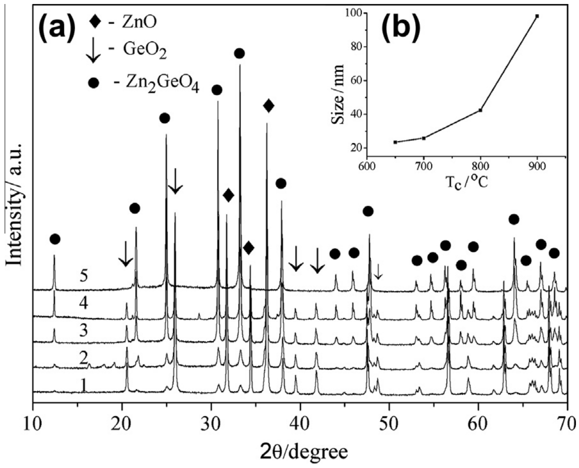

Fig. 1. (a) XRD patterns of the $ZnO–GeO_2$ mixtures (molar ratio of ZnO: GeO_2 = 2:1) calcined at different temperatures: (1) 600 °C, (2) 700 °C, (3) 800 °C, (4) 900 °C, (5) 1000 °C for 4 h, respectively. (b) Influence of the calcination temperature on grain size of Zn_2GeO_4.

$$d = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where d is the crystalline size, K is a shape factor (0.9), θ is the diffraction angle and β is the full-width at half-maximum of the peak. According to thermodynamics, the increasing temperature would lead to an increase in crystalline size. Fig. 1b showed the effect of calcination temperature (T_c) on crystalline size of Zn_2GeO_4. The main diffraction peak width of hexagonal Zn_2GeO_4 phase decreased rapidly with an increasing temperature. The crystalline size of Zn_2GeO_4 calcined at 650 °C was 23.5 nm, and increased to 98.2 nm at 900 °C.

3.1.2. HRTEM studies

Zn_2GeO_4 nanorod (calcined at 1300 °C) was exhibited in Fig. 2a. However, the nanorod was not typical shape of Zn_2GeO_4 crystallite, but just one among variety of morphologies. In Fig. 2b, we showed that HRTEM images of the Zn_2GeO_4 crystal, where the lattice planes exhibited spacings of 0.724 nm corresponding to the lattice planes (110). The diffraction spots suggested that the Zn_2GeO_4 grains had good crystallinity and possessed single crystalline structures (see Fig. 2c). EDS showed the atomic ratio of Zn to Ge is 2:0.90, indicating that the Ge-deficient Zn_2GeO_4 produced, as given in Fig. 2d.

3.1.3. TG/DSC and TMA analysis

The typical TG/DSC curves of the milled $2ZnO- GeO_2$ powders were shown in Fig. 3a. As shown in this figure, the TG curve showed that no obvious weight loss could be detected in the process. The sharp endothermal peak at 1098.9 °C could be attributed to the melt of germanium oxide. Though XRD studies suggested that pure hexagonal Zn_2GeO_4 phase was obtained at above 1000 °C, we assumed that trace of GeO_2 existed in the powders or ceramic specimens because of the uneven sintering.

Thermal mechanical analysis (TMA) of the green body illustrated that sintering curve had a sharp slope noticeably in the temperature region of 1050–1300 °C, and the radial shrinkage was −5.56%, as exhibited in Fig. 3b, which suggested that densification of Zn_2GeO_4 ceramics rapidly produced at above 1100 °C. Considering to the TG/DCS and TMA patterns, we deduced that the densification of Zn_2GeO_4 ceramics followed the liquid-phase sintering mechanism under high sintering temperature. Trace of GeO_2 melted at ~1100 °C, produced liquid phase and improved the sintering of Zn_2GeO_4 ceramics.

3.1.4. FT-IR, Raman, and XPS spectra studies of Zn_2GeO_4 powders

FT-IR spectrum of the Zn_2GeO_4 particles (calcined at 1300 °C) was shown in Fig. 4a. In the spectrum, absorption ranges of Zn_2GeO_4 particles were 535 cm^{-1} and 743–801 cm^{-1}. Yamaguchi reported that the characteristic infrared absorption ranges of Zn_2GeO_4 are as follows: υ (GeO_4) 700–800 cm^{-1} and υ (ZnO_4) 500–600 cm^{-1} [10], which were agreeable to our observation.

The local atomic structure of Zn_2GeO_4 particles (calcined at 1300 °C) was characterized by Raman spectroscopy (see Fig. 4b). We observed that the spectrum was very similar to that reported by Boppana [20]. Zhang [21] reported that peaks at 738 and 760 cm^{-1} could be attributed to ν_3 and ν_1 stretching vibration modes of $(GeO_4)^{4-}$, respectively. We thought that the Raman bands at 748, 754, and 778 cm^{-1} could be ascribed to Ge–O–Zn symmetric, defect oxygen mode and asymmetric vibrations [20], respectively.