Microwave dielectric properties of BaV$_2$O$_6$ ceramics with ultra-low sintering temperature

Cui Jin Pei[a,b], Guog Guang Yao[a,b,*] and Zhao Yu Ren[b]
[a]Institute of Photonics & Photon-Technology, Northwest University, Xi'an710069, China
[b]School of Science, Xi'an University of Posts and Telecommunications, Xi'an 710121, China

Microwave dielectric properties of BaV$_2$O$_6$ ceramics were investigated for the first time. The BaV$_2$O$_6$ ceramic was prepared by the solid-state ceramic route. The phase constitution, microstructure, and compatibility with aluminum electrode were investigated using XRD, Raman spectra and SEM. The results confirmed that that pure phase BaV$_2$O$_6$ could be obtained in the sintering temperature range of 525 °C-600 °C. With an increase in the sintering temperature, the dielectric constant (εr) and quality factor (Qxf) first increase and decrease thereafter, the temperature coefficient of resonant frequency (τf) changes slightly. The BaV2O6 ceramic sintered at 575 °C/4 hr exhibited good microwave dielectric properties of ε_r = 11.5, τ_f = 38 ppm/ °C and Qxf = 21 800 GHz (at 10.1 GHz). Moreover, the material had a chemical compatibility with aluminum powders, which represented a promising candidate material for ULTCC applications.

Key words: Dielectric properties, BaV$_2$O$_6$, sintering.

Introduction

Intensive development of wireless communication systems has resulted in an increasing demand for microwave dielectric materials with low dielectric constant (ε_r), high quality factor (low dielectric loss, Qxf > 10 000 GHz) and a near-zero temperature coefficient of resonant frequency (τ_f) [1]. In addition, it is desired to integrate the passive components to a function module by low temperature co-fired ceramic (LTCC) technology, which requires the microwave dielectric ceramics to have lower sintering temperature than that of the highly conductive and inexpensive internal electrodes such as silver and aluminum. Most of the reported LTCC material systems use glass or oxide additives to reduce their sintering temperatures by negotiating their dielectric properties [2-4]. Therefore, the search for genuine low firing ceramics has always attracted much attention.

Recently extensive efforts were made in V$_2$O$_5$-based compounds to identify novel microwave ceramic systems suitable for LTCC substrate application since they possess low or even ultra-low sintering temperature and excellent microwave dielectric properties [5-9]. In BaO-V$_2$O$_5$ binary system, four phases are formed: Ba$_3$(VO$_4$)$_2$, Ba$_2$V$_2$O$_7$, Ba$_3$V$_4$O$_{13}$ and BaV$_2$O$_6$ [10]. Among these compounds, the microwave dielectric properties of Ba$_3$(VO$_4$)$_2$, Ba$_2$V$_2$O$_7$ and Ba$_3$V$_4$O$_{13}$ ceramics have been investigated [11-13].

They show good dielectric properties with $_r$ of about 9.6-17, Qxf value in the range of 51 630-62 350 GHz, and ô$_f$ ranging from −42 ~ 40 ppm/°C. Ba$_2$VO$_6$ has orthorhombic structure with space group (C222), and its photo-catalytic property has been reported recently [14, 15]. However, its microwave dielectric properties have not been investigated to date. Moreover, since the melting point of this ceramic is about 700 °C [10], the BaV$_2$O$_6$ compound is considered to be an appropriate candidate for new ultra-low temperature co-fired ceramic (ULTCC) material. In present study, the sintering behavior, microwave dielectric properties, and chemical compatibility with Al of BaV$_2$O$_6$ ceramic are introduced as new ULTCC materials.

Experimental

Samples of the BaV$_2$O$_6$ ceramic was synthesized by the conventional solid-state methods using high-purity oxide powders (> 99%): BaCO$_3$ and V$_2$O$_5$. The pre-dried raw materials were mixed according to the desired stoichiometry of the BaV$_2$O$_6$ ceramics. The powders were ground for 7 hrs in a nylon jar with agate balls and ethanol as media. All mixtures were dried and calcined at 460 °C for 3 hrs. The calcined powders were reground for 7 hrs, dried, mixed with 5 wt% PVA as a binder, and granulated. The granulated powders were uniaxially pressed into pellets with 10 mm in diameter and 4-5 mm in height under the pressure of 200 MPa. These pellets were sintered from 500 °C to 600 °C for 4 hrs in air with a heating rate of 5 °C/min.

The bulk densities of the sintered ceramics were measured by Archimedes' method. The crystal structures

*Corresponding author:
Tel : +86-29-88166089
Fax: +86-29-88166333
E-mail: yaoguoguang@xupt.edu.cn

were analyzed using X-ray powder diffraction (XRPD) with Cu Ka radiation (Rigaku D/MAX2550, Japan). The Raman spectra were collected at room temperature using a Raman microscope (Horiba Jobin Yvon S.A.S., France) with Nd: YAG laser (532 nm) operated at 30 mw. The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Holland). The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & Schwarz, Germany) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)} \qquad (1)$$

Results and Discussion

Fig. 1 shows the XRPD patterns of BaV_2O_6 ceramics sintered at different temperatures for 4 hrs. In the sintering temperature range of 525 °C-600 °C, pure phase BaV_2O_6 was obtained within the detectable level of XRPD. Locations of diffraction peak in XRPD patterns of the sintered ceramics did not vary significantly with increasing sintering temperature. The lattice parameters of BaV_2O_6 sintered at 575 °C were calculated as a = 8.5116 Å, b = 12.4698 Å, and c = 7.8639 Å with the Jade 6.0 software.

In order to further study the crystal structure of BaV_2O_6 in detail. The room-temperature Raman spectra of BaV_2O_6 ceramics sintered at 575 °C had been recorded and the result is presented in Fig. 2. The vibration modes in the Raman spectra of the BaV_2O_6 ceramics are classified into two groups, internal and external. Yao et al. reported that the crystal structure of BaV_2O_6 consists of chains of vertex-shared VO_4 tetrahedra along the <120> direction and Ba atoms located interstitially between the chains [14]. Thus, the internal vibrations are related to the $[VO_4]^{3-}$ molecular group with a stationary mass center, the external vibrations or lattice phonons are associated with the motion of the Ba^{2+} cations and rigid molecular units [16]. The strong Raman bands observed in the 967-874 cm^{-1} can be assigned to the symmetric stretching vibration of $(VO_4)^{3-}$ ions. The symmetric bending vibrations of $(VO_4)^{3-}$ anions are observed in the region between 470 and 300 cm^{-1}, whereas that of asymmetric bending vibration is observed at 527 cm^{-1}. The Raman bands below 300 cm^{-1} are attributed to the external modes, which consist of the translational modes of the Ba^{2+}, and $(VO_4)^{3-}$ ions as well as librations of $(VO_4)^{3-}$ ions [17].

The SEM photographs of as-fired surface in BaV_2O_6 specimens sintered at various temperatures are illustrated in Fig. 3. The BaV_2O_6 sample sintered at 525 °C showed a distribution of grain sizes smaller than 2 μm and an appreciable amount of intergranular
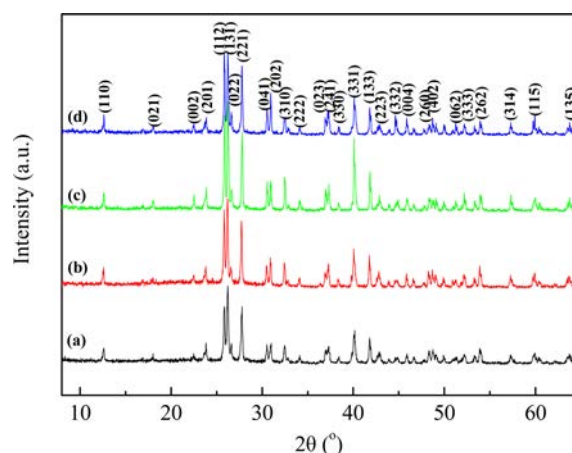

Fig. 1. XRPD patterns of BaV_2O_6 ceramics sintered at different temperatures for 4 hrs; (a) 525 °C, (b) 550 °C, (c) 575 °C, and (d) 600 °C.
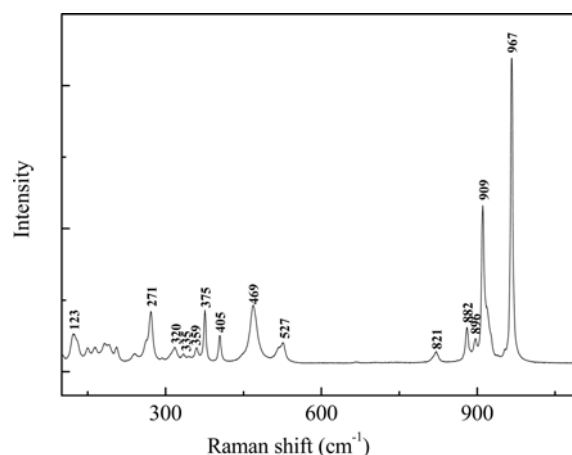

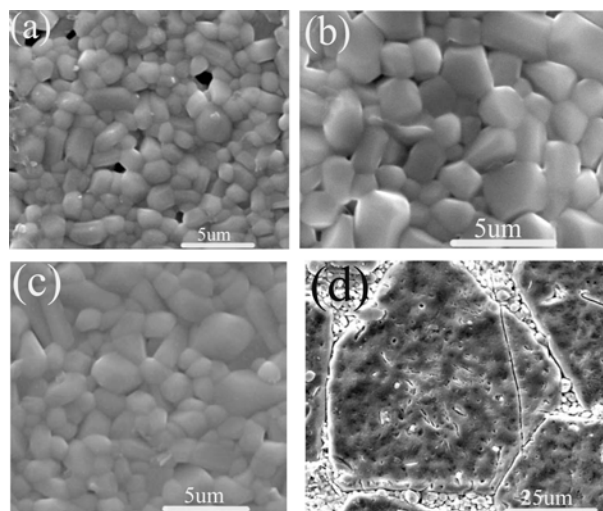**Fig. 2.** The room-temperature Raman spectra of BaV_2O_6 ceramics sintered at 575 °C.

Fig. 3. SEM images of as-fired surface in BaV_2O_6 ceramics sintered at (a) 525 °C, (b) 550 °C, (c) 575 °C, and (d) 600 °C for 4 hrs.

porosity, as seen in Fig. 3(a). The pores decreased with increasing sintering temperature. When the sample was
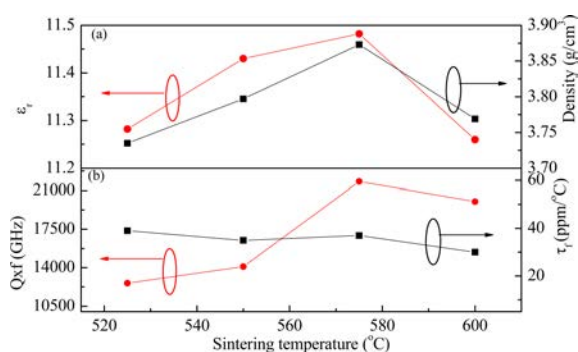
Fig. 4. Variation in (a) ε_r and density, and (b) Qxf and τ_f of BaV$_2$O$_6$ ceramics versus firing temperatures.
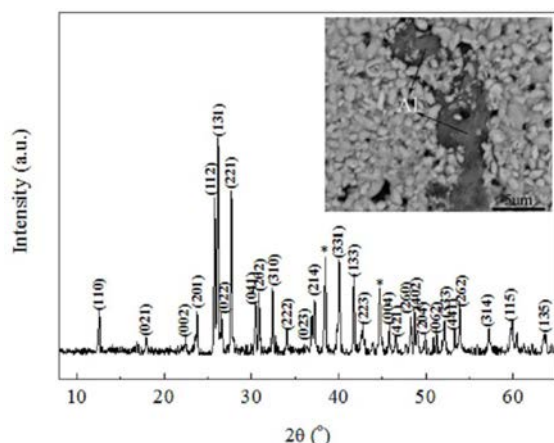
Fig. 5. XRD patterns and SEM image of BaV$_2$O$_6$ + 20 wt% Al sintered at 575 °C for 4 hrs.

sintered at 575 °C, the dense microstructures with almost no porosity could be observed, as seen in Fig. 3(c). However, abnormal grain growth was observed for BaV$_2$O$_6$ ceramic after sintering at 600 °C, which would deteriorate the density and microwave dielectric properties of specimens.

Fig. 4 illustrates the density and microwave dielectric properties of BaV$_2$O$_6$ ceramics as a function of sintering temperature. The density of the samples increased with ascending the sintering temperature. After reaching a maximum value at 575 °C, the density decreased due to the abnormal grain growth. As seen from Fig. 4(a), as the sintering temperature increased, ε_r increased with a trend similar to their density, because both the density and ε_r of ceramic are associated with the elimination of the pores [18]. In general, the dielectric loss is affected by intrinsic factors such as structural characteristics and extrinsic factors like secondary phase, grain size, densification or porosity [19, 20]. As shown in Fig. 4, the variation of Qxf is commensurate with density, suggesting the loss mechanism might be dominated by extrinsic contributions. The Qxf value increased with increasing temperature up to 575 °C, which is attributed to the increase in density and grain size. After 575 °C, the Qxf value decreased due to the abnormal grain growth, as shown in Fig. 3(d). The τ_f values did not change

remarkably with increasing sintering temperature and remained stable at about 38 ppm/°C. It is to be noted that few dielectric ceramics owing low ε_r, positive τ_f and intrinsic low sintering temperature has been reported to date [21]. In general, low ε_r materials possess large negative τ_f [22,23], however, the BaV$_2$O$_6$ ceramic exhibits an exceptionally positive τ_f and low ε_r. The positive τ_f and low ε_r of BaV$_2$O$_6$ is potentially attractive for its use as an end-member in composite ceramics with near-zero τ_f for substrate application.

To evaluate the chemical compatibility of BaV$_2$O$_6$ ceramic with aluminum electrodes, mixtures of the BaV$_2$O$_6$ powders and 20 wt% Al powders were cofired at 575 °C/4 hrs. The XRPD pattern and SEM image of the cofired sample are presented in Fig. 5. As the XRD pattern does not show the formation of any secondary phase except for BaV$_2$O$_6$ and Al, and the SEM image reveals no reaction boundary layer was detected between BaV$_2$O$_6$ and Al. These results show that the material under study has a chemical compatibility with Al.

Conclusions

A new V-based microwave dielectric ceramic BaV$_2$O$_6$ has been prepared and characterized. Pure orthorhombic phase ceramics could be obtained by the conventional solid-state route after sintering at 525-600 °C. The BaV$_2$O$_6$ ceramics sintered at 575 °C for 4 hrs showed good microwave dielectric properties of $\varepsilon_r = 11.5$, $\tau_f = 38$ ppm/°C and Qxf = 21 800 GHz (at 10.1 GHz), and it did not react with Al electrode. The unusually lower ε_r, large positive τ_f and reasonable values of Qxf in BaV$_2$O$_6$ coupled with its low sintering temperature suggested that it may be useful in the fabrication of temperature-stable composites with lower ε_r, negative τ_f and high Qxf end members.

Acknowledgments

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