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Original Article

Enhanced dielectric breakdown strength in Ni_2O_3 modified Al_2O_3-SiO_2-TiO_2 based dielectric ceramics

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ABSTRACT

Dielectric ceramics have raised particular interest since they enable pulsed-power systems to achieve high voltage gradient and compact miniaturization. In this work, x wt%Ni_2O_3 doped Al_2O_3-SiO_2-TiO_2 based dielectric ceramics were prepared using conventional solid-state reaction and the effects of Ni_2O_3 on the crystal structure, dielectric properties and dielectric breakdown strength were investigated. It was found that with the doping of Ni_2O_3, the Al_2O_3-SiO_2-TiO_2 based dielectric ceramics became denser and the distribution of each phase was more uniform. For the composition of x = 2.0, the dielectric breakdown strength was increased into 82.1 kV/mm, more than twice compared with that of the undoped one. In addition, the relationship between the dielectric breakdown strength and the resistance of Al_2O_3-SiO_2-TiO_2 based dielectric ceramics was discussed. The results show that the doping of Ni_2O_3 is a very feasible way to improve the dielectric breakdown strength and optimize the dielectric properties for the Al_2O_3-SiO_2-TiO_2 based dielectric ceramics.

1. Introduction

Compact portable pulsed-power systems have extensive application prospects in the field of dielectric wall accelerator, microwave source generator, fusion, electromagnetic rail gun, etc [1–3]. The research and manufacture of the solid dielectric materials with high dielectric breakdown strength (DBS) and excellent dielectric properties are crucial to the development of pulsed-power systems.

Currently, polymer based composites [4–6], glass-ceramics [7,8] and dielectric ceramics [9–19] have been investigated for the potential application. Polymer based materials and glass-ceramics usually possess higher DBS, but they suffer relatively serious dielectric relaxation and have larger dielectric loss in low frequency range caused by the disordered atomic arrangement in amorphous phase. In contrast, dielectric ceramics in crystalline state possess stable dielectric constant and lower loss in a wide range of temperature and frequency, but their DBS are usually lower for the existence of gaps and defects between the grains. In recent years, Al_2O_3 and TiO_2 based ceramics have attracted much attention for having higher DBS and superior dielectric properties than other chemical compounds. For example, Gilmore reported that TiO_2 might be promising candidate for pulse applications due to DBS of 35 kV/mm and high dielectric constant of 110 [12]. Al_2O_3 has good insulation properties and the role of electrical charge transport and trapping in alumina ceramics has been discussed [13]. Chen and coworkers developed a novel ceramic with DBS of 50 kV/mm by adding SiO_2 to Al_2O_3 and TiO_2 based ceramics [14,15]. Besides the chemical composition, the DBS is also related to the microstructure such as grain size, grain boundary, defect, porosity, phase structure and so on [13,16,17]. The microstructure of Al_2O_3-SiO_2-TiO_2 based ceramics became denser and more uniform by sol-gel method, and DBS has been increased from 37.45 kV/mm to 48.29 kV/mm [18]. The grain size of $(Mg_{0.9}Zn_{0.1})_2(Ti_{1-x}Mn_x)O_4$ ceramics has been decreased and DBS improved from 31.78 kV/mm to 50.24 kV/mm when x = 0.01 [19]. However, in order to develop high gradient pulsed-power systems with nanosecond-scale pulses, the dielectric materials with moderate dielectric constant (20–30) and ultra-high DBS are needed.

In the present work, to obtain higher DBS, Ni_2O_3 is added to Al_2O_3-SiO_2-TiO_2 based ceramics. Considering the change of $Ni_2O_3 \rightarrow NiO + O_2$ at high temperature during the sintering, the doping of Ni_2O_3 to Al_2O_3-SiO_2-TiO_2 based ceramics will produce Ni^{2+} and O_2, inhibit

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the generation of oxygen vacancies and thus increase the resistance of Al_2O_3-SiO_2-TiO_2 based ceramics. The effects of Ni_2O_3 on the crystal structure, bulk density, DC bulk resistivity, dielectric properties, and dielectric breakdown strength are investigated. With the increase of Ni_2O_3, the bulk density increases and the distribution of each phase is more uniform, which reduces the localization of electric field distribution. The Ni_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics have higher resistivity, DBS and superior dielectric properties compared with the undoped one. Our work provides an effective way to improve the DBS in TiO_2 based ceramics, which broaden the application of dielectric ceramics for the high gradient pulsed-power systems with nanosecond-scale pulses.

2. Experimental procedure

Proportionate amounts of reagent-grade $CaCO_3$ (98%), MgO (99.9%), α-Al_2O_3 (99.9%), SiO_2 (99.9%) and rutile TiO_2 (99.21%) as the starting reactants were mixed and ball milling for 24 h. After synthesis of the compounds at 1000 ℃ for 2 h, stoichiometric Ni_2O_3 (99.0%) was added to the composite materials and ball milling for 48 h, then the dried powers were mixed with 7 wt% PVA as binder and aging for 24 h. x wt%Ni_2O_3 (x = 0, 0.5, 1.0, 2.0, 2.5) doped 0.02CaO-0.02MgO-0.14Al_2O_3-0.20SiO_2-0.62TiO_2 (mol) ceramics with diameter of 13 mm and thickness of 0.5 mm were prepared by conventional solid-state reaction method. The optimum sintering temperatures of the samples are 1280 ℃, 1260 ℃, 1240 ℃ and 1230 ℃ for x = 0, x = 0.5, x = 1.0, 2.0 and x = 2.5 respectively. With the increase of x, the sintering temperature is decreased.

The phase structures were analyzed by X-ray diffraction (XRD, D/MAX-2550V, Rigaku, Japan) with a Cu Kα radiation. The bulk densities of the sintered samples were measured using the Archimedes method. The microstructure and chemical component elements were characterized by the scanning electron microscopy (SEM) (Magellan 400, FEI, America) equipped with an energy-dispersive spectrometer (EDS). The valence of atoms was measured by X-ray photoelectron spectroscopy (ESCAlab250, ThermoFisher, America). DC bulk resistivity was measured by high temperature four point test system (HRMS-800, Partulab, China). The frequency dependence of the dielectric constant and loss were tested using a precision impedance analyzer (E4990A, Keysight, America) from 1 kHz to 10 MHz at room temperature. The temperature dependence of the dielectric constant and loss were measured by a precision impedance analyzer (E4980A, Agilent, Palo Alto, America) from −45 ℃ to 85 ℃. The DBS was measured using a voltage-withstand testing device (SD-DC 200 kV) with the samples immersed into silicone oil to prevent surface flashover. For each composition, 10 pellets were taken to breakdown measurements. The complex impedance spectroscopy was measured by an impedance analyzer (E4990A, Keysight, America) with frequency from 20 Hz to 10 MHz and temperature from 660 to 740 ℃.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics. From the XRD patterns, we can see there are rutile TiO_2, cordierite $Mg_2Al_4Si_5O_{18}$ and anorthite $CaAl_2Si_2O_8$ crystalline phases in the Al_2O_3-SiO_2-TiO_2 based ceramics. At x = 1.0, 2.0 and 2.5, two new phases of $NiAl_2O_4$ and SiO_2 appear and the amount of $Mg_2Al_4Si_5O_{18}$ and $CaAl_2Si_2O_8$ are gradually decreasing with the increase of x, which may be due to the forming of amorphous phase.

Fig. 2(a)–(e) display the cross section SEM images of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics. With the increase of x, we know that the enrichment of black phase are gradually reducing, each phase in Al_2O_3-SiO_2-TiO_2 based ceramics is distributing more uniform, and the microstructure become denser for the rising of amorphous phase. Fig. 2(f) shows the bulk density of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics sintered at their optimum temperature and it can be observed

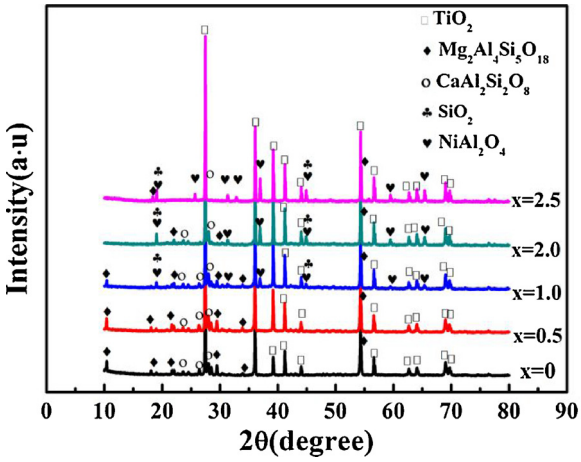

Fig. 1. XRD patterns of xNi_2O_3 ($0 \le x \le 2.5$) doped Al_2O_3-SiO_2-TiO_2 based ceramics.

that the bulk density has been improved with the increase of x. The results indicate that Ni_2O_3 plays the role of dispersant and sintering aid.

Fig. 3 illustrates the SEM images and the EDS line scanning from A to E of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics for x = 0 and 2.0 respectively. Based on the XRD and EDS analyses, the white rutile TiO_2, black cordierite $Mg_2Al_4Si_5O_{18}$ and the dark gray $CaAl_2Si_2O_8$ are all existed in the Al_2O_3-SiO_2-TiO_2 based ceramics. From the XRD, we know when $x \ge 1.0$, there exist two new phases $NiAl_2O_4$ and SiO_2. Fig. 3(c) is the local magnification of Fig. 2(d), from the Fig. 3(c) and the EDS line scanning, we can see there exist the amorphous SiO_2 phase and the light gray $NiAl_2O_4$ phase in the AB and CD region respectively at x = 2.0, which agrees well with the result of the XRD. In Fig. 3(d), the result of the EDS line scanning shows that Ti element has certain concentration in the AB region which may be influenced by the existence of the two TiO_2 grains besides the AB region.

The XPS spectra of Ni 2p of the xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics ($0 \le x \le 2.5$) are displayed in Fig. 4(a). The peaks at 856.6 eV and 874.4 eV associated with the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively and an obvious shake-up peak at 863.5 eV for x = 1.0–2.0 is a characteristic of $NiAl_2O_4$, the values are in good agreement with reported literature [20]. So the XPS spectrum reveals that the change of $Ni_2O_3 \rightarrow NiO + O_2$ has happened and the nickel exists at two valence in xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics. Fig. 4(b) shows the DC bulk resistivity of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics at room temperature. With the increase of x, the resistivity improved obviously from 8.62×10^{13} Ω·cm (x = 0) to 2.82×10^{14} Ω·cm (x = 2.0), which may be due to the reduction of pores and oxygen vacancies. But at x = 2.5, the resistivity drops which may be attribute to the increase in the content of $NiAl_2O_4$ which has a low resistivity [21].

Fig. 5(a) shows the frequency dependence of the dielectric constant and loss of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics (x = 0–2.5) from 1 kHz to 10 MHz at room temperature. The dielectric constant exhibits excellent frequency stability and the dielectric loss of all samples are below 0.003 in the frequency range. Fig. 5(b) presents the dielectric constant and loss of the xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics (x = 0–2.5) at 1 kHz as a function of temperature from -45°C to 85°C. It can be found that with the increase of x, the dielectric constant of xNi_2O_3 doped Al_2O_3-SiO_2-TiO_2 based ceramics slightly decreases from 29.3 (x = 0) to 25.0 (x = 2.5). While the dielectric loss decreases from 0.0028 (x = 0) to 0.0010 (x = 2.0) firstly, then increases to 0.0016 at x = 2.5. The dielectric loss is concerned with the DC bulk resistivity and the relaxation polarization existed in ceramics. The change of the dielectric loss is consistent with the change of the DC bulk resistivity. At x = 2.5, the dielectric loss become larger instead of smaller which may be attributed to the decrease of DC bulk resistivity