Influence of CaF$_2$ on the structure and dielectric properties of Ag(Nb$_{0.8}$Ta$_{0.2}$)O$_3$ ceramics

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Abstract
Ag(Nb$_{0.8}$Ta$_{0.2}$)O$_3$ ceramics were prepared by the traditional solid-state reaction method. The effect of CaF$_2$ addition on the structure and dielectric properties of Ag(Nb$_{0.8}$Ta$_{0.2}$)O$_3$ ceramics was investigated. The addition of CaF$_2$ led the ceramics to a larger grain size and distortion of lattice. With the addition of 4.5 wt.% CaF$_2$, the permittivity of the ceramics increased from 442 to 1028, the dielectric loss decreased sharply from $6.12 \times 10^{-3}$ to $8.6 \times 10^{-4}$, and the temperature coefficient of capacitance decreased from 1834 ppm/°C to $-50$ ppm/°C (at 1 MHz). These results indicated that the high permittivity was related with a large grain size, a low grain boundary density, and the weak Ta–O or Nb–O bond strength caused by the addition of CaF$_2$.

Keywords: microwave materials; Ag(Nb,Ta)O$_3$; solid-state reaction method; dielectric properties

1. Introduction

Perovskite-type materials possess excellent properties that make them potentially useful for industry applications, such as dielectric resonators. Recently, an investigation of Ag(Nb,Ta)O$_3$ dielectrics pointed to a very promising high-permittivity microwave material [1-3]. However, the development of the materials with high permittivity is hindered by the correlation between the permittivity and two other important dielectric properties: the dielectric loss and the temperature dependence of the permittivity [4].

Ag(Nb$_{0.8}$Ta$_{0.2}$)$_1$-xSb$_x$O$_3$ solid solutions were prepared with a permittivity of 825 and a dielectric loss of 0.0023 [5]. CuO-doped Ag(Nb$_{0.8}$Ta$_{0.2}$)$_1$-xSb$_x$O$_3$ ceramics were fabricated with a permittivity of 415 [6]. Recently, Ag$_{1-x}$Bi$_x$NbO$_3$ systems were investigated; excellent temperature-stable dielectrics were obtained at $x = 0.25$, where $\varepsilon_r = 192$ ppm/°C, $\varepsilon_r \approx 600$, and $\tan \delta \approx 10^{-4}$ (at 1 MHz) [4]. To adjust the dielectric properties, sintering aids were usually added to ceramics. Fluorides, such as LiF, MgF$_2$, CaF$_2$, and PbF$_2$ with low melting point, were the modifier for sintering capacitors and microwave ceramics in low sintering temperature [7-9]. CaF$_2$ could promote sintering, and the permittivity increased with increasing CaF$_2$ concentration [10-12].

In this work, CaF$_2$ was used to develop materials with high permittivity and low dielectric loss. The influence of CaF$_2$ on the structure and dielectric properties of Ag(Nb$_{0.8}$Ta$_{0.2}$)O$_3$ ceramics was investigated.

2. Experimental

Ag(Nb$_{0.8}$Ta$_{0.2}$)O$_3$ (ANT2) perovskite was synthesized using the solid-state reaction technique with powders of Nb$_2$O$_5$, Ta$_2$O$_5$, and Ag$_2$O. The powder mixtures were weighed and then mixed using de-ionized water and zirconia milling media for 2 h. Phase formation was investigated on raw materials mixture using a thermo-gravimetric analysis (TG) combined with differential thermal analysis (DTA). According to the result of thermo-gravimetric analysis, the mixed powders were calcined at 800°C and then milled for 4 h. The grinded powders were granulated by mixing them in a 7 wt.% binder, and the granules were pressed into disks of 10 mm in diameter and 1-1.5 mm in thickness. The pellets were sintered at 1100-1150°C. CaF$_2$ with appropriate mass ratio was used as an addition before granulation.

Phase identification of the sintered samples was performed by an X-ray diffractometer (RIGAKU D/Max) using Cu $K\alpha$ radiation. Microstructures were examined using a scanning electron microscope (Philips XL30). Thermal behavior was performed by a thermo-gravimetric Analysis
combined with differential thermal analysis (Model STA409EP, Netzsch, Germany). The density was measured using the Archimedes method (Mettler Toledo XS64). The capacitance and dielectric loss were measured at 1 MHz with a capacitance meter (HP4278A). The temperature coefficient of capacitance (TCC) was tested with a GZ-ESPEC oven and an HM 27002 C-T Meter Model. Raman measurements were carried out at room temperature (Bruker FS100). The excitation source was the 1064 nm line with 100 mW Raman laser power. The obtained Raman spectra were recorded with a resolution of approximately 2 cm\(^{-1}\). To determine the dielectric properties in the frequency range from 1 kHz to 1 MHz, the capacitor performances were measured using a digital electric bridge (TH 2816) and a capacitance meter (HP4285A).

3. Results and discussion

3.1. Study of ANT2 phase formation

Phase formation was explored by TG/DTA on raw materials mixture of Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), and Ag\(_2\)O calcined in air (Fig. 1(a)). XRD patterns were also reported. The mass loss observed at 150°C and 330°C was related to H\(_2\)O loss and Ag\(_2\)O decomposition (Fig. 1(b)). The ANT2 phase formation began at about 450°C and finished at around 930°C. After calcining at 550°C, XRD analysis revealed the presence of raw materials with ANT2 phase. At 550°C, ANT2 phase was predominant with a few impurities, whereas, at 930°C, ANT2 phase was completely formed (Fig. 1(c)).

XRD patterns of ANT2-xCaF\(_2\) (x = 0 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 4.5 wt.%) ceramics are shown in Fig. 2. A single-phase perovskite structure was observed. The influence of CaF\(_2\) concentration on diffractions of X-ray diffraction of the samples can be observed in the variations of intensity and full width at half maximum (FWHM) of diffraction peaks of the ceramics. These characteristics were utilized to determine the crystallinity. The crystallinity of the samples was estimated according to the integral area of diffraction peaks. The results revealed that the crystallinity decreased with the increase of CaF\(_2\) concentration. Based on the Jade 5.0 software, the crystallinity could be calculated using the following equation:

\[
M = \frac{I'}{I} \times 100\%
\]

where \(M\), \(I'\), and \(I\) are the crystallinity, the intensity of crystalline portion, and total intensity of crystalline and non-crystalline portion, respectively. The crystallinity of ANT2-xCaF\(_2\) (x = 0 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 4.5 wt.%) ceramics was 83.71%, 83.42%, 82.45%, 68.27%,

![Fig. 1](image)

(a) TG/DTA for the mixture of Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), and Ag\(_2\)O; (b) XRD pattern for the mixture of Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), and Ag\(_2\)O calcined at 330°C; (c) XRD patterns for the mixture of Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), and Ag\(_2\)O calcined at 550°C and 930°C.