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Temperature-stable and high-ε dielectric ceramics based on Ag $(Nb_{1-x}Ta_x)O_3$

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Abstract

The dielectric properties of novel dielectric system $AgNb_{1-x}Ta_xO_3$ (ANT) have been studied in this paper. In this system, the temperature coefficient of capacitance (TCC) can be adjusted to $0 \pm 30 \times 10^{-6}/^{\circ}C$ by choosing proper molar ratio of Nb^{5+} to Ta^{5+}. When 2 wt% glass is added to the ceramics, the sintering temperature is reduced to 960 °C, which restrains Ag^+ decomposition in ambient atmosphere. It is noted that the dielectric loss reduces further after adding 2.5 wt% Sb_2O_5. The dielectric properties of the resultant samples are as follows: dielectric constant $\varepsilon \approx 512$, loss tangent $\tan\delta \approx 5.2 \times 10^{-4}$, and TCC $\approx 10 \times 10^{-6}/^{\circ}C$.

Keywords: Sintering; Dielectric properties; Niobates; Tantalates; Capacitor

1. Introduction

Recently, a novel system $AgNb_{1-x}Ta_xO_3$ (ANT) with ultra-high dielectric constant is preliminarily investigated which can meet the demand for multilayer ceramic capacitors and microwave dielectric filters with much smaller sizes. There are two techniques to prepare this dielectric material. The first technique is to mix Ag_2O, Nb_2O_5 and Ta_2O_5 powders and then sinter at intermediate temperature. The second is to mix Nb_2O_5 and Ta_2O_5 firstly according to certain ratio then calcine at 1200 °C, finally adding Ag_2O to obtain mixture and sintering at a specified temperature.

According to the related reports, $AgNb_{1-x}Ta_xO_3$ delectric decomposes easily during the sintering process and results in the deteroration of the dielectric properties. For example, when $x = 0.5$, the decomposition takes place at 1100 °C as follows[1]:

$$104AgNb_{1/2}Ta_{1/2}O_3 \xrightarrow{-26Ag_2O} 26Ag_2(NbTa)O_{11} \xrightarrow{-10Ag_2O} 4Ag_2(NbTa)_{26}O_{69} \xrightarrow{-3Ag_2O} 13Ag_2(NbTa)_3O_{26} \xrightarrow{-13Ag_2O} 52(NbTa)_2O_5$$

So, it is necessary to restrain decomposition during the sintering process.

Based on the investigation of Matjaz Valant,[2] when sintered in the oxide atmosphere, the decomposition of the ANT dielectric can be restrained effectively. However, the processing is very complex.

Through our research, the temperature coefficient of capacitance (TCC) can be adjusted to $0 \pm 30 \times 10^{-6}/^{\circ}C$ by choosing proper molar ratio of Nb^{5+} to Ta^{5+}. In this paper, it is emphasized to restrain the decomposition by adding glass and to decrease the dielectric loss by adding dopant.

2. Experimental procedure

The starting powders were analytical reagents Ag_2O, Nb_2O_5 and Ta_2O_5. The mixture was calcined through the traditional solid-state reaction to prepare ANT system and then proper dopants and glass were added to improve the dielectric and sintering properties. The powders were pressed into disks and sintered in air at 950–1200 °C.

The dielectric properties at room temperature were characterized by an LCR meter (HP4285A) at 1 MHz. TCC of the dielectric constant was measured at 1 MHz by another LCR meter (HP4278A) equipped with a thermostat in the temperature range from room temperature to 85 °C. The microstructures were characterized by scanning electron microscopy (SEM).

3. Results and discussion

3.1. The effects of glass on ANT system

As mentioned above, the most important problem of the ANT system sintered in air is the decomposition at higher sintering

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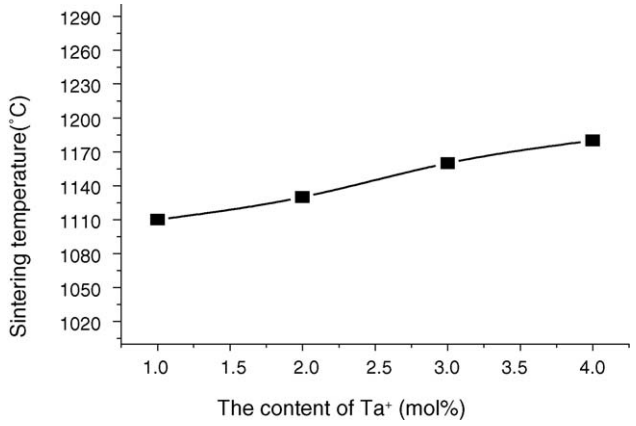

Fig. 1. Sintering temperature vs. the content of Ta^{+}.

temperature. So the purpose of this experiment is to restrain the decomposition.

The relationship between the sintering temperature of ANT system and Ta^{5+} content is shown in Fig. 1, which indicates that the sintering temperature increases gradually with increasing Ta^{5+} content.

The decomposition of ANT system accelerates with increasing of the sintering temperature. Therefore, the sintering temperature could be lowered by decreasing Ta^{5+} content. However, it could hardly lower the sintering temperature below the decomposition temperature effectively. Proper flux must be chosen for this system.

Figs. 2 and 3 are, respectively, the SEM micrographs of undoped samples sintered at 1130 °C and doped samples with 2 wt% glass. It can be observed that the samples added by glass are denser than the undoped samples. The sintering temperature of the samples in Fig. 3 was 960 °C, which is below the decomposition temperature of the ANT system.

Fig. 4 illustrates the variation of the dielectric loss ($\tan\delta$) as the function of glass content.

The dielectric loss varies slightly below 2 wt% glass but sharply when the content exceeds 2 wt%. Considering that the sintering temperature decreases with the increasing glass content, the value of the content should be limited to 2 wt%, and then the system with better properties is obtained.

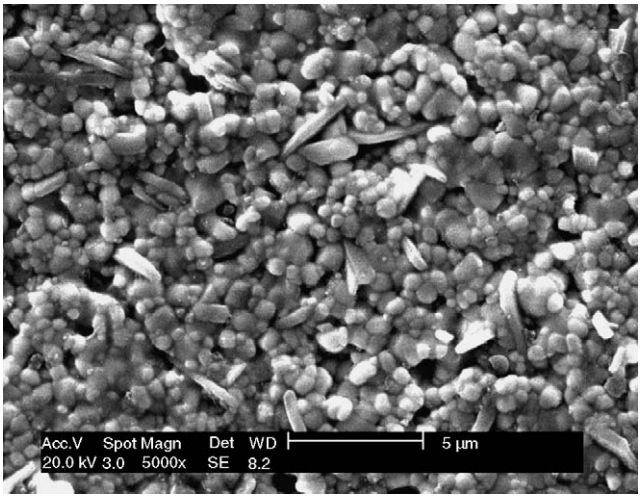

Fig. 2. SEM micrographs of the undoped samples.

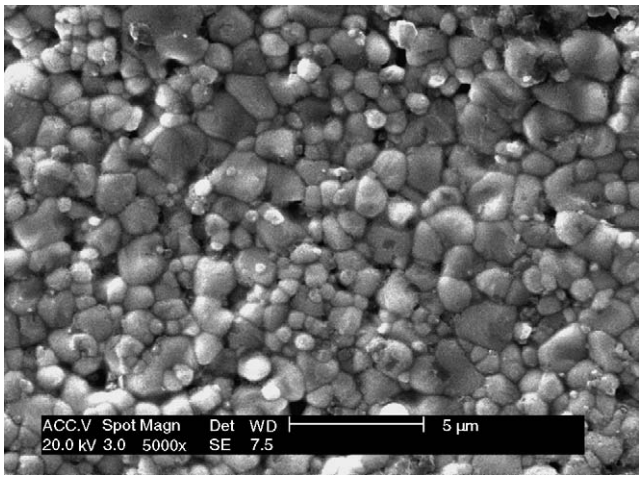

Fig. 3. SEM micrograph of the sample with 2 wt% glass.

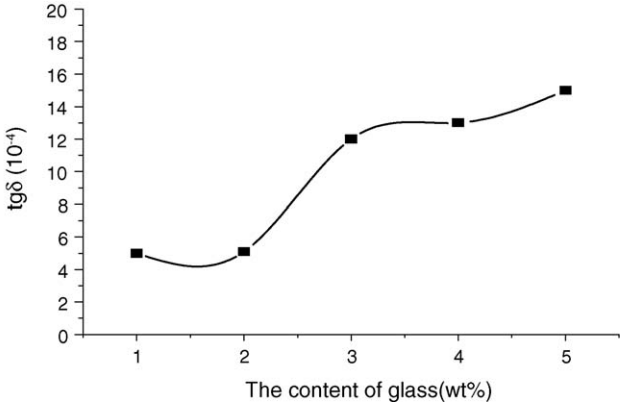

Fig. 4. Dielectric loss $\tan\delta$ vs. the content of glass.

3.2. The effects of Nb/Ta on the dielectric properties

The dielectric properties of the ANT system with different ratios of Nb/Ta are researched, as shown in Table 1.

It is clear that the TCC values decrease with increasing Ta^{5+} content, because TCC of $AgNbO_3$ is positive while $AgTaO_3$ is negative.[3,4] When the ratio of Nb/Ta is 0.8/0.2, TCC of the ANT system approaches to $10 \times 10^{-6}/°C$ which satisfies the NPO specification.

Table 1
The influence of Nb/Ta on the dielectric properties of ANT system (at 1 MHz)

Nb/Ta	$\tan\delta$ ($\times 10^{-4}$)	ε	I_R (Ω)	TCC ($\times 10^{-6}/°C$)
0.9/0.1	7.4	529	$>10^{12}$	+428
0.8/0.2	5.2	512	$>10^{12}$	+10
0.7/0.3	7.5	460	$>10^{12}$	−421
0.6/0.4	8.0	415	$>10^{12}$	−960

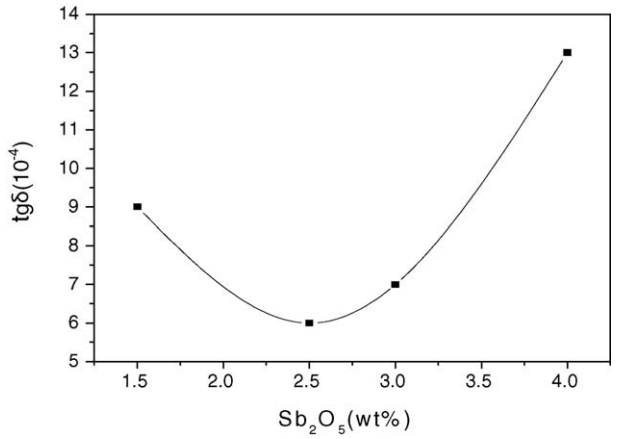

Fig. 5. Effect of Sb_2O_5 content on the loss.

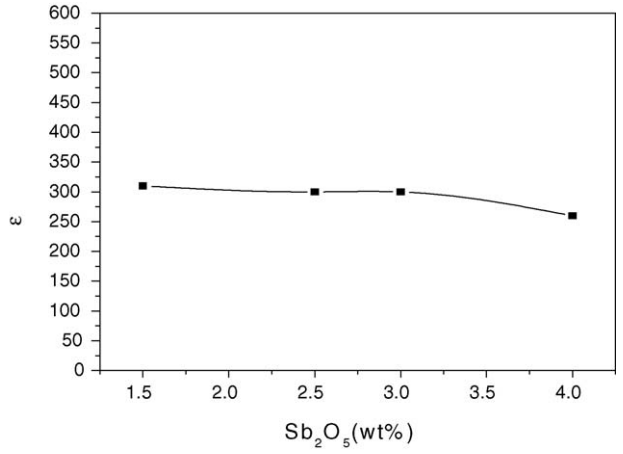

Fig. 6. Effect of content of Sb_2O_5 on ε.

3.3. The influence of Sb_2O_5 additive

It indicates that the dielectric loss decreases with increasing Sb_2O_5 content as shown in Fig. 5. However, when its content exceeds 2.5 wt%, $\tan\delta$ value rises sharply. Since this system is perovskite structure, the tolerance factor of the structure is expressed as $r_A + r_O = t\sqrt{2}(r_B + r_O)$, where r_A, r_B and r_O are the radii of the A-site ions, B-site ions and the oxygen ions, respectively. In the structure, Sb^{5+} ions partly substitute for Nb^{5+} and Ta^{5+} in B-site because its valency is close to that of Nb^{5+} and Ta^{5+} but a little smaller. Therefore, the tolerance factor becomes large and the relaxation polarization weakened and the dielectric loss of the system decreases accordingly. But if the content of Sb_2O_5 exceeds 2.5 wt%, they might enrich at grain boundary to form secondary phase, which leads to the increasing of the dielectric loss.

Fig. 6 shows the relationship between the dielectric constant and Sb_2O_5 content. It can be observed that permittivity varies slightly with the content of Sb_2O_5. Therefore, the influence of dopant on the dielectric loss of the system is focused on in experiment.

4. Conclusions

The sintering and the dielectric properties of ANT system are improved by adding 2 wt% glass; moreover, the sintering temperature reduces to 960 °C, which is below the decomposition temperature of ANT system. When the ratio of Nb/Ta is 0.8/0.2, TCC of ANT system approaches to $10 \times 10^{-6}/°C$, which satisfies the NPO specification. In addition, the dielectric loss decreases with increasing Sb_2O_5 content below 2.5 wt%.

The dielectric properties of the resultant ceramics are of permittivity about 512, temperature coefficient of capacitance about $10 \times 10^{-6}/°C$ and loss tangent, $\tan\delta$ about 5.2×10^{-4}.

Acknowledgements

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