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Temperature-Stable Super High Permittivity Dielectric Ceramics Based on $(Ag_{1-x}Na_x)(Nb_{1-y}Ta_y)O_3$ System

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Abstract. The dielectric properties of $(Ag_{1-x}Na_x)(Nb_{1-y}Ta_y)O_3$ were studied in this paper. The molar ratios of Ag/Na and Nb/Ta were quite important to adjust dielectric properties of the system. The ceramic material with high permittivity and low dielectric loss can be obtained in the cases where Ag/Na ratio is 3/2 and Nb/Ta ratio is 3/2. In addition, the dielectric loss was reduced by preparing the precursor in advance.

Keywords: $(Ag_{1-x}Na_x)(Nb_{1-y}Ta_y)O_3$, dielectric properties, precursor

1. Introduction

With the increasing development in information industry and mobile communication, the electronic devices face the challenge of high property, high stability, miniaturization and integration, which creates a demand for novel electroceramics with high permittivity and reliability.

According to the formula $f_r \approx C/D\sqrt{\varepsilon}$ where f_r is the resonance frequency, D is the size of the microwave devices, C is the speed of the light, ε is relative permittivity, the dimension of the device is inversely proportional to the square root of permittivity when f_r maintains constant. Thus the key of the miniaturization of the devices is to improve permittivity of dielectric materials. Many investigations on materials with higher permittivity have been carried out. From last decade, a new type of dielectric system with higher dielectric constant [1–3] (above 400) was of concerned, i.e. $(Ag_{1-x}Na_x)(Nb_{1-y}Ta_y)O_3$ The better characteristics make the system suitable for practical applications. However, the compound decomposes easily during synthesis and sintering according to the previous research results. For this reason, the synthesis and the resultant compound must be processed in oxygen pressure atmosphere and the process are rather complex. On the basis of the study in this paper, $(Ag_{1-x}Na_x)(Nb_{1-y}Ta_y)O_3$ (ANNT) system was obtained by substitutions of Na^+ for Ag^+ and Ta^{5+} for Nb^{5+}. The synthesis and sintering processes are simplified.

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2. Experimental Procedure

The raw materials were Ag_2O, Na_2CO_3, Nb_2O_5 and Ta_2O_5. All the reagents used in the experiment were analytical pure. The ANNT system was heat-treated at certain temperatures 1100°C and the obtained powders were added by proper additives Bi_2O_3, MnO_2 and glass to improve the dielectric and sintering properties. The total contents of the additives were no more than 7% in weight percent. Appropriate mixtures of the additives were premilled, mixed with ANNT powders and then milled, dried, pressed into disc-shaped form, and then sintered at 960–1150°C in air. The loss tangent and capacitance of the samples were measured by HP4278A at 1 MHz and the temperature coefficient of capacitance (TCC) was measured at 1 MHz using GZ-ESPEC and HM 27001 Capacitor C-T Meter Model. The insulation resistance was examined by Super-High Resistance Meter Model EC36. Model 2038 X, Rigaku was employed to analyze the X-ray diffraction patterns of the samples.

3. Results and Discussion

3.1. *The Effect of Different Ag/Na Ratio on Dielectric Properties of the System*

The following figures showed the XRD patterns when X values were 0.3 and 0.4 respectively. As shown in Figs. 1 and 2, X-ray diffraction pattern peaks of $AgTaO_3$, $AgNbO_3$, $NaTaO_3$, $NaNbO_3$ were at similar location. It suggested that they all had the perovskite structure and ANNT solid solution formed. The Bragg's peak near 30 degrees indicated the presence of Bi_2O_3. It can be inferred that the system didn't decompose because the peaks of Ag and Ag_2O weren't found from XRD.

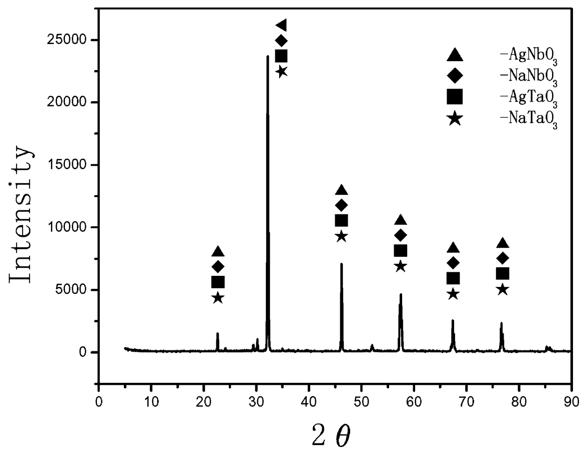

Fig. 1. XRD of the system when $x = 0.3$, $y = 0.4$.

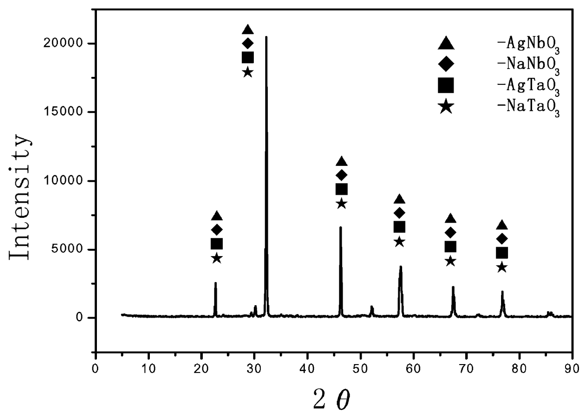

Fig. 2. XRD of the system when $x = 0.4$, $v = 0.4$.

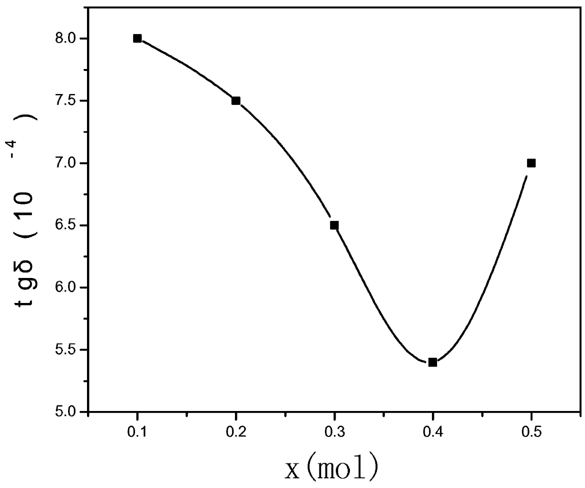

Fig. 3. Relation between dielectric loss and molar content of Na^+ (when $y = 0.4$).

The radii of Na^+ and Ag^+ are respectively 0.115 and 0.10 nm. In the formula $1 - \frac{R_A}{R_B} < 15\%$ which determines the formation of the solid solution, R^+_{Na} and R^+_{Ag} were introduced into the expression, then we obtained $1 - \frac{0.102}{0.115} = 11.3\%$ less than 15%. In addition, Na^+ and Ag^+ have the same ionic valence, this system can form perfect solid solution . Different contents of Na^+ and Ag^+ had significant effect on the dielectric properties of the system. Higher dielectric constant and lower dielectric loss can be obtained by adjusting the different ratio of Ag^+ and Na^+. The relationship between the dielectric properties of the system and the ratio of Ag/Na were illustrated by Figs. 3, 4 and 5. There is an optimum

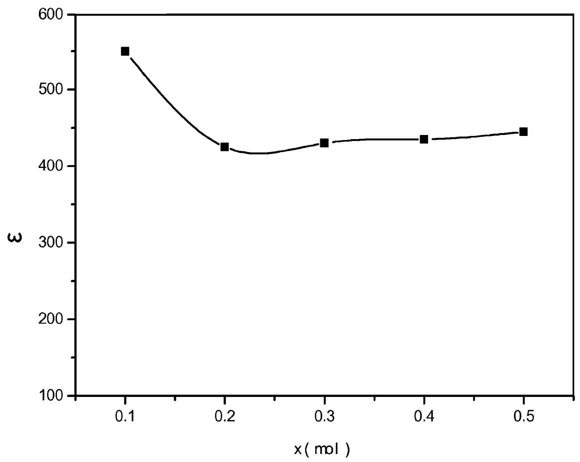

Fig. 4. Relation between dielectric constant and molar content of Na^+ (when $y = 0.4$).

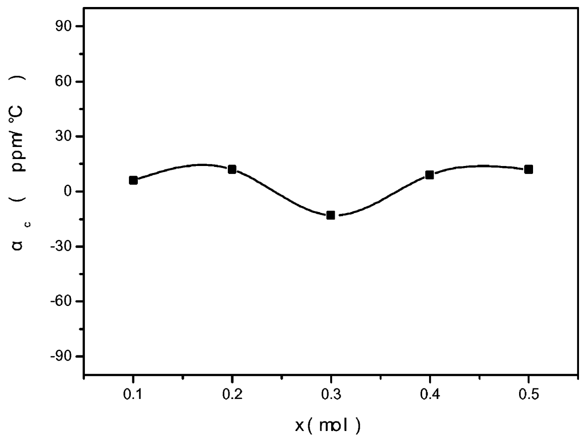

Fig. 5. Relation between TCC and molar content of Na^+ (when $y = 0.4$).

value ($x = 0.4$) in the dielectric loss versus Na^+ content curve. But the sintering temperature increased with the addition of Na^+, when x value exceeded 0.4, the surface of the sample became black, which indicated that decomposition became obvious and the dielectric loss increased accordingly. From Fig. 4, the addition of Na^+ lowered the dielectric constant but it maintained constant when the content exceeded 0.1.

3.2. *The Effect of Different Nb/Ta Ratio*

It can be testified that different molar ratio of Nb/Ta has an great effect on dielectric properties of the system in the experiment. The results were shown in Figs. 6, 7 and 8.

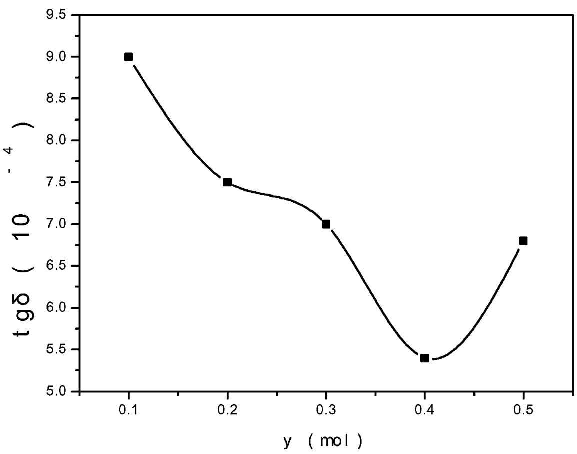

Fig. 6. Dielectric loss vs. y value when $x = 0.4$.

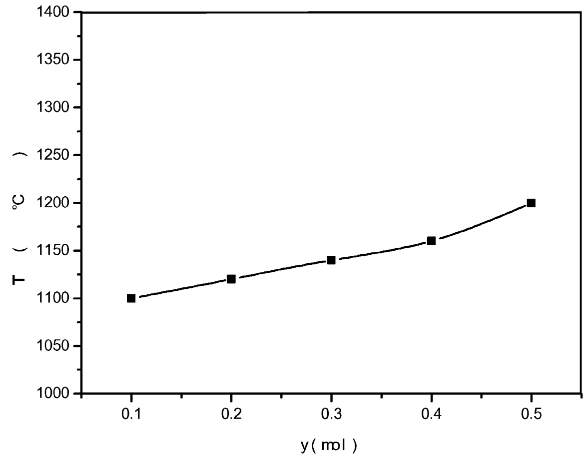

Fig. 7. Sinter temperature vs. y value when $x = 0.4$.

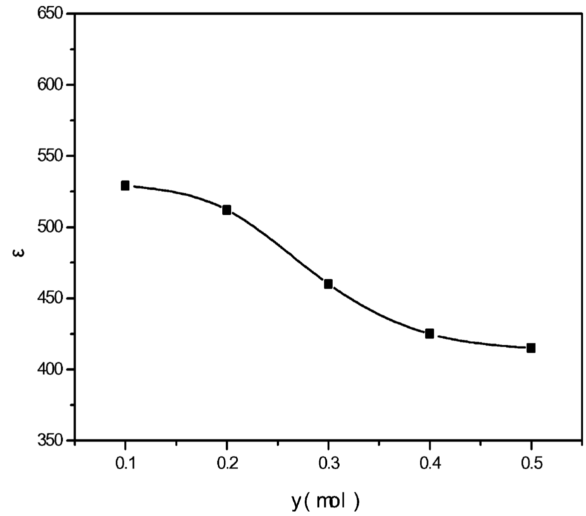

Fig. 8. Permittive vs. y value when $x = 0.4$.

From the above figures, when the molar content of Ta^{5+} was 0.4, the dielectric loss reached the lowest point, permittivity kept high value above 400, while the sintering temperature increased with Ta^{5+} content.

3.3. *The Effect of Different Synthesized Technique*

The key of the investigation is to lower the dielectric loss of the system effectively, so the proper process, especially the synthesis, could decrease the loss significantly.

In this experiment, the raw materials were compared by two synthetic methods. One [4, 5] was to

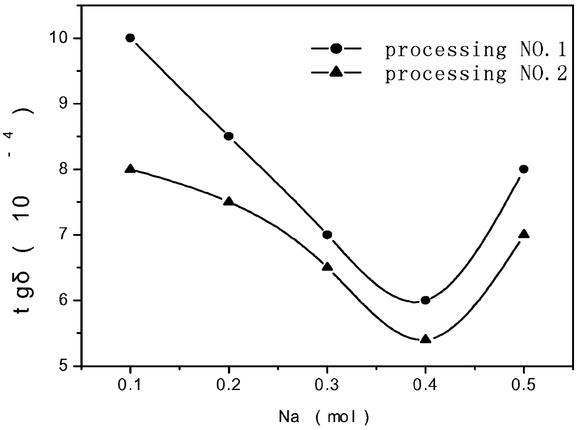

Fig. 9. Effect of different processes on the dielectric loss.

mix $(Ag_{1-x}Na_x)TaO_3$ and $(Ag_{1-x}\ Na_x)NbO_3$ according to molar fraction and processed by solid state reaction as mentioned earlier. The other was to mix Ta_2O_5 and Nb_2O_5 at a certain ratio and synthesize at 1200 °C, then add Na_2CO_3, Ag_2O and additives Bi_2O_3, MnO_2 and glass, which were used to control sintering temperature, reduced the possibility of decomposition of Ag and thus improve the dielectric properties. The samples were finally fired at 1140°C. There were obvious differences in two processes as shown in Fig. 9. The second synthetic method could lower the dielectric loss effectively.

The dielectric properties of resultant ceramics are of permittivity about 450, temperature coefficient of capacitance about 13×10^{-6}/°C, loss tangent tg δ below 5.5×10^{-4} and high insulation resistivity above $10^{13}\Omega$·cm.

4. Conclusion

1. In $(Ag_{1-x}\ Na_x)(Nb_{1-y}Ta_y)O_3$ ceramic, when molar content of Na^+ was 0.4, the dielectric loss of the system was lowered below 5.5×10^{-4}.
2. When the molar ratio of Ta/Nb was 2/3, the system exhibited better dielectric properties. The loss wass 5.5×10^{-4} and the permittivity was 340.
3. The dielectric loss can be reduced effectively by preparing the precursor in advance.

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