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# Investigation of $Ag(Ta,Nb)O_3$ as tunable microwave dielectric

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**Abstract**

$Ag(Ta,Nb)O_3$ (ATN) has been investigated as a candidate material for an application in tunable high frequency devices. $AgTa_{0.1}Nb_{0.9}O_3$ as a bulk ceramic shows moderate permittivity of $\varepsilon = 310$ and visible tunability $\tau = (\varepsilon(0) - \varepsilon(E_{max}))/\varepsilon(0)$ of 16% for an applied field of 10 kV/cm at room temperature. $AgTa_xNb_{1-x}O_3$ powders with $0 \leqslant x \leqslant 0.4$ have been prepared by mixed oxide technique. Permittivity, losses and tunability of ATN bulk ceramic and screen printed thick films have been characterized at frequencies $<1$ MHz in the temperature range from $-150$ °C to $+120$ °C. Increasing the tantalum content leads to an increase of the tunability and a shift of the point of maximum tunability to lower temperatures. ATN thick films have also been characterized up to 12 GHz in the temperature range from $-30$ °C to $+100$ °C by using coplanar waveguide resonators. A decrease of tunability to $\tau < 1\%$ with increasing frequency has been observed. The beginning of dielectric relaxation is observed at frequency of about 8 GHz.



*Keywords:* Dielectric properties; Niobates; Porosity; Sintering; Tantalates

## 1. Introduction

Ferroelectric materials like $(Ba,Sr)TiO_3$ (BST), or $Ba(Zr,Ti)O_3$ (BZT) are promising candidates for application in tunable microwave devices like phase shifters, tunable filters and varactors.[1–3] In comparison to the above-mentioned material systems, ATN combines the advantages of low permittivity and small dielectric dispersion in a wide frequency range from 1 kHz to 100 GHz.[4] Non-tunable ATN bandpass filters for use at microwave frequencies up to 2 GHz with $Q$-values up to 700 have already been produced.[5]

Although various papers describe the structure and properties of ATN,[6–8] only a few of them give a more detailed description of the electrical properties of the tunable monoclinic–monoclinic M1–M2 phase transition. In Ref. 9 the M1–M2 phase transition is reported to be strongly dispersive with a ferroelectric relaxor-like character. In Ref. 10 ATN thin films fabricated by pulsed laser deposition have been characterized up to 1 MHz with interdigital capacitors (IDC). The capacitors showed a tunability of up to 6.8% and losses smaller than 0.3%. Although recently ATN has successfully been fabricated as thick film and characterized up to 12 GHz,[11] the strong decrease of the ATN tunability at about 10 GHz is still not completely understood.

This paper compares the low frequency dielectric properties of tunable ATN bulk ceramics and thick films at the M1–M2 phase transition. The ATN films are also characterized in the high frequency region using a coplanar waveguide resonator.

## 2. Material preparation and experimental methods

$AgTaO_3$ (ATO) and $AgNbO_3$ (ANO) powders have been prepared by the mixed oxide method. To avoid a reduction of $Ag_2O$, preparative tasks have been carried out in a darkroom. To prevent metallic silver precipitates, the calcination has been carried out in oxygen atmosphere as reported in Ref. 7. The calcination parameters were 900 °C, 8 h for ATO and 900 °C, 4 h for ANO. ATO and ANO have been weighed out in stoichiometric proportions to prepare $Ag(Ta,Nb)O_3$ bulks and powders for thick film paste.

Bulk ceramics have been cold isostatically pressed at 200 MPa and sintered at the temperatures $T_s = 1100$ °C + 200 °C·$(1-x)$, where $x$ denotes the Ta ratio. A porosity of 4% has been determined by image processing methods based on SEM pictures of polished samples. The grain size of the ATN bulks varies from 40 to 10 μm.

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Before preparing the paste for thick films, ATN powders have been calcinated a second time at 1030 °C. The paste has been screen printed on polished 99.6% $Al_2O_3$ substrates of 635 μm thickness.

A Siemens D5000 X-ray diffractometer has been used for XRD studies to determine the maximum sintering temperature. ATN powder has been mixed with 10 wt.% $Al_2O_3$ powder and sintered at different temperatures. The measured XRD patterns of $AgTa_{0.2}Nb_{0.8}O_3$ powder are shown in Fig. 1. Starting from room temperature, no additional phases can be found up to 1100 °C. At 1150 °C, $AlNbO_4$ and $AlTaO_4$ second phases can be observed.

Additionally performed thick films to substrate adhesion tests revealed an optimum sintering temperature of 1060 °C.

The film thickness is 3 μm for a single printing step and about 6 μm after a second printing step after 24 h of drying. The grain size and porosity of the thick films discussed in this paper was 3–4 μm and 24%, respectively.

The low frequency (1 kHz to 1 MHz) measurements have been performed with an Alpha-H High Resolution Dielectric Analyzer (novocontrol) with Broadband High Voltage Extension to overlay a DC voltage up to 150 V to the measurement signal. The bulk samples were cut into disks of 1 mm thickness and 6 mm diameter. Thin gold electrodes were sputtered on both faces of the disk to form plate capacitors. The thick film properties have been measured with the help of IDC structures, and the electrical parameters have been derived as described in Refs 11 and 12.

For the high frequency measurements (3–12 GHz), a 8510C vector network analyzer (Agilent Technologies) in combination with a climatic chamber (System Weiss/Typ WK1-180/40) for temperatures from −40 °C to +180 °C was used. Thick films with 6 μm thickness have been used for the high frequency measurements. A coplanar waveguide (CPW) resonator structure as described in Ref. 11 has been used. The material parameters of ATN thick films for low and high frequencies have been calculated from the effective permittivity and the quality factor $Q = 1/\tan\delta$ by using conformal mapping methods as described in Refs. 12–15.

## 3. Results and discussion

Fig. 2 shows the temperature dependence of dielectric permittivity of $AgTa_{0.4}Nb_{0.6}O_3$ bulk ceramics. Two monoclinic–monoclinic phase transitions (M1–M2 and M2–M3) indicated by a local maximum of $\varepsilon_r$ can be observed over the temperature range from −130 °C to +230 °C: the M1–M2 phase transition at −95 °C and M2–M3 at +100 °C. M1–M2 shows a tunability of 20% at 500 V/mm whereas no tunability can be observed at the M2–M3 phase transition. The small irregularity of the curve at about room temperature is due to the change of the sample holder when changing from cryostat to oven measurements.

The tunable M1–M2 phase transition can be shifted to higher temperatures by decreasing the tantalum ratio (Fig. 3). A concurrent decrease of the local maximum of permittivity can be observed until it almost disappears for pure $AgNbO_3$. The permittivity of the $AgTa_{0.2}Nb_{0.8}O_3$ samples is 30% higher than in Ref. 7 but matches well with the results of the samples with other tantalum ratios. The difference can be due to slightly different material preparation. For ATN90 the temperature of maximum tunability for bulk ceramics at 100 kHz is at room temperature.

Table 1 shows the tunability $\tau_{max}$ at maximum applied electric field $E_{max}$ and losses $\tan\delta$ of the ATN bulks at the point of the local maximum of permittivity, which is at the same time the point of maximum tunability. The theoretical value for $\tau_{max}$ for ATN with 40% tantalum would be higher than for 20% tantalum due to the

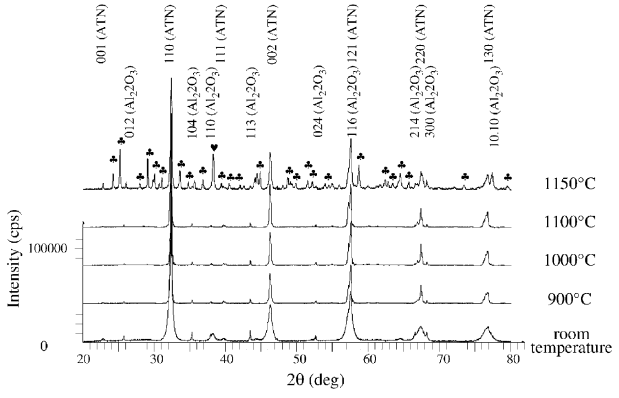


Fig. 1. XRD $\theta$–$2\theta$ scans in Cu$K_\alpha$ radiation for $AgTa_{0.2}Nb_{0.8}O_3$ mixed with 10% $Al_2O_3$ powder and sintered at different temperatures. Symbol ♣ marks the reflections of $AlNbO_4$ and $AlTaO_4$, (PDF card 41-0347 and 25-1490) and ♥ marks the reflections of Ag (PDF card 22-0471).

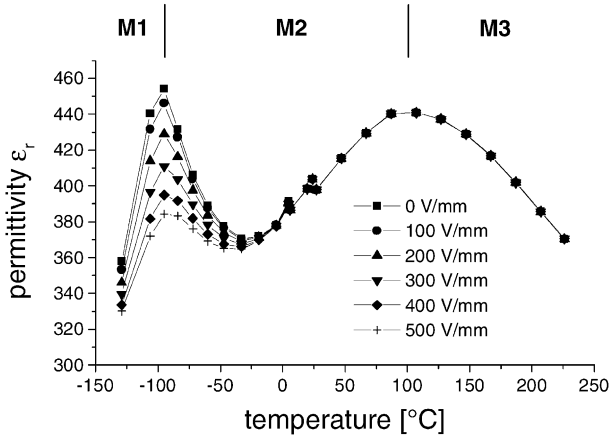


Fig. 2. Temperature dependence of dielectric permittivity of $AgTa_{0.4}Nb_{0.6}O_3$ bulk ceramics at 100 kHz.

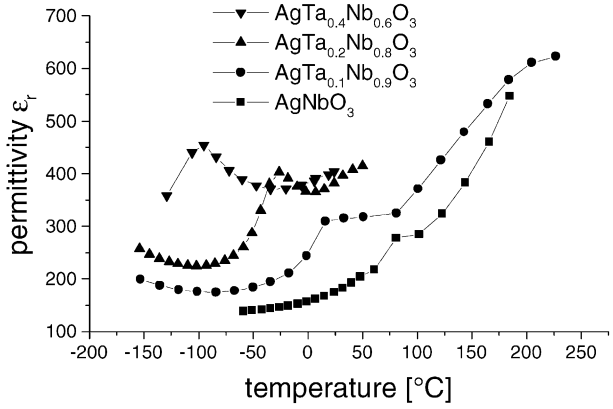


Fig. 3. Temperature dependence of dielectric permittivity of ATN bulk ceramics with different tantalum ratios (100 kHz).

Table 1
Tunability $\tau_{max}$ at maximum applied electric field and losses tan$\delta$ of the $AgTa_xNb_{1-x}O_3$ bulk ceramics with different tantalum ratios $x$ (100 kHz)

| $x$ | Temperature at $\tau_{max}$ (°C) | $E_{max}$ (kV/mm) | $\tau_{max}$ (%) | tan$\delta$ |
|---|---|---|---|---|
| 0.4 | −106 | 0.5 | 15 | |
| 0.2 | −26 | 0.8 | 27 | <0.014 |
| 0.1 | 17 | 1 | 16 | <0.015 |
| 0 | 82 | 1 | 1 | |

nonlinear field dependency of $\varepsilon_r$. Therefore a decrease of the tantalum ratio causes a decrease of $\tau_{max}$ too.

Fig. 4 shows the temperature dependence of dielectric permittivity of $AgTa_{0.1}Nb_{0.9}O_3$ (ATN90) thick films. Due to porosity, the permittivity is about half the one of the corresponding bulk. The maximum tunability is 16% at 33 °C. The measurement values of the permittivity fit well with the theoretical values $\varepsilon*(p)$ of samples with the porosity $p$ obtained with the simplified Bruggeman formula for inhomogeneous symmetrical media Ref. 16 with air as second medium although the grain size of bulk and thick film differs. This indicates

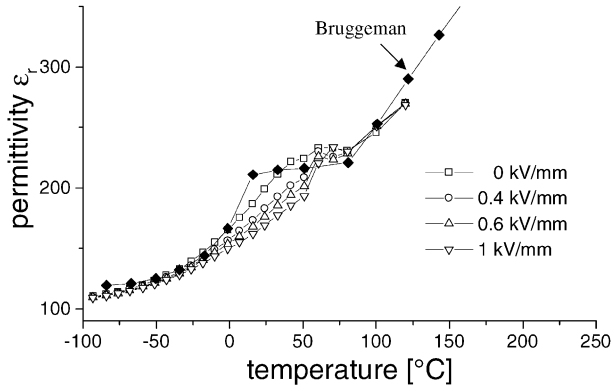


Fig. 4. Temperature dependence of dielectric permittivity of ATN90 thick films (100 kHz) and the theoretical curve for ATN90 with 24% porosity calculated from the corresponding ATN90 bulk with the Bruggeman formula.[15].

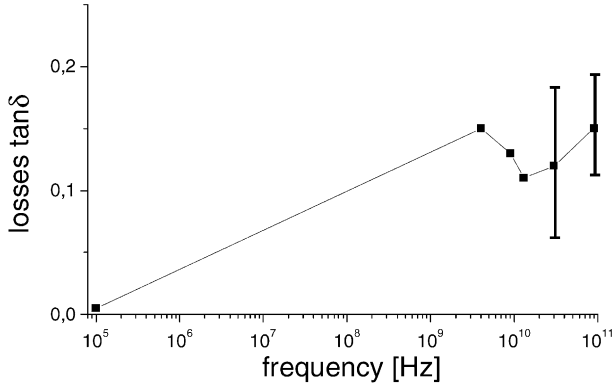


Fig. 5. Frequency dependence of the losses of porous ATN90 thick films at room temperature.

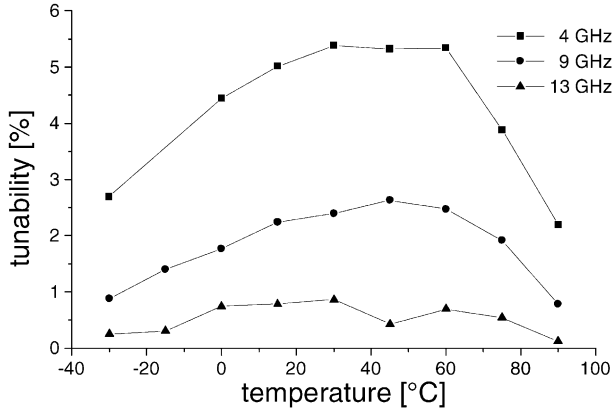


Fig. 6. Temperature dependence of the tunability of ATN90 in the low GHz region.

that the grain size has almost no influence on the permittivity of ATN in the low frequency region.

$$\varepsilon^*(p) = \varepsilon_r \cdot (1 - 3p/2) \quad (1)$$

The losses of ATN90 thick films at room temperature increase for increasing frequencies (Fig. 5). From 100 kHz to 13 GHz a relaxation can be observed. The increase of losses from 30 to 90 GHz measured with an open resonator method[17] at the Institut für Materialforschung I (IMF I, Forschungszentrum Karlsruhe) is most probably due to phonon scattering effects.

Fig. 6 shows the temperature dependence of tunability of ATN90 thick films at different frequencies. At low GHz frequencies a shift of the maximum tunability to 40 °C can be observed. Due to relaxation the tunability decreases from 5% to less than 1% from 4 to 13 GHz. At 4 GHz the tunability of more than 5% remains very stable from 30 to 60 °C.

## 4. Conclusions

Dense ATN bulk ceramics and thick films with 24% porosity have been prepared. The tunable region of

ATN is the M1–M2 phase transition which can be shifted to higher temperatures by decreasing the tantalum ratio, but this additionally decreases the tunability.

The porosity dependence of $\varepsilon_r$ of ATN90 can be described by the Bruggeman formula with an error $<10\%$, and it shows no dependency on the grain size. This leads to the assumption that the change in size from 40 to 3 μm does not lead to changes in the internal stress in grains.

The increase of losses in the low GHz range due to relaxation is accompanied by a shift of the maximum tunability from about 30 up to 45 °C. Therefore, the optimum tantalum ratio for a room temperature application of ATN as tunable ceramic in low GHz range under 8 GHz is about 20%, which would additionally increase the tunability.

If no possibility is found to shift the relaxation to frequencies higher than 30 GHz, for example, by further reduction of the grain size, the application of ATN as tunable microwave ceramic is limited to the low GHz region.

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