

Ag(Nb,Ta)O₃-based ceramics with suppressed temperature dependence of permittivity

Matjaz Valant^{a,*}, Danilo Suvorov^a, Christian Hoffmann^b, Helmut Sommariva^b

^a“Jozef Stefan” Institute, Jamova 39, 1000 Ljubljana, Slovenia

^bEPCOS OHG, Siemensstrasse 43, Deutschlandsberg, Austria

Abstract

Different methods for the suppression of the temperature coefficient of permittivity of Ag(Nb,Ta)O₃-based ceramics have been experimentally tested, as a result two methods, isovalent doping on the B-site and microstructural engineering, were combined to produce a Ag(Nb,Ta)O₃-based ceramic with a temperature stable dielectric constant. Although the AgNbO₃ and AgTaO₃ exhibit complete solid solubility, special attention was devoted to maintaining the highest possible level of non-equilibrium in the Ag(Nb,Ta)O₃-based ceramics. The influence of particular compositional and processing parameters on the microstructure and temperature dependence of permittivity was investigated. Based on our observations, the powder processing, phase composition and the firing conditions were optimized to produce Ag(Nb,Ta)O₃-based ceramics with a permittivity of 430, a temperature coefficient of permittivity < 50 ppm/K, $\tan\delta = 2 \cdot 10^{-4}$ (at 1 MHz) and a Q -value (at 1 GHz) = 700. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Consumer demands for multi-functional pocket- or credit-card-sized devices are forcing the pace in the development of the microwave wireless-communication and information systems. Such level of miniaturization can only be realized by introducing dielectric materials with substantially increased permittivity (κ') the physical property which is related to the dimensions of any high-frequency component (e.g. resonators, filters). For the dielectric resonator the relationship connecting the diameter (D) and permittivity with its resonant frequency (f_r) is:

$$f_r \approx \frac{c}{D\sqrt{\kappa'}}$$

where c is the velocity of light. Over the last 20 to 30 years a significant reduction in the size of microwave devices was achieved by substituting air cavities ($\kappa' = 1$) with ceramic resonators made from Ba-polytitanates¹

and MgTiO₃-CaTiO₃² ($\kappa' = 20-40$) and then by ceramic resonators based on the Ba_{6-x}R_{8+2/3x}Ti₁₈O₅₄ ($R = \text{La-Gd}$) system ($\kappa' = 70-90$).³ The development of materials with even higher permittivity is hindered by the unfortunate correlation between the permittivity and two other important dielectric properties: the dielectric losses ($\tan\delta$ is inversely proportioned to the Q -value) and the temperature dependence of the permittivity (τ_ϵ)—both of these properties are known to be adversely affected by an increase in the permittivity.⁴⁻⁶ Here we report on the development of a microwave material based on the Ag(Nb_{1-x}Ta_x)O₃ (ANT) solid solution which is characterized by low dielectric losses, a temperature-stable permittivity and, most importantly, a very high permittivity of 430. Properties like these will allow us to produce electronic components with a significantly reduced size and/or a much-increased capacity.

Previous studies on ANT, performed by Volkov et al.⁷ indicated that ANT has some potential as a material for wireless-telecommunication technology due to low dielectric losses combined with an extraordinarily high permittivity. The problem is that, it suffers from a high temperature dependence of permittivity and therefore, it has never been seriously considered as a possible substitute for the established microwave dielectric materials.

* Corresponding author. Tel.: +386-1-477-3547; fax: +386-1-426-3126.

E-mail address: matjaz.valant@ijs.si (M. Valant).

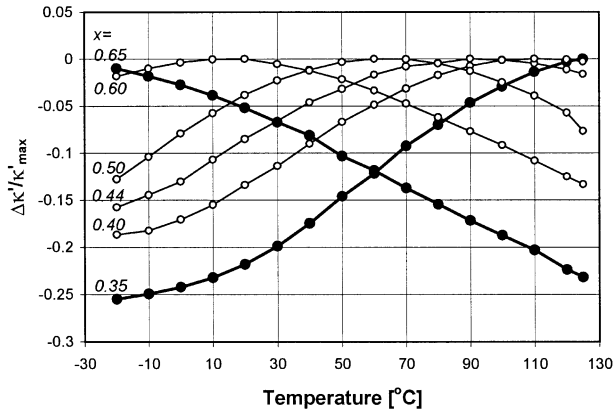


Fig. 1. Temperature dependence of the permittivity as a function of x in $\text{Ag}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ ceramics sintered to $\sim 97\%$ of theoretical density. Thick lines are used to indicate the compositions with monotonically increasing to monotonically decreasing temperature dependence ($x=0.35$ and $x=0.65$).

However, by applying a novel technique which combines isovalent cation substitution with microstructural engineering we have been able to suppress the temperature dependence below the level required for bandpass filters and capacitors (50 ppm/K) and turned ANT into a material which is ready for commercial exploitation.

2. Experimental procedure

We synthesized ANT-based compositions using the solid-state reaction method. First, Nb_2O_5 and Ta_2O_5 were reacted at 1200°C for 20 h, after which we added Ag_2O to the reaction mixture and fired it at 970°C for 10 h to form the ANT. The subsequent sintering of the pelletized powders was carried out in closed crucibles at 1100°C for 5 h in an oxygen atmosphere.^{8,9} The dielectric properties were measured at 1 MHz and ~ 2 GHz.

3. Results and discussion

In the temperature interval of the interest, -20 to $+80^\circ\text{C}$, $\text{Ag}(\text{Nb}_{0.5}\text{Ta}_{0.5})\text{O}_3$ exhibits a broad permittivity maximum at $\sim 60^\circ\text{C}$, with the maximum temperature dependence of permittivity at any point in the interval being ~ 1300 ppm/K (see Fig. 1, curve $x=0.5$); this is much too large for commercial applications. In order to control the temperature dependence of permittivity it is necessary to induce slight modifications to the oxygen sublattice of the crystal structure, and this is normally achieved by chemical substitutions.¹⁰ In the case of ANT we explored the influence of two different substitutional mechanisms on the temperature dependence of permittivity. The first mechanism, where the x -value in $\text{Ag}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ was varied, can be regarded as an isovalent substitution, the second is an aliovalent co-substitution which is represented by the formula $(\text{Ag}_{1-x}\text{Sm}_x)(\text{Nb,Ta})_{1-x}\text{Ga}_x\text{O}_3$. For both mechanisms the response of the temperature dependence of permittivity to the variation in x is similar and in accordance with other ferroelectric and antiferroelectric solid solutions. The change in the composition induces a shift in the temperature at which the permittivity maximum occurs but does not significantly influence the shape or the slope of the curves (see Fig. 1 for isovalent substitution), which would be necessary for the suppression of the temperature dependence.

Although isovalent substitution was shown to be ineffective in suppressing the temperature dependence of permittivity, Fig. 1 shows one very important feature: just by varying the Nb-to-Ta ratio, the permittivity variation in the temperature range of interest alters from a monotonically increasing to a monotonically decreasing trend. Therefore, by combining two such phases into a dense ceramic the compensation of the individual temperature dependencies may be expected.

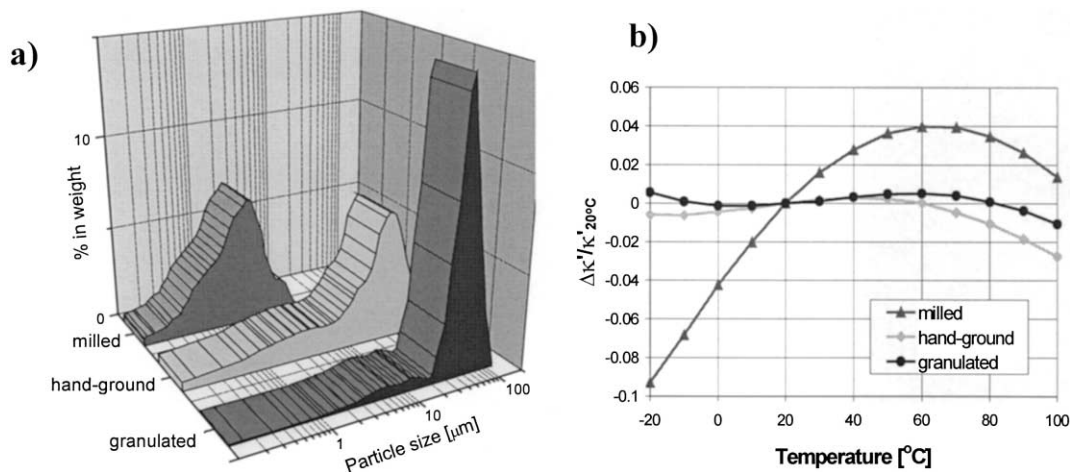


Fig. 2. (a) Particle size distribution of the ANT powders prepared by three different processing routes: milling for 30 min at 150 rpm in a ZrO_2 mill, hand-grinding and granulating and (b) temperature dependence of the permittivity of the ceramics with the composition 45 wt.% $\text{Ag}(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$ –55 wt.% $\text{Ag}(\text{Nb}_{0.35}\text{Ta}_{0.65})\text{O}_3$ sintered from these powders. All samples are sintered to $\sim 97\%$ of theoretical density.

In theory, ceramics composed of two phases (α and β) would exhibit properties according to the logarithmic mixture rule for permittivity¹¹ and its temperature derivative for τ_ε :

$$\log \kappa' = (1 - \nu)\log \kappa'(\alpha) + \nu\log \kappa'(\beta)$$

$$\tau_\varepsilon = (1 - \nu)\tau_\varepsilon(\alpha) + \nu\tau_\varepsilon(\beta)$$

where ν is the volume fraction of the phase β . The major limitation in applying this technique for the compensation of the temperature dependence of permittivity arises from the thermodynamic incompatibility of the

phases at sintering temperatures. Only thermodynamically compatible phases can be sintered into the α - β composite ceramics without producing any redundant reaction phase(s). In the case of ANT all the solid-solution compositions are mutually incompatible and react to form the intermediate composition (e.g. $\text{Ag}(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3 + \text{Ag}(\text{Nb}_{0.35}\text{Ta}_{0.65})\text{O}_3 \rightarrow 2\text{Ag}(\text{Nb}_{0.50}\text{Ta}_{0.50})\text{O}_3$). From the point of view of the dielectric properties, instead of a compensated temperature dependence of permittivity, such ceramics would exhibit a temperature dependence with a pronounced permittivity maximum which is characteristic of the single-phase ANT ceramic.

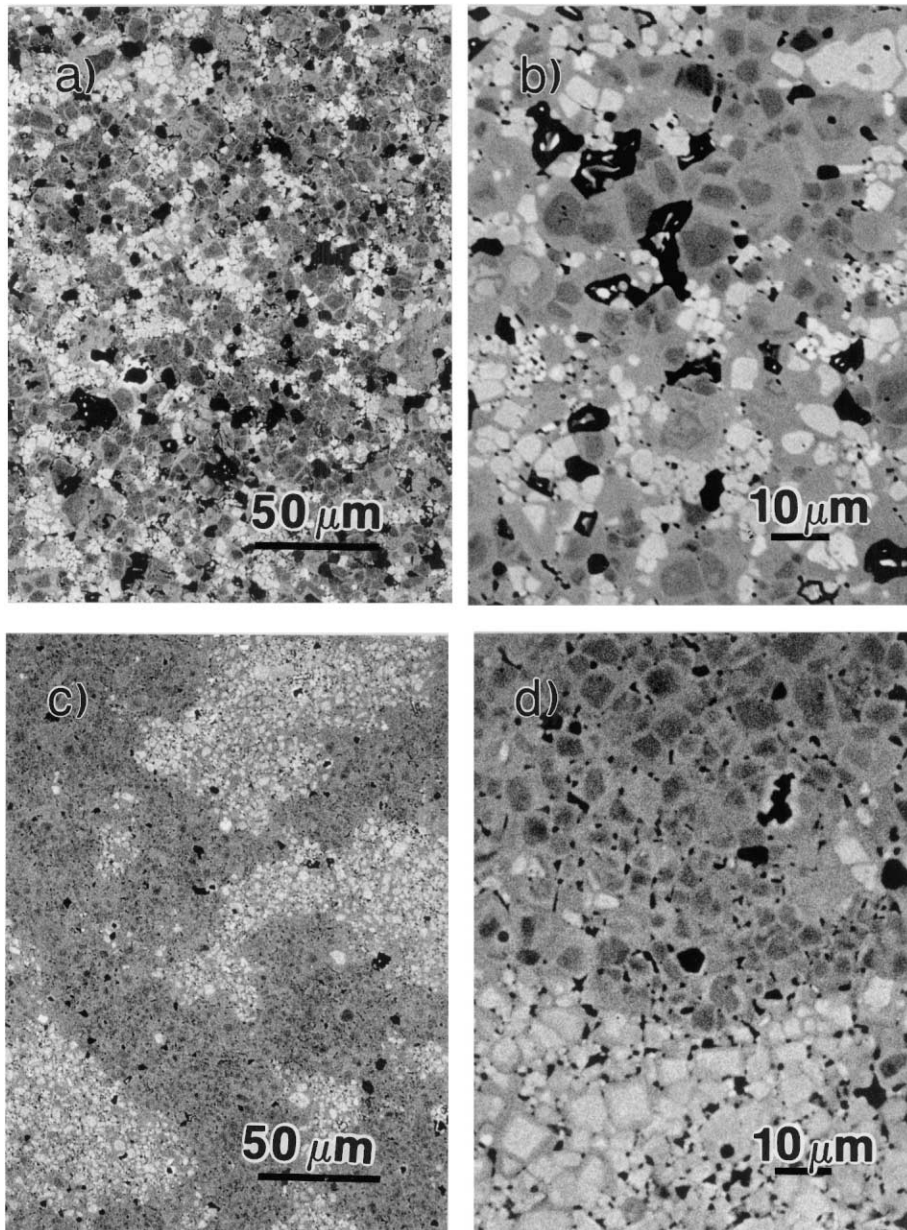


Fig. 3. Scanning electron microscope images of the microstructures of the ANT-ANT composite ceramics showing a phase distribution in the ceramics prepared from the hand-ground (a and b) and granulated powders (c and d) (dark phase, $\text{Ag}(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$; light phase, $\text{Ag}(\text{Nb}_{0.35}\text{Ta}_{0.65})\text{O}_3$, grey phase, the reaction product).

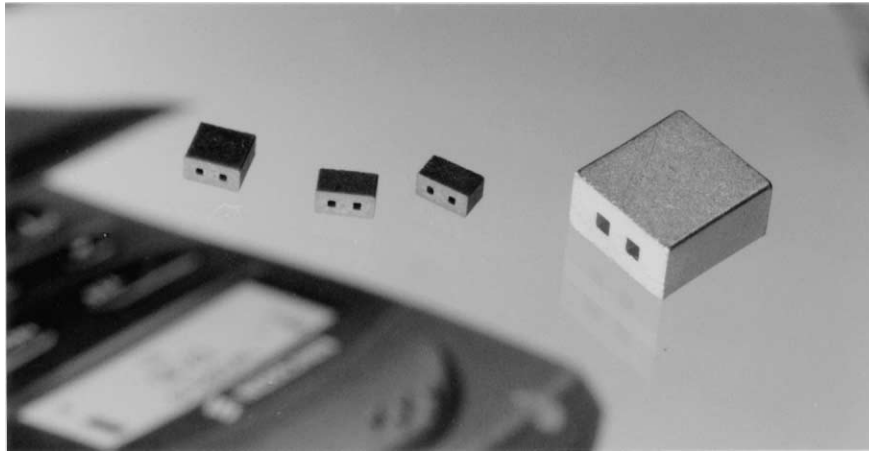


Fig. 4. Bandpass filters (1.8 and 0.9 GHz) produced from the ANT–ANT composite ceramics and a commercial 1.8 GHz bandpass filter produced from the material based on $\text{Ba}_{6-x}\text{Nd}_{8+2/3x}\text{Ti}_{18}\text{O}_{54}$ with the permittivity ~ 90 (for the size comparison).

In order to use this method to suppress the temperature dependence of permittivity of ANT ceramics we need to overcome the thermodynamic incompatibility by slowing down the kinetics of the reaction. This can be done by making use of the fact that the kinetics of the solid-state reaction are related to the particle size of the powders. At a certain particle size the kinetics of the reaction is slower than the kinetics of sintering, and with a further increase in the particle size the degree of thermodynamic non-equilibrium in densely sintered ceramics increases. To test this approach we chose two ANT compositions: $\text{Ag}(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$ and $\text{Ag}(\text{Nb}_{0.35}\text{Ta}_{0.65})\text{O}_3$. Within the range -20 to 120 °C these materials exhibit an increasing and decreasing temperature dependence of permittivity, respectively. We calcined the ANT compositions three different ways to obtain three different particle size distributions (Fig. 2a). They were either hand-ground, milled to an average particle size of ~ 1.5 μm , or granulated to ~ 45 μm . Each powder type was mixed, pressed, sintered and then analyzed with respect to its microstructural and dielectric properties. On the basis of preliminary experiments performed with the hand-ground powders, the optimum compensation of the temperature dependence of permittivity was obtained with a mixture of 45 wt.% of $\text{Ag}(\text{Nb}_{0.65}\text{Ta}_{0.35})\text{O}_3$ and 55 wt.% of $\text{Ag}(\text{Nb}_{0.35}\text{Ta}_{0.65})\text{O}_3$. Fig. 2b shows that the temperature dependence of such ceramics is significantly lower than that of the ceramics produced from the mixture of powders which were milled to an average particle size of ~ 1.5 μm . The reason for the difference can be found by looking at the microstructure of the ceramics. In the case of the milled powder, both phases reacted completely to form the intermediate $\text{Ag}(\text{Nb}_{0.485}\text{Ta}_{0.515})\text{O}_3$ composition: an equilibrium single-phase ceramic with dielectric properties characteristic of the single-phase ANT solid solution. In the case of the hand-ground

powder, the kinetics of the reaction was obviously too slow to reach equilibrium during sintering and the ceramic still contains the starting phases in addition to a significant concentration of reaction product (Fig. 3a and b).

We expected a further reduction in the interaction between the phases when the fraction of fine particles was eliminated from the ANT powders. We were able to achieve that by granulating the milled powders to obtain a sharp particle size distribution with an average size of ~ 45 μm (see Fig. 2). A microstructural analysis of the ceramics sintered from a mixture of granulates confirmed this reduced interaction. Large clusters of both phases are visible (Fig. 3c and d) with only a thin interaction layer on the grain boundaries. In accordance with the discussed correlation, we found the temperature dependence of permittivity was further reduced, and on the steepest part of the curve reached a value of only ~ 40 ppm/K (Fig. 2b). The permittivity of this ANT–ANT composite ceramic remained very high ($\kappa' = 430$) and the material exhibited low dielectric losses: $\tan\delta = 2 \cdot 10^{-4}$ (at 1 MHz) and Q (at 1 GHz) = 700.

4. Conclusion

The properties of these ANT–ANT composite ceramics are compatible with the requirements for several microwave electronic components, e.g. bandpass filters, high-capacity NP0 multilayer capacitors, and would lead to the significant miniaturization of these devices. For the case of bandpass filters, an eight-times volume reduction could be expected, see (Fig. 4), allowing the production of ceramic filters with the size of surface acoustic wave (SAW) filters, but with significantly improved power handling and low dielectric losses across a wide temperature range. For capacitor tech-

nology, the implementation of ANT would lead to a new category of multilayer capacitors with characteristics between those of standard NP0 and X7R types. In addition, the replacement of high-frequency polymer capacitors (PPS-type) with ANT capacitors in, for instance, Bluetooth modules and the loop-filters of cellular phones offers the possibility for further size reduction and the enhancement of performance and reliability.

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