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Review

Review of Ag(Nb, Ta)O_3 as a functional material

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Abstract

Recent research activities on functional properties and applications of Ag(Nb,Ta)O_3-based materials are reviewed and critically discussed. Fundamental aspects of these materials, such as crystal chemistry, lattice dynamics and phase formation, are explained first. Further, a focus is placed on the development of state-of-the-art applications for passive components, piezoelectrics and tuneable thin films. Many areas are identified where further research should focus. This includes open questions from the fundamental segment of research as well as challenges of the applied development. The review clearly presents potentials of the Ag(Nb,Ta)O_3-based materials but also reveals an incomplete understanding of these materials.

Keywords: Dielectric properties; Ferroelectric properties; Functional application; Capacitors; Ag(Nb,Ta)O_3

Contents

1. Introduction

Because of recent developments in telecommunications, electro-optics and piezoelectric components perovskite niobates and tantalates have been placed on a short list of functional materials for future technologies. Several unrelated scientific discoveries, political decisions and economical trends have made investments into investigation of these materials even more courageous and, in turn, an important fundamental knowledge was generated, a number of devices was constructed and significant industrial profits were gained. A few examples of these events are:

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- a discovery of ultra-low loss microwave ceramics based on the perovskite tantalates, which initiated extensive studies on mainly a $A^{2+}(B^{2+}_{1/3}Ta_{2/3})O_3$ type of the perovskites;
- a high market price of the tantalum, which re-directed the studies onto the alternative perovskite niobates;
- an ecologically driven quest for lead-free piezoelectrics, where a $A^{+}NbO_3$ type of the perovskites show a high potential;
- laser technologies, holographic techniques, integrated optics, surface-acoustic-wave (SAW) applications and high-frequency telecommunication signal processing has made progress into the everyday use; $LiNbO_3$ and $LiTaO_3$ single crystals have became strategic materials.

Although researchers have looked on these materials from a number of different angles there is one particular family of the perovskite niobates/tantalates, which surprisingly has been left aside. Perovskites from a $AgNbO_3$–$AgTaO_3$ system have not been so widely investigated so far as their alkaline analogues. There were many reasons for this, however, with a further development in this field they have vanished one after another.

The first of the major problems relates to the synthesis and sintering of the $Ag(Nb,Ta)O_3$ ceramics. The synthesis has been thought to be difficult due to a thermodynamic instability of the Ag^+ ion at elevated temperatures. Intuitively, this would suggest that the solid-state synthesis using a metal-silver or oxide powder is not possible. Researchers have soon disproved this thesis and determined conditions for the solid-state synthesis.[1] Furthermore, for a range of the $Ag(Nb,Ta)O_3$ compositions rich on Ta a decomposition temperature is lower then the sintering temperature. This makes the sintering extremely complicated and expensive but recent developments in the field of low-temperature sintering has shown ways to overcome the problem. In addition, wet-chemistry methods for the synthesis of the $Ag(Nb,Ta)O_3$ powders were developed, which give a very fine and active powder with significantly lower sintering temperature. Today $Ag(Nb,Ta)O_3$ is also used in forms of thin films or single crystals where the sintering is not required.

Secondly, $Ag(Nb,Ta)O_3$ has been considered a costly material and devices made of it economically unattractive. Therefore, industrial interest for this material has been low and research on it inhibited. One reason has been the high and unstable prices of tantalum. As a consequence of the mobile telecommunication expansion the prices for tantalum jumped to around US$ 350/lb in 2001, up from US$ 40/lb in 1997. However, instead of continuing to grow, the mobile telephone market and the aerospace industry turned downward in 2001 and tantalum prices started to fall sharply. By the end of 2001 the prices were back to the pre-boom levels, and in early 2005, the spot prices remained below US$ 40/lb. In 2005, the principal end-use markets for tantalum, such as mobile phones and other electronic equipment, aerospace and automobile manufacturing, have returned to a long-term growth trend. That will not, however, fully translate into additional demand for tantalum. As a result of a progressive trend in device miniaturization a unit consumption of component materials is significantly reduced. The material is used in forms of thick and thin films with a minimal consumption of the material and an insignificant contribution to the price of the entire device. Tantalum is also losing market share to other materials, such as ceramics, aluminium and niobium in applications where it previously had little competition such as microwave filters and capacitors. It is also believed that the price for tantalum will stabilize due to a commercialization of new deposits of tantalum. Some large projects in Egypt, Saudi Arabia and Canada are in advanced stages of development and could be operational in the fairly near future.[2] Taking in account the prospect of the low and stable tantalum prices and the decreased unit consumption of the material the concerns related to the economical viability of $Ag(Nb,Ta)O_3$ are considerably reduced.

Researchers are becoming aware of the unexplored possibilities for the use of $Ag(Nb,Ta)O_3$ and many laboratories are resuming the work on this material. The majority of today's investigations on $Ag(Nb,Ta)O_3$ are focused on technologies based on thick and thin films and differ from those, in which $Ag(Nb,Ta)O_3$ was investigated and used as a bulk material. In this review of the perovskites from the $AgNbO_3$–$AgTaO_3$ system we will focus mainly on the development of technological applications of these materials (Table 1). But we also highlight fundamental work that correlates functional properties of $Ag(Nb,Ta)O_3$ with its crystal chemistry.

2. Crystal chemistry, lattice dynamics and dielectric properties

Modern devices do not only exploit dielectric properties but a vast spectrum of functional properties of $Ag(Nb,Ta)O_3$. Nevertheless, dielectric and ferroelectric properties are by far the most important in the applications of these materials and to

Table 1
Functional properties of $Ag(Nb,Ta)O_3$-based materials

Composition	Form	Properties	Application	Reference
$Ag(Nb_{0.65}Ta_{0.35})O_3$–$Ag(Nb_{0.35}Ta_{0.65})O_3$ composite	Ceramics	$\varepsilon = 430$, $\tau_\varepsilon < 50$ ppm/K, $\tan\delta = 2 \times 10^{-4}$ at 1 MHz Qxf = 700 GHz at 2.4 GHz	Filters, capacitors	23
$(Ag_{0.9}Li_{0.1})NbO_3$	Ceramics	$P_r = 23\ \mu C/cm^2$ $E_c = 22$ kV/cm	Ferroelectrics devices	46
$AgNbO_3$	Single crystal	$d_{31} = 130$ pC/N, $k_{31} = 70.5\%$	Piezoelectric devices	32
$Ag(Nb_{0.8}Ta_{0.2})O_3$	Ceramics	$\tau = 27\%$ at 800 V/mm $\varepsilon \sim 400$ $\tan\delta < 0.014$ at 100 kHz	Voltage tuneable devices	48
$Ag(Nb_{0.8}Ta_{0.2})O_3$	Thick film	$\tau = 19\%$ at 1.2 kV/mm $\varepsilon \sim 350$ $\tan\delta = 0.005$		49
$AgNbO_3$ on SRO/LAO	Spin-coated thin film	$\tau = 21.4\%$ at 1.9 kV/mm $\tan\delta = 0.020$ at 100 kHz		29
$Ag(Nb_{0.62}Ta_{0.38})O_3$ on LAO	PLD thin film	16.8% at 200 kV/cm $\varepsilon = 224$ $\tan\delta = 0.0033$ at 1 MHz		52

understand their fundamental nature the crystal chemistry and the lattice dynamics must be analysed. A considerable body of work in this direction was led by two teams from the University of Silesia and the University of Metz and thanks to them an impressive body of knowledge about the characteristics of the $Ag(Nb,Ta)O_3$ materials was gathered.[3–11] For the purpose of this paper the final results of their studies will be reviewed while for the fine details of the research readers are advised to refer to the publications listed below.

Initial papers about phase transitions and their influence on the dielectric properties were published by Reisman and Holtzberg,[12] and Francombe and Lewis[1] in the late 50s and the work was resumed in the seventies[13] when the first spectroscopic data were published.[14] In the mid 80s Kania[5] and Pawełczyk[7] published two papers, which even today represent comprehensive information on the relations between the phase transition and the dielectric properties in the $AgNbO_3$–$AgTaO_3$ system. This information provided a basis for the further more detailed investigations of this system. The same group had worked on the end members of this system already before but has just few years ago came towards the conclusive results, which describe the crystal chemistry and the nature of the phase transitions of $AgNbO_3$. Fig. 1 is from the original work of these two authors and shows the correlation between the phase transition sequence and the permittivity.

$Ag(Nb,Ta)O_3$ undergoes a rich sequence of displacive phase transitions, which are driven by a successive tilting of oxygen octahedra. Because of this the crystal structure becomes more and more distorted with a decrease in temperature. Finally, this distortion, results in a displacement of cations from their Wyckoff positions and a creation of dipolar moments and ferroic states.

2.1. C phase

The high-temperature cubic $AgNbO_3$ phase is stable above 579 °C. The transformation temperature decreases almost linearly with increase in Ta concentration to 497 °C for $AgTaO_3$. A structural refinement of neutron diffraction data of all the $AgNbO_3$ phases was performed by Sciau et al.[15]. The C phase was described with the $Pm\bar{3}m$ (No. 221) space group and no disorder was found in this phase. With a decrease in temperature the C phase undergoes the tilting of oxygen octahedra to transform into the T phase.

2.2. T phase

The octahedra in the tetragonal T phase are tilted around the *c*-axis and the structure can be described with the *P*4/*mbm* (No. 127) space group. A disorder is possible in this phase due to local faults in the oxygen octahedron tilt scheme and consequent local appearance of anti-phase tilting. The disorder can be frozen and so influencing the structures and the properties of the lower phases. The $AgNbO_3$ T phase is stable down to 387 °C. With increasing Ta concentration the transformation temperature slightly increases to ∼430 °C.

2.3. O phase

At the transition of the T phase into the O phase the distortion of the lattice continues by condensation of the octahedron tilting around the *b*-axis. This tilting does not influence the position of the Nb ions while the Ag ions are slightly displaced along the *b*-axis. The space group that describes this phase is

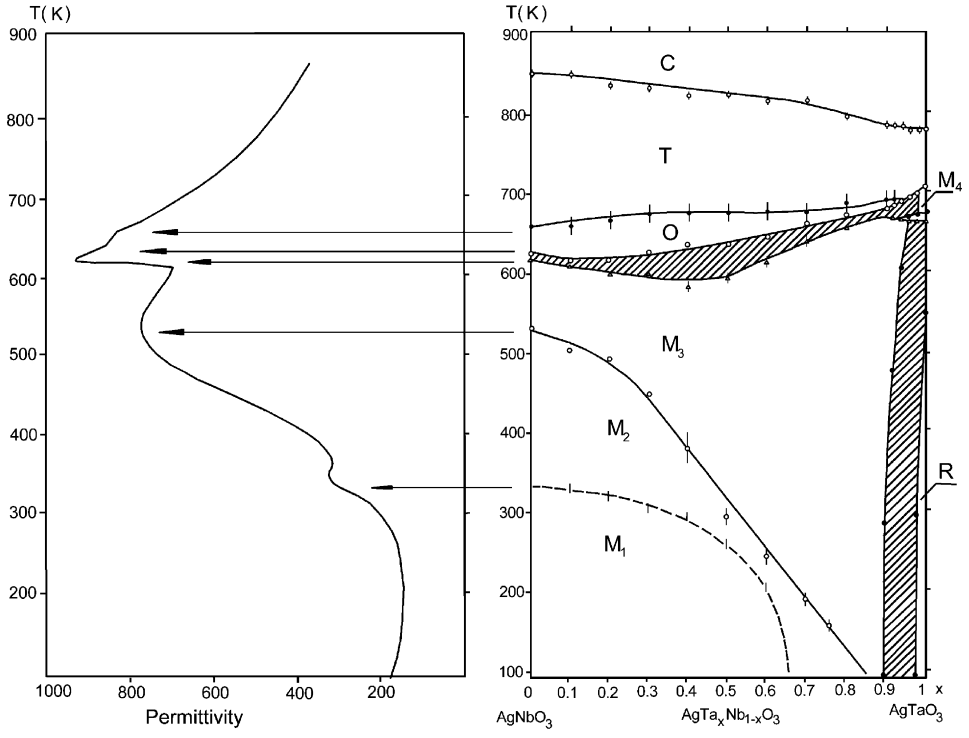


Fig. 1. $AgNbO_3$–$AgTaO_3$ phase diagram according to Pawełczyk[7] and permittivity of $AgNbO_3$ as a function of temperature according to Kania.[5] The arrows denote the correlation between the phase transition temperatures and the temperatures of the dielectric anomaly.

according to Sciau et al. *cmcm* (No. 63) [15] and to Ratuszna et al. *Pmmn* (No. 59).[11] In his $AgNbO_3$–$AgTaO_3$ phase diagram Pawełczyk described a phase field below the O phase as a field of a coexistence of the O and M phase (hatched area in the original figure).[7] Later Kania disproved this and confirmed the existence of another orthorhombic phase (O2).[16] No investigations of the symmetry of the O2 phase has been carried out so far.

The O phases do not extend completely to $AgTaO_3$. Instead a monoclinic distortion (M4) appears for $AgTaO_3$, which is different to that of $AgNbO_3$ at lower temperatures. The M4 phase dominates in the temperature range from 436 to 402 °C and starts to disappear below this temperature. It takes only around 5% of Nb on the B-site to stabilize the O phases.

2.4. M phases

The monoclinic M phases (M1, M2 and M3) are by far the most important for the application of the $AgNbO_3$–$AgTaO_3$ system in electronic devices. This is because these phase fields extend through the working temperature of these devices and because the phases exhibit ferroic states with many unique features.

Again, the transition from the O phase to the M3 phase is associated with further distortion of the crystal lattice. The oxygen tilting advances and for the M phases also appears around the *a*-axis and causes a significant Nb displacement (Fig. 2).[15] All M phases can be satisfactorily described by the Pbcm space group and the same octahedral tilting scheme. The tilting causes an antiparallel displacement of Ag and Nb in the [1 1 0] cubic direction and consequently a long-ordered antiferroelectric state. Different M phases cannot be resolved using diffraction techniques, DTA or domain structure studies[17] but can be observed only as a diffuse maxima in a ε''(T) dependence. They are related to the different states of Nb ion displacement. A slim ferroelectric hysteresis, which was observed for $AgNbO_3$ at room temperature, can be rationalized by a presence of clusters of a local polar ordering occurring around structural defects.[18] In contrast, an ab initio study of the room temperature $AgNbO_3$ phase showed on a preferential ferroelectric ordering over the antiferroelectric.[19]

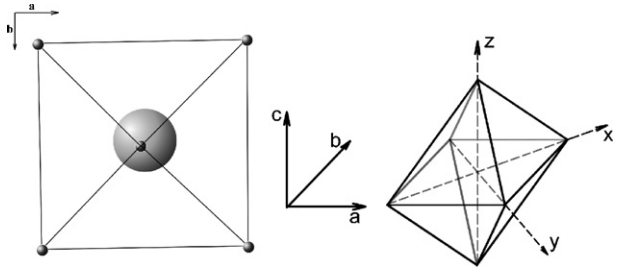


Fig. 2. The view along the (0 0 1) direction shows a crystal structure fragment of $AgNbO_3$. The displacement of the Nb ion from the centre of octahedron is illustrated for M3 phase at 372 °C. The atomic coordinates published in Ref. [15] were used for the octahedron construction and calculations. The displacement vector is (0.1046, 0.0424, and 0.0646 Å) where *x*-, *y*-, and *z*-axes are defined as shown.

Analyses of lattice dynamics have shown that the Nb ions have a great influence on Raman spectra, phase transitions and dielectric properties.[6,10,20] The niobium relaxation motion is attributed to high frequency dispersion, which gives rise to high and frequency stable (up to more than 100 GHz) permittivity. In addition, an absence of any further lower-frequency dispersion keeps the dielectric losses on a low level and makes the $Ag(Nb,Ta)O_3$ very attractive for technical applications.[21]

The increase in Ta concentration in $Ag(Nb,Ta)O_3$ influences the properties through the reduction in the concentration of Nb oscillators. As a result the permittivity decreases and the modes in the Raman and IR spectra, which are related to the Nb motion, decrease in intensity. The M3–M2 transition temperature decreases almost linearly with increasing Ta content. At ~90% of Ta on the B-site the M3 phase becomes unstable and the rhombohedral modification starts to appear in a coexistence with the M3 end member. The M2–M1 transition has not been yet investigated and for now the only evidence for the existence of the low-temperature phase is a slight anomaly in ε''(T) [6] and in a temperature variation of unit-cell parameters.[15]

3. Synthesis and sintering

3.1. Solid-state synthesis

The main problems in the solid-state synthesis of the $Ag(Nb,Ta)O_3$ compounds are related to oxidation and reduction characteristics of Ag and Ag^+ species. Usually the synthesis starts from the mixture of Nb/Ta oxide and Ag_2O. At slightly elevated temperature (~200 °C) Ag_2O decomposes into metal Ag and oxygen. This would imply that the same results should be obtained when the metal Ag powder is used as a silver source in the initial mixture. However, the kinetics of the reaction are very much slower in this case and a final product is typically not single phase. It is still not understood why this difference occurs.

At the reaction temperature Ag_2O is thermodynamically unstable but nevertheless, oxidation of the metallic silver occurs simultaneously during the reaction with $(Nb,Ta)_2O_5$. We investigated the oxygen transport during the synthesis and the results of a thermogravimetric analysis clearly show the initial release of oxygen during the decomposition of Ag_2O. This process is followed by a mass gain during the reaction of Ag, $(Nb,Ta)_2O_5$ and O_2 from atmosphere. The amount of oxygen released is equal to the mass gain (Fig. 3) which confirms that all the silver that was reduced, was re-oxidized and consumed during the reaction.

The next important issue related to the solid-state synthesis of $Ag(Nb,Ta)O_3$ relates to a homogeneity of a B-site cation distribution. In the case when all the three oxides are mixed and reacted at around 900 °C the perovskite phase does form but it is very unlikely that a fully homogeneous distribution of Nb and Ta over the B-site will be obtained at such a low-temperature. A routine X-ray diffraction analysis will not reveal this problem but some functional properties could be significantly influenced.[22] An example is the temperature dependence of permittivity, which is a very important parameter for microwave filters

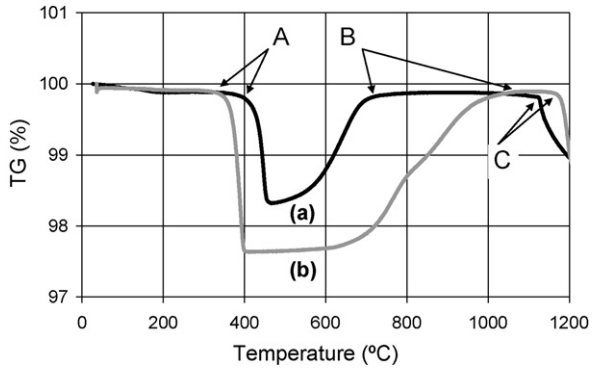


Fig. 3. Thermogravimetric analysis of mixtures of Ag_2O and, Nb_2O_5 (a) and Ta_2O_5 (b). The evolved-gas and X-ray diffraction analysis showed that a mass change occurs because of a release of oxygen and a pick-up of the oxygen during the decomposition of Ag_2O and formation of $Ag(Nb,Ta)O_3$ (A . . . start of Ag_2O decomposition, B . . . start of $Ag(Nb,Ta)O_3$ formation, C . . . start of $Ag(Nb,Ta)O_3$ decomposition).

or capacitors. We performed a model experiment where the properties of homogeneous $Ag(Nb_{0.5}Ta_{0.5})O_3$ ceramics were compared with properties of inhomogeneous ceramics of same overall composition.[23] A different level of the homogeneity was obtained by mixing together two kind of powders, $Ag(Nb_{0.65}Ta_{0.35})O_3$ and $Ag(Nb_{0.35}Ta_{0.65})O_3$, with different particle size. After sintering a significant difference in the temperature dependences of the permittivity was observed ranging from the dependence typical for homogeneous $Ag(Nb_{0.5}Ta_{0.5})O_3$ to those theoretically estimated for the two-phase system using the logarithmic rule. The experiment clearly showed that for a highly reproducible industrial production of these materials the B-site cation distribution should be closely controlled.

A much more homogeneous $Ag(Nb,Ta)O_3$ compound can be synthesized when Nb_2O_5 and Ta_2O_5 are pre-reacted at >1200 °C to form a homogeneous solid solution. The formation of $(Nb_{1-x}Ta_x)_2O_5$ solid solution can be monitored using X-ray powder diffraction. Completely homogeneous solid solutions, $Nb_2O_{5(ss)}$ and $Ta_2O_{5(ss)}$, can be obtained in the concentration range $x < 0.25$ and $x > 0.51$, respectively.[24,25] In the intermediate concentration range both solid solution end members coexist and the homogeneity is again not perfect. However, no problems with the homogeneity of the final perovskite compound were observed experimentally when the synthesis was conducted in this manner.

3.2. Sintering

The problem that must be overcome during the sintering of a powder from the $AgNbO_3$–$AgTaO_3$ system is a thermal decomposition of the compound driven by the reduction of the Ag^+ ion. It is reasonable to expect, and it was also many times empirically confirmed,[26] that oxygen partial pressure influences the decomposition process. The chemistry of the decomposition process has been described in detail and it was shown that during the sintering an oxygen atmosphere is essential.[26] However, with the increase in Ta, the sintering temperature increases, as it is a case for many other Nb and Ta analogues. This means that even a pure oxygen atmosphere does not prevent the decomposition during sintering. In such cases, an increasing amount of black silver precipitates can be visually detected in otherwise yellow/orange ceramics. In our study we used thermogravimetric analysis to trace the onset temperature of the decomposition (see Fig. 3). It was shown earlier that during the decomposition, oxygen evolves, which reduces mass of the sample. In air the start of the decomposition of $AgNbO_3$ and $AgTaO_3$ was determined to be at 1122 (±2) and 1172 (±3) °C, and in oxygen atmosphere at 1138 (±2) and 1200 (±10) °C, respectively.

To avoid the presence of the silver precipitates during sintering researchers have used different techniques. A simple technique is to enclose a compacted sample into a corundum crucible or tube and suppressed the decomposition by suppressing dissociation of Ag_2O and volatilization of Ag.[5,26] Successful sintering of the powders from the entire compositional range was performed using this technique. However, it is unsuitable for larger scale industrial production. Because of this, the research focused on alternative ways of sintering applying an understanding of low-temperature sintering techniques and wet chemistry.

Here it is important to mention an ill understood microstructural phenomenon that so far has been described in only two papers,[27,28] i.e. a formation of Ag nano-precipitates within the $Ag(Nb,Ta)O_3$ matrix. These precipitates should not be confused with the large micrometer-size precipitates appearing during sintering. Verwerft et al.[28] reported that they observed the formation of these nano-precipitates during *in situ* heating experiments after heating $AgNbO_3$ through the O–M phase transition at 337 °C. Furthermore, TEM studies of a number of different $Ag(Nb,Ta)O_3$ compositions detected the nano-precipitates in all investigated samples (Fig. 4). The question regarding the reasons for their formation remains unanswered. Can their presence be avoided by better processing or are they a constituent part of a high-temperature equilibrium? Neither crystallographic nor spectroscopic investigation has taken into account their presence, although a process, responsible for their formation could cause a stoichiometric deficiency, structural changes and changes in the dynamics of the lattice vibrations.

3.3. Wet-chemistry methods

Wet-chemistry methods for a synthesis of $Ag(Nb,Ta)O_3$-based compounds were used for the purpose of reducing the sintering temperature of powder or preparing thin films. Authors have described two different chemical routes: an alkoxide and a citrate route.

The alkoxide route was described by Telli in his doctoral thesis.[29] He dissolved Nb and Ta ethoxides in 2-methoxyethanol and pyridine. He used pyridine to avoid silver precipitation and stabilize the solution after the 2-methoxyethanol solution of $AgNO_3$ was added. The chemical solution was dried at 200 °C in air to get a solid precursor. The solid precursor crystallized in one step at 650 °C into $Ag(Nb,Ta)O_3$. He showed that the same route could be applied for all the compositions from the $AgNbO_3$–$AgTaO_3$ system. For the synthesis of thin films the obtained solution was deposited by spin-coating on a substrate and heat treated.

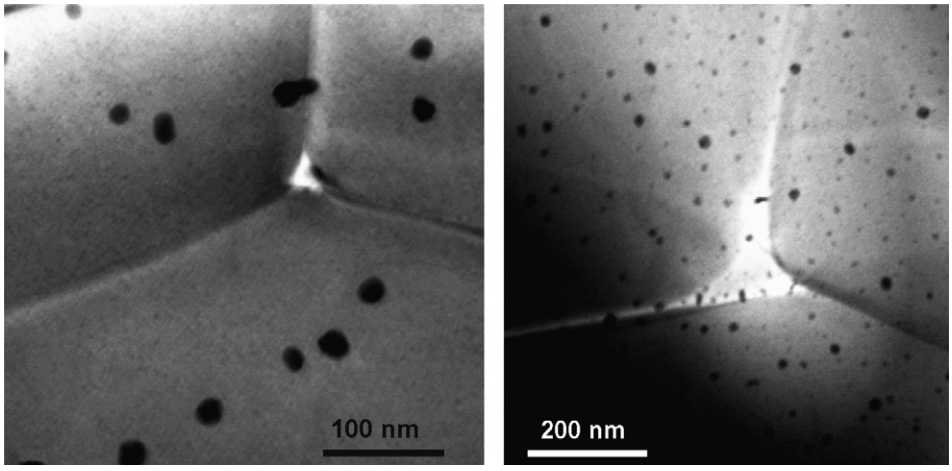


Fig. 4. STEM image of a $Ag(Nb_{0.5}Ta_{0.5})O_3$ microstructure showing the black nano-precipitates inside the crystal matrix.

Xiao et al.[30] report a citric self-combustion method where starting oxides or nitrates were dissolved in a mixture of hydrofluoric and nitric acid. The citric acid was added to start the condensation. Such a precursor was heated under an infra-red lamp to evaporate the solvent and calcined. During this process the self-combustion occurred and subsequent calcination at 800 °C led to the formation of a fine powder with a particle size of 30–40 nm.

Due to the use of hydrofluoric acid and the hazard of an uncontrolled combustion, we developed another citric route for the synthesis of $Ag(Nb,Ta)O_3$. The starting reagent was NbF_5, which was weighed out in a humidity-free atmosphere and dissolved in water. Thus, a solution with the accurate Nb-concentration of 0.2 mol/l was obtained. The stoichiometric amount of $AgNO_3$ was dissolved in the Nb solution. To start the condensation, citric acid and ethylenglycol were added in the ratio 7.5:1. After heating at 80 °C for 3 h the solution become a viscous gel suitable for a spin-coating. No self-combustion occurred during this treatment. Thermal analysis showed that all the organics could be removed by the heat treatment of the gel at 550 °C and a well crystallized $AgNbO_3$ product could be obtained at 800 °C.

3.4. Single crystals

A number of structural and spectroscopic investigations has been performed on $Ag(Nb,Ta)O_3$ single crystals as well as some characterization of electrical properties. An understanding of functional properties of the single crystals and their anisotropy is fundamental for thin film studies and piezoelectric applications.

Fairly large single crystals can be grown by a molten salt method. Łukaszewski et al.[31] used NaCl as a flux for the growth of the $AgNbO_3$ crystals. From a mixture of Ag_2O, Nb_2O_5 and NaCl (1:1:1) melted at 1200 °C and cooled at 17 °C/h they obtained crystals up to 15 mm large. The Ta analogue was grown with the use of either AgCl or V_2O_5 as a flux. The crystals grew in needle-like or plate-like forms with dimensions up to 3 mm × 3 mm × 1 mm.

Saito et al.[32] used a slow cooling method to grow Li-doped $AgNbO_3$ single crystals. The calcined powder was heated in a corundum crucible up to 1220 °C, kept at this temperature for 3 h and then slowly cooled with 4 °C/h to 950 °C. During this process the crystallites grew with maximum volume around 2 mm^3.

4. Passive dielectric components

The development of the $Ag(Nb,Ta)O_3$-based materials for passive dielectric components was triggered by an unique combination of several physical characteristics of these materials; (i) an unusually high permittivity, the atomistic background of which already has been discussed in this paper, (ii) modest dielectric losses as a consequence of an absence of any low-frequency dispersion, (iii) a prospect for a low-temperature dependence of the permittivity and (iv) a fairly low sintering temperature, which for Nb-rich members can be as low as 1000 °C. Without much further adjustments the permittivity (400–600) and the dielectric losses ($\tan\delta = 2 \times 10^{-4}$ at 1 MHz, $Q = 700$ at 1 GHz)[23] are good enough for these kinds of applications, however, the temperature dependence of the permittivity on certain parts of the curve exceeds 1000 ppm/K and is therefore problematic. Consequently, much research is focused into stabilizing the temperature dependence of the permittivity.

From an analysis of the dielectric properties of the $AgNbO_3$–$AgTaO_3$ system, performed by Kania,[5] we can see that around room temperature and in the compositional range between $Ag(Nb_{0.6}Ta_{0.4})O_3$ and $Ag(Nb_{0.4}Ta_{0.6})O_3$ the temperature dependence of the permittivity somewhat flattens with opposite trends for the both end members (Fig. 5). This is the reason why the development focused on this particular compositional range. The maximum temperature dependence of the permittivity in this compositional interval is around 1300 ppm/K while the required dependence should be in a range below 100 ppm/K. Unfortunately, the final suppression cannot be achieved just by a further adjustment of the Nb to Ta ratio. The change in this ratio only influences a position of the phase transition, i.e. the position of the dielectric "hump" moves to a lower temperature with an increase in the Ta concentration, while the steepness of the curves remains the same.[23]

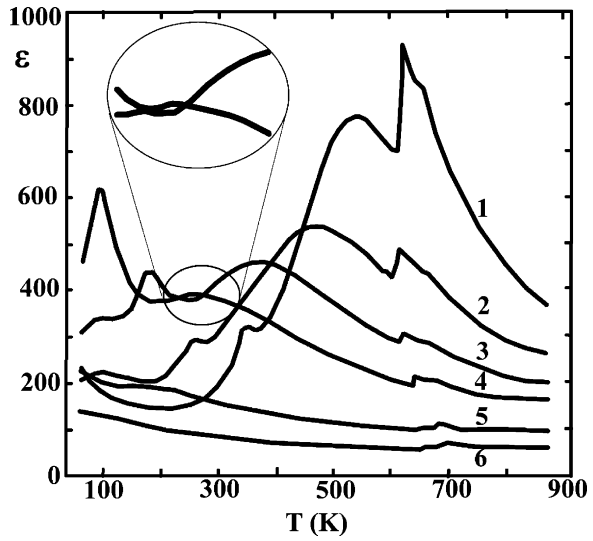
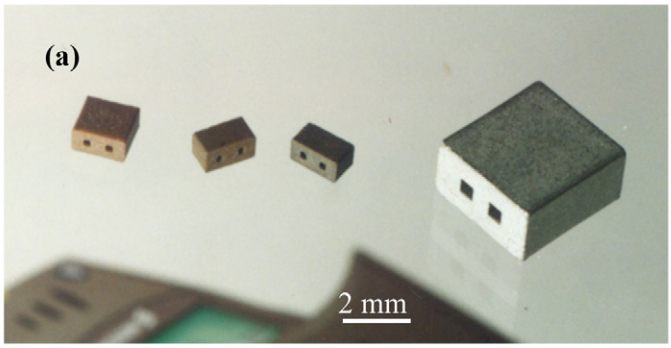


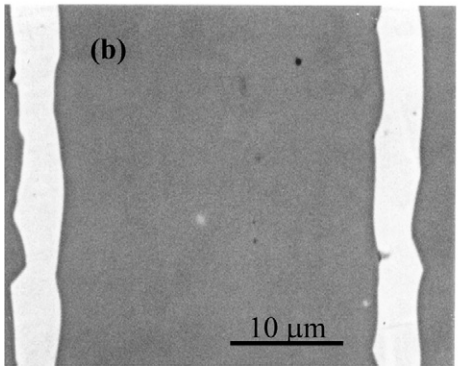
Fig. 5. Temperature and compositional dependence of permittivity for ceramics from the $Ag(Nb_{1-x}Ta_x)O_3$ solid solution system according to Kania[5] (1. . .x = 0, 2. . .x = 0.2, 3. . .x = 0.4, 4. . .x = 0.6, 5. . .x = 0.8, 6. . .x = 1.0). The inset detail shows an interval around room temperature, in which the search for the temperature stable dielectrics has been focused.

Researchers have tried to suppress the temperature dependence of the permittivity by an isovalent substitution of Ag with Li^+, Na^+ or K^+.[33–36] Systematic studies of an influence of these dopants on the dielectric properties were performed. No change in the symmetry of the phases is induced with a modest Na^+ and K^+ doping (<10%) and the temperature dependence remains of the characteristic shape for undoped $Ag(Nb,Ta)O_3$ with no significant improvement in the steepness of the curve. A 5% of the Ag substitution by Li induces the change in the symmetry from orthorhombic to rhombohedral. The temperature characteristics of the permittivity change significantly and Li-doped $Ag(Nb,Ta)O_3$ becomes proper ferroelectrics with very interesting properties for ferroelectric applications.

The only approach described so far to suppress the temperature dependence of the permittivity successfully was the one reported by Valant et al.[23,37,38] By a controlled powder morphology and a careful selection of firing conditions an inhomogeniety on the B-sites of $Ag(Nb,Ta)O_3$ was deliberately generated. The different $Ag(Nb,Ta)O_3$ phases present in such ceramics exhibited different temperature dependences of the permittivity, which produced a compensated overall temperature dependence of such ceramics. On the steepest part of the curve the temperature dependence of permittivity reached a value of only ∼40 ppm/K.

The properties of such ceramics were compatible with the requirements for several microwave electronic components, e.g. band-pass filters, high-capacity NP0 multilayer capacitors, and their use would lead to a significant miniaturization of these devices. For the case of band-pass filters, an eight-fold reduction in volume could be expected (Fig. 6), 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.[39] For capacitor technology, the implementation of $Ag(Nb,Ta)O_3$ 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 $Ag(Nb,Ta)O_3$ capacitors in, for instance,





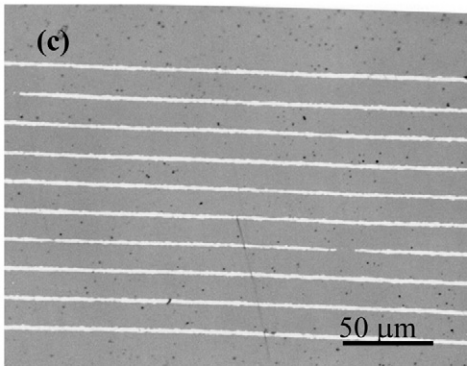


Fig. 6. (a) A 1.8 and 0.9 GHz band-pass filters based on $Ag(Nb,Ta)O_3$ ceramics and a commercial 1.8 GHz band-pass filter produced from a material based on $Ba_{6-x}Nd_{8+2/3x}Ti_{18}O_{54}$ with permittivity ∼90 (for a size comparison); (b) and (c) microstructure of a PPS-type multilayer capacitor produced from $Ag(Nb,Ta)O_3$.

Bluetooth modules and the loop-filters of cellular phones offers the possibility for further size reduction and the enhancement of performance and reliability.[40]

Because of a relatively low sintering temperature $Ag(Nb,Ta)O_3$ is also considered as a potential material for an LTCC technology. Researchers have attempted to develop the LTCC-compatible $Ag(Nb,Ta)O_3$-based material for an integration of embedded capacitors, antennas and resonators. The development was focused in a further reduction of the sintering temperature on a level suitable for the LTCC technology (~900 °C). A promising approach is to use CuO as an additive.[41] Full densification of $Ag(Nb_{0.5}Ta_{0.5})O_3$ was achieved at 900 °C after addition of 1 wt.% of CuO. The dielectric properties were not adversely influenced by this addition. In addition, taking advantage of the compositional inhomogeneity, as described in Ref. 23, the temperature dependence of permittivity was reduced to <180 ppm/K. Unfortunately, no explanation of the CuO interaction with the matrix phase was given in Ref. 41. It was later confirmed that Cu-ions incorporate into the $Ag(Nb,Ta)O_3$ crystal structure[42] but the substitution mechanism is not yet clear. Li et al.[43] report on a successful decrease in the sintering temperature of the $Ag(Nb,Ta)O_3$ ceramics by a glass addition. By the addition of 2 wt.% of glass they decrease the sintering temperature to 960 °C and keep the dielectric losses low, $\tan\delta < 10^{-3}$. Unfortunately, they do not report on the composition of the glass nor do they give any detailed analysis of the phase interactions and dielectric properties, etc. They also report a beneficial influence of a Sb_2O_5 addition on the dielectric losses but again without any comprehensive analysis of its interaction with the matrix phase.

The development of the passive components based on $Ag(Nb,Ta)O_3$ is still in an early stage. Much more basic knowledge is needed to improve functional properties such as dielectric losses and temperature dependence of permittivity, dielectric strength, aging, leakage . . . In addition, processing of the powder and a production of the components is far from being optimized. On several segment the work with $Ag(Nb,Ta)O_3$ relies on empirical recognitions and could be, with further understanding of the chemistry and physics of the $Ag(Nb,Ta)O_3$-based systems, brought onto a much higher level. An example is substitutional chemistry of $Ag(Nb,Ta)O_3$, which so far is insufficiently understood. A more comprehensive understanding of phenomenological correlations between the isovalent/aliovalent substitutional mechanisms, crystallography and functional properties is required. In combination with this research, a detailed research of reaction mechanisms and conditions, and sintering behaviour of the substituted $Ag(Nb,Ta)O_3$ would be needed to overcome problems, which are present in the production of the $Ag(Nb,Ta)O_3$-based components, especially to improve reproducibility and to further decrease the sintering temperature to a level where the thermal decomposition does not cause complications.

Another characteristic of the permittivity, which is very interesting from a fundamental standpoint but troublesome for technological exploitation of $Ag(Nb,Ta)O_3$ is a significant dielectric thermal hysteresis.[35,44] Its origin and nature is not understood yet. It is hypothesized that the M_3–O_1 phase transition is of a martensitic type, where the phase transition temperature is strongly influenced by external or internal stress.[35] At present, no experimental evidence has been put forward to support the hypothesis. Moreover, our experiments on this topic do not confirm this hypothesis. It can be seen from Fig. 7 that the thermal hysteresis is not present only at the M_3–O_1 phase transition but also at other transitions. In addition, for Li-doped $Ag(Nb,Ta)O_3$ where the M_3–O_1 transition not even exist the themal hysteresis can be detected as well. More work is needed to explain the origin of the hysteresis and prevent or immobilize its adverse effect on the properties of the passive components.

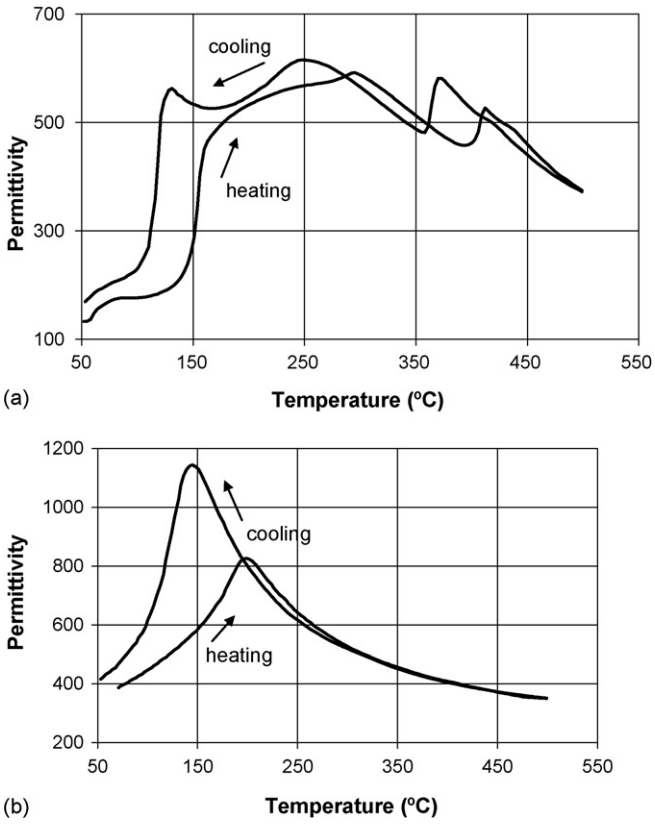


Fig. 7. Thermal hysteresis of permittivity for $AgNbO_3$ (a) and $(Ag_{0.87}Li_{0.13})(Nb_{0.6}Ta_{0.4})O_3$ (b) ceramics, measured at 1 MHz.

5. Piezoelectric response

An off-centering of A-site ions in a perovskite lattice is shown to be essential for a strong piezoelectric response. As Pb ions show an outstanding off-centering that gives rise to a large internal polarization and a strong coupling to electric fields, their perovskite compounds are used in high-performance piezoelectric devices such as actuators, motors, sensors, and transducers. Recently a quest for environmental acceptable lead-free piezoelectrics with performance similar to lead-containing materials triggered extensive research all around the world. Density functional theory calculations showed that Ag ions in the perovskite are ferroelectrically active and, if crystalo-chemical conditions are right, can off-center as much as the Pb ions.[45] This suggests that by a proper modification

of the crystal lattice of $Ag(Nb,Ta)O_3$ ferroelectricity can be enhanced and a high piezoelectric response achieved.

The only substituent, which so far was experimentally confirmed to induce the strong ferroelectricity in $Ag(Nb,Ta)O_3$, is Li. Li^+ incorporates on the Ag site according to formula $(Ag_{1-x}Li_x)(Nb,Ta)O_3$ and occupies the off-centered position, which creates an additional dipole moment.[35] The remanent polarization and coercive field are increased by several orders of magnitude compared with undoped $Ag(Nb,Ta)O_3$. On ceramic samples with composition of $(Ag_{0.9}Li_{0.1})NbO_3$ Sakabe et al.[46] measured the remanent polarization (P_r) and coercive field (E_c) to be 23 μC/cm^2 and 22 kV/cm, respectively (pure $AgNbO_3$ exhibits $P_r = 0.095$ μC/cm^2 and $E_c = 2.9$ kV/cm). Interestingly, Saito et al.[32] determined a significantly lower P_r on single crystals. They measured P_r of only 10.7 μC/cm^2 and E_c of 21.2 kV/cm. Nevertheless, of importance are their measurements of piezoelectric constants on the same single crystal. The piezoelectric constant d_{31} was measured to be 130 pC/N, which is close to soft PZT ceramics (171 pC/N), but they also measured very high k_{31} of 70.5% that is twice as high as that for PZT. On ceramic samples of the similar composition the piezoelectric constant were somewhat smaller but still surprisingly high, $d_{33} = 66$ pC/N and $k_{33} = 48\%$.[47]

These data indicate that the $Ag(Nb,Ta)O_3$-based ceramics can be considered as promising lead-free piezoelectric materials. The cost of the materials can impede a commercialization of bulk piezoelectric devices based on $Ag(Nb,Ta)O_3$, such as e.g. actuators. But for piezoelectric devices in a form of thick and thin films the material consumption is very low and this cost is not expected to inhibit commercialization. Unfortunately, so far there has been no investigations performed on the piezoelectric response of the $Ag(Nb,Ta)O_3$-based thick and thin films. The studies should focus on an investigation of an influence of strain, generated during the deposition, and its relaxation on the ferroelectric and piezoelectric properties of the $Ag(Nb,Ta)O_3$-based films. The clamping of the film on the substrate is another feature which influences the piezoelectric response of the thin films and should be evaluated. In addition, different orientations of epitaxially grown films should be investigated with respect to the strain and electric properties. The quantum-size effect and its influence on the hysteresis and piezoelectricity of these films should also be characterized.

6. Thick and thin films

Current research on the $AgNbO_3$–$AgTaO_3$ system is focused on thin and thick film synthesis and investigation of their dielectric properties and dielectric tuneability. The reasons that make this field of research attractive are various. The entire development of the electronic industry is shifting from bulk components to integrated devices based on thick or thin film technology, which is significantly cheaper in a mass production. In the case of the $Ag(Nb,Ta)O_3$-based films this is even more pronounced due to the lower material consumption of relatively expensive oxides. Preliminary studies on single crystals indicate that much better properties can be expected from the epitaxially grown films than from the bulk ceramics where the random grain orientation, and a presence of porosity and grain boundaries represent extrinsic factor that affect key properties adversely.

6.1. Thick films

A preliminary research of Zimmermann et al.,[48] performed on bulk ceramics, provided the guidance for further work on screen printed thick films. Two-phase transitions around room temperature, M_1–M_2 and M_2–M_3, were examined on bulk samples and the authors clearly showed that only the M_1–M_2 phase transition is tuneable. By changing the Ta:Nb ratio the M_1–M_2 transition was brought towards room temperature. The highest tuneability (τ) was achieved for $Ag(Nb_{0.8}Ta_{0.2})O_3$ with the M_1–M_2 transition at −26 °C. When the transition was shifted to the room temperature by decreasing the Ta concentration to 10% the tuneability decreased to 16% (1 kV/mm). Such powders were used to prepare a paste for a screen printing of 3–6 μm thick films on Al_2O_3 substrate. For electrical measurements at low frequencies an interdigital capacitor (IDC) structure was sputtered on the thick films while for high frequencies a coplanar waveguide technique was used. The measurements showed that the dielectric properties of the fired thick films were in the main influenced by their porosity. For the dense films the dielectric properties were very close to the bulk materials while, as expected, for the porous films the permittivity was much lower. Interestingly, the tuneability was not so much affected by the porosity. The relative tuneability remained on the level of the bulk materials with 19% (1.2 kV/mm) and 16% (1 kV/mm) for $Ag(Nb_{0.8}Ta_{0.2})O_3$ and $Ag(Nb_{0.9}Ta_{0.1})O_3$, respectively.[49]

For possible applications in tuneable microwave devices, such as phase shifters, tuneable filters and varactors, these films were also characterized in the frequency range from 4 to 13 GHz. The tuneability decreases with frequency to 5% at 4 GHz and <1% at 13 GHz. This is accompanied with an increase in dielectric losses to $\tan\delta \sim 0.15$ at 10 GHz. It is suggested that the reason for such behaviour is in the presence of a relaxation at around 30 GHz, most probably due to phonon scattering effects.[50] If this problem is not overcome in the future the use of these thick films will be restricted to the low-GHz applications.

6.2. Chemically deposited thin films

Telli in his doctoral thesis[29] reports on successful formation of epitaxial thin films by spin-coating of chemical solutions on (0 0 1) $LaAlO_3$ and (0 0 1) $SrRuO_3$/(0 0 1) $LaAlO_3$ (SRO/LAO) substrates. He prepared three compositionally different films, $AgTaO_3$, $AgNbO_3$ and $Ag(Ta_{0.5}Nb_{0.5})O_3$, and determined their dielectric tuneability. The tuneability is again significantly lower then that for the bulk materials but for one particular case, when the $AgNbO_3$ was deposited onto the SRO/LAO substrate, a remarkably high tuneability was measured. At a negative bias of −140 kV/cm the tuneability of 12.8% was measured and 21.4% for the opposite bias of 190 kV/cm. The polarity dependence is due to use of asymmetric electrodes (Pt and SRO) with different leakage current. He also determined dielectric properties of the films and for majority of the films the permittivity and the

losses roughly correspond to those of the bulk materials. In a few cases, a shift in the transition temperature, which most probably occurs because of the induced strain in the film, significantly influences the room temperature permittivity. Such an example is $Ag(Ta_{0.5}Nb)O_3$ on SRO/LAO where the M_2–M_3 transition shifts from around 50 °C, as typical for the bulk ceramics, to −150 °C. Even more interesting is $AgNbO_3$ on the SRO/LAO substrate where the measurements indicated that the phase-transition sequence completely changes. No detailed analysis of the observed phase-transition sequence was performed but the effect results in a remarkable deviation of the room temperature permittivity of the thin film ($\varepsilon_r = 550$) from values typical for the bulk ($\varepsilon_r = 120$). Nevertheless, the thin films retained moderate dielectric losses, which is very important for possible applications. A relatively low dielectric strength of the film prevents the achievement of even higher values for tuneability and if future developments can improve the dielectric strength then $AgNbO_3$ could be a good substitute for lossy $(Ba,Sr)TiO_3$ for applications where the low dielectric losses are required.

6.3. Physically deposited thin films

The only group that has so far reported synthesis and studies of $Ag(Nb,Ta)O_3$ thin films is the group from Royal Institute of Technology, Sweden.[51–54] They synthesized and characterized the $Ag(Nb_{0.62}Ta_{0.38})O_3$ thin films deposited on $LaAlO_3$, MgO, $Pt_{80}Ir_{20}$ and Al_2O_3 substrates. For the deposition they used a pulse-laser deposition technique with a 248 nm KrF excimer laser, 350 mTorr of oxygen pressure in a deposition chamber, 550 °C substrate temperature and 3–4 J/cm^2 laser energy density. Typically their films were 400 nm thick.[51]

Comprehensive crystallographic analyses of these films showed that only the film grown on the $LaAlO_3$ (0 0 1) substrate exhibit very high *c*-axis orientation (0 0 1) of the prototype unit-cell with strictly a cube-on-cube epitaxial relationship.[52] Some small deviation from the composition of the target was detected presumably due to a discriminated thermalization (increase in Ta content) and volatilization of Ag. The effect of this compositional shift on the functional properties was not investigated. Films grown on the MgO substrate show a lower *c*-axis orientation but can be still considered as pseudo-epitaxial. The major part of the film crystallized in the cube-to-cube epitaxial relationship while the minor part in a diagonal-to-edge relationship.[53] The latter is energetically unfavourable because of a high in-plane tensile stresses due to a structural mismatch on the interface. Deposition on a polished polycrystalline $Pt_{80}Ir_{20}$ substrate resulted in a preferentially (0 0 1)-oriented film which contained a small concentration of a $Ag_2Nb_4O_{11}$ phase.[51] On the single-crystal Al_2O_3 substrate the film was single phase but polycrystalline.[54]

The characterization of the thin films was mainly oriented into their possible application in tuneable devices. The IDC structures were defined on the thin films, typically having five pairs of 1-mm long fingers with 4-μm gap.[54] The thin films with a composition of $Ag(Nb_{0.62}Ta_{0.38})O_3$ were deposited on the different substrate and characterized with respect to their dielectric properties, dielectric tuneability, relaxation characteristics during switching cycles, leakage current and conduction mechanisms. Superior overall performances were exhibited by the $Ag(Nb_{0.62}Ta_{0.38})O_3$ film deposited on $LaAlO_3$ substrate.[52] the tuneability was measured to be 16.8% at 200 kV/cm. At the same time the dielectric losses were rather low, $\tan\delta = 0.0033$ (at 1 MHz). The permittivity was determined to be 224 (at 1 kHz) with a small frequency dependence of only 5.8% up to 1 MHz. The leakage current was as low as 230 nA/cm^2 and resistivity 4.4×10^{-11} Ω cm at 100 kV/cm^2. Using substrates other than $LaAlO_3$ particular characteristics can be better, e.g. lower dielectric loss for a MgO substrate, but the overall performance deteriorates. Taken as a whole, the performance of the $Ag(Nb_{0.62}Ta_{0.38})O_3$ film deposited on the $LaAlO_3$ surpass the performances of $(Ba,Sr)TiO_3$, which today is regarded as a prime candidate for the electrically tuneable devices. Taking into account that not much work has been done so far on an optimization of these characteristics of the $Ag(Nb,Ta)O_3$ thin films we can expect even further improvements and serious consideration of these materials in commercial tuneable devices.

7. Summary and future work

As a result of an enthusiastic work of a small number of research groups the fundamental aspects of the $Ag(Nb,Ta)O_3$ materials are well understood. Not many open fundamental questions have remained to be answered. Maybe one of the most intriguing questions to be answered is the reason for the appearance of the nano-size silver precipitates within the $Ag(Nb,Ta)O_3$ crystal matrix.[27,28] Researchers have mainly considered the $Ag(Nb,Ta)O_3$ ceramics as a metal-silver free if no black silver precipitates were observed and no silver diffraction lines were present. But, using these two methods the nano-size inclusions cannot be detected although their overall concentration can be fairly significant. The observed silver deficiency in the thin films[52] might be related to the same phenomena as the appearance of the silver inclusions in the bulk. We also observed a related phenomena during a deposition of $Ag(Nb_{0.5}Ta_{0.5})O_3$ thin films on $LaAlO_3$ substrates. An accurate X-ray diffraction analysis of an apparently single-phase epitaxial film showed traces of metallic silver. No other phase was detected, which again implies significant cation deficiency in the $Ag(Nb,Ta)O_3$ crystal matrix. However, the defect chemistry of $Ag(Nb,Ta)O_3$ in the form of bulk or thin films has so far never been a topic of comprehensive studies. Such results could give us valuable directions for the synthesis of a metallic-silver pure material with superior properties.

The production of $Ag(Nb,Ta)O_3$ powder is fraught with problems related to the synthesis of the material. The formation of $Ag(Nb,Ta)O_3$ is highly sensitive to firing conditions, starting materials, powder packing, etc. and sometimes fails without any obvious reason. Despite this, no detailed study of the formation mechanism and reaction kinetics has been reported so far. It is taken for granted that the high oxygen vapour pressure is required during the synthesis of this material although the critical process, which determines the kinetics of the reaction, has never been determined. Understanding of the formation processes would allow an optimization of powder production in

terms of a synthesis of purer powders, reproducibility, economic efficiency and optimal scale-up of production. In addition, an understanding of the solid-state reaction mechanism and its energetics is essential for studies of the processes occurring during the combustion of gels or the deposition of thin films. The latter includes several different processes, in which we have absolutely no insight. These are a thermalization of the species by the laser, mass transport from the target through the plum and a condensation of the thin films on the substrate.

Compared with the fundamental aspects of the research the applied research is still in a very early stage. Possibly, the only segment, which has been examined in some detail, is the area of passive bulk components. A great deal of work is required in the areas of the integrated passive component, piezoelectricity, thin films, properties of compositionally modified $Ag(Nb,Ta)O_3$, etc. It is impossible to comment within this paper on all the particular topics which need to be addressed in the future, but a short list of the most promising future research direction is given below:

- Development of $Ag(Nb,Ta)O_3$-based compositions for an integration of the passive components into LTCC systems. An interaction of sintering aids, such as CuO, glasses . . ., should be determined to optimise the microstructure and consequently the properties. Even more important, the chemical compatibility and cofiring characteristics with base LTCC materials must be carefully studied and optimized.
- The influence of the thermal hysteresis on the functional properties in the temperature-variable environment should be determined. It is important to know its atomistic origin.
- The substitutional chemistry of $Ag(Nb,Ta)O_3$ is poorly investigated. For only few substituents (Na, K, Li and Bi) all the substitutional parameters have been determined while a large number of other ions have never been tested. It would be interesting to understand their influence on the crystallographic parameters as well as on the functional properties.
- It is known that the Li incorporation in $Ag(Nb,Ta)O_3$ induces a strong ferroelectricity and rather high piezoelectric coefficients. No systematic search for other dopants, which might enhance the ferroelectricity even further and give even higher piezoelectric coefficients, has been performed so far although the quest for lead-free piezoelectrics is still ongoing.
- No investigation of the piezoelectric properties of $Ag(Nb,Ta)O_3$-based thin films has been reported so far. The investigation is needed to understand the influence of chemical composition, strain, clamping and quantum-size effect on the functional properties of such films.
- No substituted $Ag(Nb,Ta)O_3$ has been tested for dielectric tuneability.

The investigation of $Ag(Nb,Ta)O_3$ has gone through periods of high and low intensity. Work on the materials started in late 50s and resumed intensively in 80s. Another peak was seen in the late 90s and in the first years of the new century. In the last few years the frequency of publications has diminished but research continues within the industrial laboratories. Unfortunately, their achievements are not always publicly revealed. Still, the $Ag(Nb,Ta)O_3$-based material remains on the list of potential functional materials for future applications and represents a topic, which is surprisingly relatively unexplored. In addition to the established electronic applications there are numbers of potential applications from different fields where $Ag(Nb,Ta)O_3$ should be considered from the outset. A good example are investigations of photophysical and photocatalytical properties of $Ag(Nb,Ta)O_3$. It was shown that these materials, especially in a combination with sacrificial agents, can be used as a new visible-light-driven photocatalyst with the ability to split water into oxygen and hydrogen.[55,56] Because of its excellent piezoelectric properties $Ag(Nb,Ta)O_3$-based materials could be considered as a ferroelectric component for the development of multiferroic composite materials. Similarly, the investigations of electrocaloric effect for the development of alternative cooling techniques would also be highly interesting.

$Ag(Nb,Ta)O_3$ is a perovskite with a highly flexible crystal structure, which can be modified in a way so as to induce different ferroic effects. At present we do not know the limits of this family of materials and this is good news. It means that with future work we can even improve properties further, exploit the physical effect and develop a number of technologically very attractive $Ag(Nb,Ta)O_3$-based compositions.

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