

Session 1

Materials & Processes

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Ceramic System with High Dielectric Constant for COG Capacitors

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Abstract

The number of single phase ceramic materials which can be used to produce multilayer ceramic capacitors (MLCC) with COG specification is limited. This limitation is the result of the interrelationship between the dielectric constant and its temperature coefficient. Materials with a high dielectric constant in general exhibit high temperature coefficients of the same making them unsuited for COG components. In order to overcome this problem EPCOS has investigated multi-phase material systems based on $\text{Ag}_2\text{O-Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5$ to fulfil COG or near COG specifications.

Introduction

High-permittivity ceramics with relative permittivities exceeding 1000 are generally based on ferroelectric materials (class II dielectrics). Due to the ferroelectric nature the temperature coefficient of capacitance (TCC) of these materials is poor and results in capacitance changes of at least several percent. Materials with significant lower temperature coefficients of capacitance can be found among the ceramic systems used in microwave applications. These materials are characterized by very low dielectric loss factors and their high temperature stability (class I dielectrics). The thermal behaviour in these systems is expressed as the change of resonant frequency with temperature (TCf). The TCf value can be near zero in a temperature range between -45°C up to $+85^\circ\text{C}$. Unfortunately the dielectric constant of these materials is relatively small compared to ferroelectric materials. Ceramics from the $\text{BaO-RE}_2\text{O}_3\text{-TiO}_2$ (RE = rare-earth metal) system rate among the materials with the highest dielectric constants in the range of 100 [1].

Materials from the system $\text{Ag}_2\text{O-Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5$ are capable candidates to close that gap between class I and class II dielectrics. Permittivities in this system are found to be around 400 and the temperature coefficient of permittivity can be shifted by the Nb / Ta ratio from positive to negative values. The preparation of a single phase material with a near zero temperature coefficient needs rather high efforts in solid state processing in order to achieve sufficient batch to batch reproducibility. An easier access is found by mixing two phases x1 and x2 of $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ with positive and negative temperature coefficient resp. leading to a multiphase system [2].

The Material System $\text{Ag}_2\text{O-Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5$

Early investigations of AgNbO_3 and AgTaO_3 compounds showed weak indications of ferroelectricity at temperatures below 348K and 180K, respectively. [3] Dielectric spectroscopy up to 30 GHz did not reveal any dielectric dispersion. Therefore the dielectric properties at microwave frequencies were studied. Compositions in the range of $0.46 < x < 0.54$ for $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ exhibit permittivity values above 400 with reasonably low dielectric loss factors. The temperature dependence of permittivity is low but not linear and shifts with the composition. These results make the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system interesting for microwave and multilayer capacitor applications. While requirements for microwave applications demand high temperature stability of dielectric properties which can only be achieved by phase mixing the freedom to define the temperature characteristic of a capacitor enables the usage of single phase materials.

Various attempts were made to describe the phase relations in the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system. An extensive review and major contributions can be found at Valant *et al.* [4] The structure can be considered as a pseudo-cubic perovskite with Ag on A-sites and Nb/Ta on B-sites. Deviations of the A/B ratio from one result in the formation of secondary phases like Ag inclusions for Ag-excess and $\text{Ag}_2(\text{Nb,Ta})_4\text{O}_{11}$ for Ag-deficiency. In the case of Ag-excess one can observe a reduction in the isolation resistance and in the long term stability under DC bias. The Ag-deficient secondary phase influences the temperature coefficient in the low temperature range. At temperatures higher than 1050 °C the perovskite decomposes into Ag_2O (which instantaneously is reduced to Ag) and $\text{Ag}_2(\text{Nb,Ta})_4\text{O}_{11}$ (as well as other compounds with reduced Ag-content).

Processing

The homogeneous Nb-Ta-distribution in the entire perovskite is an important issue for the long term stability of the ceramics especially under the electric field conditions of multilayer capacitors. Applying the mixed oxide route the use of a proper $(\text{Nb,Ta})_2\text{O}_5$ precursor is an essential prerequisite for a high quality powder processing. Conventional solid state reactions for the formation of such a precursor from Nb_2O_5 and Ta_2O_5 need temperatures exceeding 1200°C and a high energy milling process to retain a defined grain size to achieve the necessary reactivity. For an industrial scale production such a process is practically inapplicable. The required homogeneity, purity and fineness of the precursor can be achieved by e.g. co-precipitation of Nb-Ta-compounds from a solution or by nano-dispersion of Nb- and Ta-hydroxides with subsequent calcination.

In the phase formation process of $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ the dispersion of the precursor with the silver compound is of much less concern due to the high mobility of silver and silver ions. Silver can be added in different forms whereas Ag_2O or Ag_2CO_3 are the most practicable ones. Nevertheless the comparison between Ag_2O and Ag_2CO_3 as starting compound showed distinct differences which are attributed to different reaction mechanisms. It was observed that higher calcination temperatures were required to achieve the same powder quality when Ag_2CO_3 was used. Nevertheless Ag_2CO_3 was preferred because of its better homogeneity.

The higher process temperatures for Ag_2CO_3 could be compensated by the usage of fine grained co-precipitated $(\text{Nb,Ta})_2\text{O}_5$ precursors. shows fully reacted ATN material from the $\text{Ag}_2\text{CO}_3 - (\text{Nb,Ta})_2\text{O}_5$ route after calcination at 800°C .

Capacitors are made by multilayer technology which includes the processes of tape casting, printing of the inner electrode pattern, stacking and cutting and finally the co-firing of this layered ceramic metal composite. For the tape casting the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system turned out to be stable also in water based slurries. For the sintering an oxygen atmosphere is advantageous because the stability region of the perovskite is extended to higher temperatures due to the fact that the decomposition reaction involves the formation of oxygen.

Flux development for low firing temperatures

Sintering the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system needs temperatures near 1200°C , which implies partial decomposition leading to the negative effects on the materials properties mentioned in previous sections. For multilayer components this sintering temperature further requires the use of silver/palladium alloys with a rather high content of the costly palladium. The use of a proper flux will reduce the sintering temperature and enhance the densification of the ceramics. In the case of the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system it will also simplify the thermal processes because of firing in air instead of oxygen. The major phases of liquid phase sintering include particle rearrangement, solution/precipitation, grain growth and equilibration of the grain boundary phase. During this equilibration the flux in some cases reacts with the main phase and may practically disappear. With an appropriate flux sintering temperature can be set below 950°C yielding dense microstructure and stable properties.(Fig. 1)

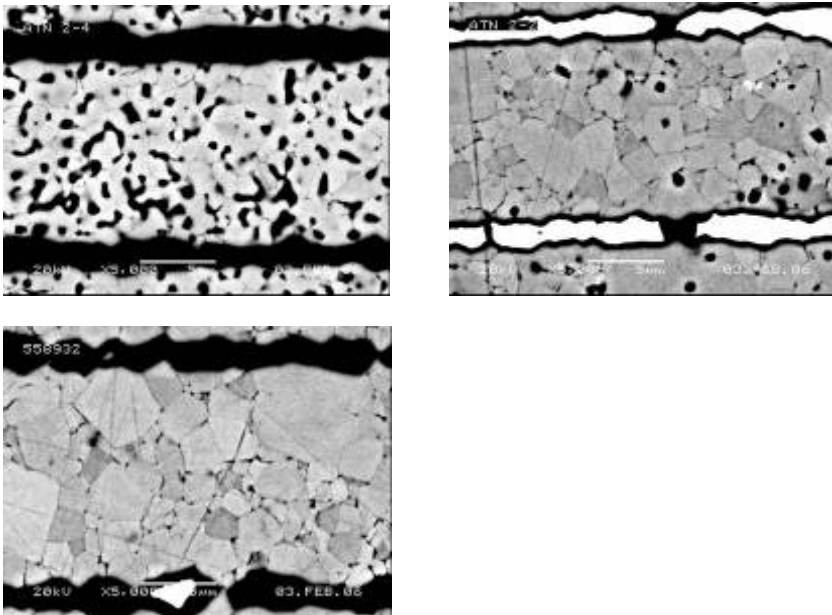


Fig. 1 SEM images of etched components with different degrees of porosity

From the variety of fluxes found in the literature (see for example [5], [6]) we chose H_3BO_3 and Lithium-compounds for our testing program. In the case of H_3BO_3 we assume that boron is not incorporated into the perovskite lattice. Any stoichiometric consideration of the boron in the formulation of the perovskite resulted in the expected formation of secondary phases. Most of the added boron is evaporated during sintering. In contrast lithium compounds form a liquid phase but the lithium subsequently is incorporated in the perovskite lattice, where it occupies A-sites replacing the silver ions [5]. If this is not accounted for, an A/B-ratio > 1 is created, which results in a poor isolation resistance because of the formation of silver as secondary phase. The solubility limit of Li in the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system was estimated to be between 10 mol% and 15 mol%. The incorporation of 7,5 mol% of Li causes ferroelectricity with a phase transformation from monoclinic to rhombohedral. The Curie temperature for that transformation depends on the Nb/Ta-ratio. For Nb/Ta = 1 a Curie temperature of about 80°C is observed [5].

Reliability Issues

Especially in multilayer capacitor components, where usually higher electric fields than in microwave components are applied, the life-time of the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system is limited mainly by resistance degradation, as it is the case for most of dielectric materials. Although the degradation mechanisms and the defect chemistry of this system are not completely consistent up to now, some empirical conclusions can be drawn.

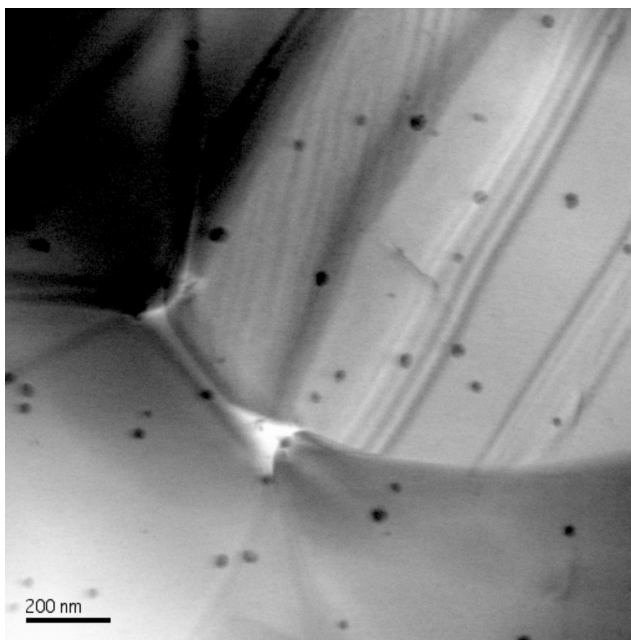


Fig. 2 TEM image of silver precipitates in $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ ceramics

In general it is observed that the isolation resistance and consequently the life-time are reduced by processes, which are linked to the formation of silver precipitates in the ceramics. (Fig. 2) Such silver precipitates may originate from a silver excess in the formulation or by thermal decomposition of the perovskite during sintering, which in turn is favoured by a low oxygen partial pressure. Therefore sintering should be carried out at temperatures as low as possible, but it has to be taken into account that a high porosity (particularly open porosity) leads to a low isolation resistance and accelerated degradation. Highly porous ceramics exhibits a pronounced photochemical effect, which can be observed as an intensive darkening of the material when exposed to daylight. A homogeneous and fine grained starting powder strongly enhances the densification of the ceramics. This requires the use of a Nb-Ta-precursor with a grain size below 500 nm. Hence the calcination temperature can be minimized, which in turn lowers the energy and time of the milling process for the calcined powder to achieve a small grain size. Further such a highly reactive starting powder needs a minimum of flux leading to a more homogeneous grain growth and to a reduction of negative effects of excessive grain boundary phase.

Reliability measurements were conducted on multilayer capacitor test structures with 25 ceramic layers. The fired ceramic thickness was 11 μm . All samples were fired to full density at temperatures between 920°C and 980°C. Highly Accelerated Life Test (HALT) conditions were 150 °C and 64 V. Fig. 3 demonstrates that lower sintering temperatures increase reliability. The data from the sample fired at 920°C suggests that two failure mechanisms overlap.

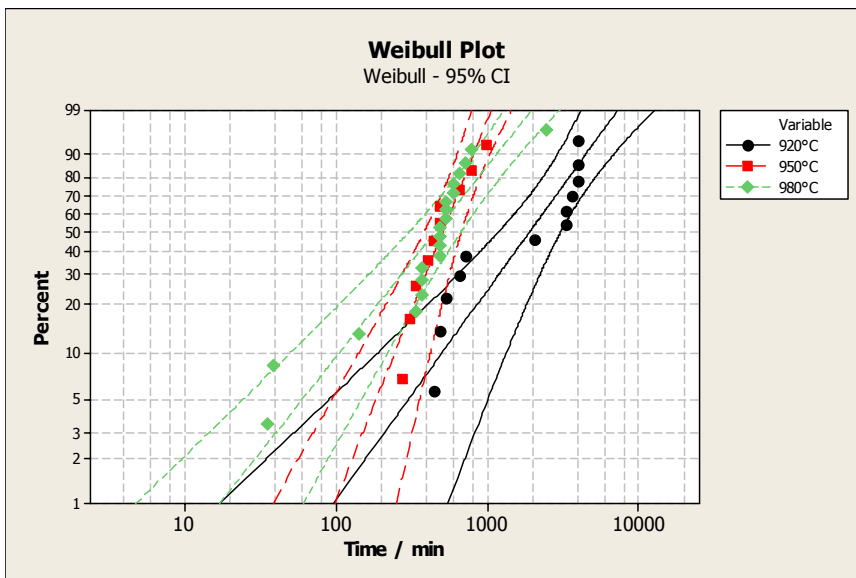


Fig. 3 Highly Accelerated Life Test results (150 °C, 64 V) as function of sintering temperature

Conclusion

Capacitors with COG or near COG characteristic and permittivity above 400 can be achieved in the $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ system. It has been shown that different processing problems related to the nature of the material have to be conquered to increase reliability of these components. Because of the decomposition of $\text{AgNb}_{1-x}\text{Ta}_x\text{O}_3$ it is necessary to decrease the sintering temperature to a minimum. At the same time it is essential to reach a maximum of densification due to problems related to open porosity and silver migration. Both problems can be solved with fine grained $(\text{Nb}, \text{Ta})_2\text{O}_5$ precursors and improved processing. The sintering temperature can be further decreased by the introduction of flux materials. H_3BO_3 was found to have least impact on the dielectric properties and the reliability. Multilayer structures of ATN ceramic with H_3BO_3 addition fired at 920°C performed best in highly accelerated life tests.

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