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Suppressed temperature dependence of the resonant frequency of a $AgNb_{0.5}Ta_{0.5}O_3$ composite vs. single-phase ceramics

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Abstract

$AgNb_{0.5}Ta_{0.5}O_3$ ceramics were synthesized and analyzed, with respect to their dielectric properties, in the radio- and microwave-frequency ranges. The influences of different synthesis conditions were investigated and correlated with the difficulties in preparing single-phase ceramics, as a consequence of the inhomogeneous distribution of Nb and Ta ions and the decomposition of the matrix phase. The results revealed that with the simple mixing of all three oxides and subsequent firing in air, it is possible to prepare composite material that is attractive for microwave applications due to inhomogeneity of the B-site cation distribution – a well-known issue that was in our case shown to be an advantage for decreasing the temperature dependence of the resonant frequency over a broad temperature range. On the other hand, we also succeeded in fabricating single-phase ceramics with a very high density through the initial formation of a precursor and sintering in an overpressure of oxygen.

Keywords: $AgNb_{0.5}Ta_{0.5}O_3$; Composite ceramics; Single-phase ceramics; Suppressed temperature dependence; Microwave dielectric

1. Introduction

$AgNb_{1-x}Ta_xO_3$ ceramics with a composition near to $x = 0.5$ exhibit the highest potential for microwave applications compared to all the other compositions in the system, due to the local maximum of the dielectric constant in the exploitable room-temperature range and moderate dielectric losses. One of the first more detailed investigations of processing and dielectric characterization for compositions with $0 \leq x \leq 0.7$ was given by Kania.[1] A high temperature dependence of permittivity, which had for a long time been considered as problematic, was successfully suppressed by fabricating composite ceramics prepared from a mixture of 45 wt.% of $Ag(Nb_{0.65}Ta_{0.35})O_3$ and 55 wt.% of $Ag(Nb_{0.35}Ta_{0.65})O_3$.[2] The properties of such ceramics became acceptable for several microwave electronic components. However, this is a complex synthesis procedure, since two different single-phase solid solutions have to be prepared first and the powder morphology has to be carefully controlled. Thus, the first objective of this research was to develop a simpler synthesis procedure, based on mixing all three oxides (Ag_2O, Nb_2O_5 and Ta_2O_5) at the beginning, and firing the mixture in air, which could give us equivalent results in terms of dielectric performance. It turned out that the very well-known problem of the inhomogeneous distribution of Nb and Ta ions in the $AgNb_{1-x}Ta_xO_3$ can be advantageous for preparing material with temperature-stable dielectric properties.

On the other hand, much effort has been invested so far in preparing single-phase $AgNb_{0.5}Ta_{0.5}O_3$ with a high density. Despite the technological importance of these materials, their crystal structures and phase transitions were, up until recently, still a subject of debate, as a consequence of the complex types of octahedral tilting and the cation displacements. The $AgNb_{0.5}Ta_{0.5}O_3$ exhibits orthorhombic *Pbcm* symmetry at room temperature with the lattice parameters $a_c\sqrt{2} \times a_c\sqrt{2} \times 4a_c$ ($a_c \approx 4$ Å refers to an ideal cubic perovskite cell).[3–6] Upon cooling from the high-temperature cubic phase, $AgNb_{0.5}Ta_{0.5}O_3$ has been reported to undergo a series of structural phase transitions: $C \leftrightarrow T \leftrightarrow O_1 \leftrightarrow O_2 \leftrightarrow M_3 \leftrightarrow M_2 \leftrightarrow M_1$. All the M-structures exhibit an orthorhombic *Pbcm* symmetry in the rhombic orientation, while O_1 and O_2 are the phases with an orthorhombic symmetry in the parallel orientation. T and C denote the phases with tetragonal and cubic symmetry, respectively. The problem

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with the inhomogeneity of the perovskite phase was solved by the pre-reaction of Nb_2O_5 and Ta_2O_5 to form a precursor with the nominal composition $(Nb_{1-x}Ta_x)_2O_5$. Another problem that must be overcome during the sintering of a powder is the thermal decomposition of the $AgNb_{0.5}Ta_{0.5}O_3$ compound, which under normal conditions starts at a temperature that is not high enough for efficient densification. Therefore, a flow or an atmosphere of oxygen was used in some investigations to postpone the onset of decomposition. The second object of this study was thus to explore the influence of the oxygen overpressure during the sintering process, to retard the decomposition process even more and, consequently, to achieve a higher density for the sintered ceramics. It is the first time that an oxygen overpressure has been used for this kind of investigation. Finally, we compared the dielectric properties of the as-prepared samples with samples that were sintered in air.

2. Materials and methods

Two solid-state reaction procedures were applied to prepare the $Ag(Nb_{0.5}Ta_{0.5})O_3$ material from reagent-grade Nb_2O_5 (99.9985% pure, Lot 24794; Alfa Aesar, Germany), Ta_2O_5 (99.993% pure, Lot 61001144; Alfa Aesar, Germany), and Ag_2O (99.99% pure, Lot F18T065; Alfa Aesar, Germany).

In the first procedure (classic route) all three powders were weighed and then mixed, using conventional ball milling with yttrium-stabilized-zirconia balls in ethanol for 1 h at 300 rpm. The pelletized powder mixture was calcined at 900 °C for two 10-h periods in air with intermediate cooling and milling. The pre-reacted samples were milled to an average particle size of <1 μm, compacted into disks, cold isostatically pressed at 700 MPa and sintered at a selected temperature (1040 °C, 1080 °C, 1120 °C, 1160 °C, 1200 °C) for 5 h in air. The heating/cooling rate was 10 °C/min.

In the second procedure (precursor route) a $(Nb_{1-x}Ta_x)_2O_5$ precursor was synthesized first, by homogenizing Nb_2O_5 and Ta_2O_5 powders in ethanol and then pre-reacting them at a temperature of 1200 °C for two 10-h periods in air with intermediate cooling and crushing. The as-prepared precursor was milled for 1 h at 300 rpm. Before Ag_2O was added to the precursor in an appropriate amount, the precursor was thoroughly dried at 600 °C for 1 h. This mixture was pre-reacted in an oxygen overpressure (0.6 MPa) at temperatures of 900 °C and 1100 °C for 5 h with intermediate cooling and crushing. The resulting powder was milled for 1 h. The subsequent sintering of the pelletized and cold isostatically pressed powders was carried out in an oxygen overpressure at the same temperatures as the samples in the first procedure, except for 1040 °C. The heating/cooling rate was 10 °C/min.

The microstructures were examined using scanning electron microscopy (SEM, Model JSM 5800; JEOL, Tokyo, Japan) coupled with an energy-dispersive X-ray spectrometer (EDS, Model Oxford-Link Isis 300; Oxford Instruments, Oxford, U.K.).

Powder X-ray diffractometry (XRD) data for the phase identification of the calcined and sintered samples were collected on a diffractometer with θ–2θ Bragg–Brentano geometry (X'Pert PRO, PANalytical, The Netherlands) and an incident-beam monochromator (Johansson monochromator). The following scanning parameters were used: 2θ range from 20° to 80°, step size 0.017° and time per step 200 s.

A heating microscope (Hesse Instruments) was used to measure the linear shrinkage of the pellet. The experiment was conducted at a heating rate of 10 °C/min in air up to 1300 °C. The densities of the sintered samples were determined using Archimedes' method in ethanol.

The dielectric properties were measured in the radio- and microwave-frequency regions. The low-frequency dielectric properties were measured using a LCR meter (Model 4284A; Hewlett–Packard, USA) at frequencies from 1 kHz to 1 MHz in the temperature range from −153 °C to +600 °C. Silver paste was fired on the samples before the measurements. The microwave dielectric properties were determined using a network analyzer (Model E8361C; Agilent Technologies, USA) and the cavity-reflection method.[7] The sintered samples act as cylindrically shaped dielectric resonators with a thickness-to-diameter ratio of ∼0.40.

3. Results and discussion

3.1. Classic route

The XRD analysis of the samples after the first and second calcination steps at 900 °C for 10 h revealed the same diffraction patterns and suggests a single $Ag(Nb_{0.5}Ta_{0.5})O_3$ perovskite phase (PDF card 010 79 6964) with an orthorhombic *Pbcm* (no. 57) symmetry, which is in agreement with the neutron-diffraction study conducted by Levin et al.[3] The as-prepared powder was examined with the heating microscope, and the results showed an onset of shrinkage near 850 °C, reaching the maximum shrinkage at 1120 °C. Based on this, a range of sintering temperatures from 1040 °C to 1200 °C was chosen. After a subsequent sintering at 1040 °C or 1080 °C for 5 h, the XRD patterns show the presence of the same diffraction maxima; however, they show narrower and sharper peaks, indicating the improved crystallinity of the sintered material compared to the calcined one. The samples sintered at 1120 °C, 1160 °C and 1200 °C contain a perovskite matrix, as well as some other crystalline secondary phases, which can be attributed to the decomposition process.[8] For the sample sintered at 1120 °C, mainly the $Ag_2(Nb,Ta)_4O_{11}$ phase (PDF cards 000 21 1345 and 000 21 1086) and small amounts of $Ag_8(Nb,Ta)_{26}O_{69}$ (PDF card 000 51 0374) phase can be identified, whereas for the samples sintered at 1160 °C and 1200 °C, besides the metallic silver, the $Ag_8(Nb,Ta)_{26}O_{69}$ phase was found (Fig. 1). For the sample sintered at 1120 °C no diffraction peaks corresponding to elemental silver can be observed as a consequence of the small amount of decomposition products and the volatility of the released silver.

The SEM micrograph of the sample sintered at 1040 °C reveals the presence of secondary phases, which appear as dark and bright phases due to the different atomic number *Z*. The observed secondary phases can be attributed to the inhomogeneous distribution of the Ta and Nb ions over the B-site in the perovskite structure as a result of the low sintering temperature.