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High frequency dielectric properties of hot-pressed $Ag(Nb_xTa_{1-x})O_3$ solid solutions E-P-09

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Abstract

The objective of this paper was to determine the dielectric properties of $AgNb_{1/2}Ta_{1/2}O_3$ (referenced ANT22) sintered at low temperature without any addition or substitution.

Hot-pressing was performed to decrease the sintering temperature. By this way, high density were achieved. The resulting samples were compared with conventionally sintered ANT22 and with copper oxide added ANT22.

The highest densities were obtained for the hot-pressed samples compared with the CuO added ones. We concluded that the dielectric losses of the hot-pressed and copper oxide added ANT22 were very similar at high frequency ($f > 1$ MHz), indicating that copper oxide does not degrade the ANT22 properties.

Conversely, low frequency dielectric properties were different, with a strong dielectric relaxation for the hot-pressed samples.

Keywords: Hot-pressing; Dielectric properties; Perovskites; Capacitors; ANT ($AgNb_{1-x}Ta_xO_3$)

1. Introduction

Development of microwave electronic devices (telecommunications, Radar or medical applications) demands high-permittivity materials with low loss and low sintering temperature since the major concerns are miniaturization and cost reduction. Over the last 20–30 years, a significant reduction in size of microwave devices was achieved by substituting air cavities (dielectric constant: $K = 1$) by ceramic resonators that have $K = 25$–30 with $Q \times f = 100{,}000$–$200{,}000$ GHz and then $K = 80$–90 with $Q \times f = 5000$ GHz. However the increase of K results in a decrease of $Q \times f$ and in a stronger temperature dependence of the permittivity.

Dielectric materials based on $Ag(Nb_xTa_{1-x})O_3$ solid solution (ANT) meet the majority of commercial requirements because of their high permittivity and moderate dielectric losses. Without sintering aids, the $Ag(Nb_xTa_{1-x})O_3$ solid solutions (ANT) require high sintering temperature (1200 °C) that results in Ag evaporation.[1,2]

Copper oxide added to ANT (referenced CuO–ANT), allows reducing this temperature by 300 °C but an increase of dielectric losses was observed.[3]

The objectives of the present study were:

- to sinter $AgNb_{1/2}Ta_{1/2}O_3$ at low temperature without any addition;
- to evaluate the dielectric properties over a wide frequency range;
- to correlate with the physico-chemical properties.

2. Experimental procedure

$AgNb_{1/2}Ta_{1/2}O_3$ perovskite was synthesized using solid-state chemical reaction with the following raw materials: Ag_2O Alfa Aesar, Ta_2O_5 Alfa Aesar, Nb_2O_5 Alfa Aesar or HJD (see Table 1). The powders were weighed and then mixed, using attrition-milling with zirconia–cerium balls in water for 1 h. ANT behaviour during the calcination was studied by thermo differential analysis coupled with a Thermo Gravimetric Analysis noted TDA/TGA (SDT 2960, TA Instruments Model). According to the Nb_2O_5 grain size, the mixed powders were calcined at 740 °C (Nb_2O_5 HJD) and 990 °C (Nb_2O_5 alfa) for

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Table 1
Raw materials characteristics

Powders	Mean grain size (μm)	Specific area (m^2/g)
Raw materials		
Ag_2O	4 ± 0.5	0.35 ± 0.05
Ta_2O_5	1 ± 0.2	2.8 ± 0.1
Nb_2O_5 HJD	0.3 ± 0.1	8.35 ± 0.1
Nb_2O_5 alfa	5 ± 0.5	0.3 ± 0.05

2 h in air and then milled for 30 min. Phase identification of the samples was performed using X-ray diffractometry at room temperature (XCPS 120 INEL). Specific area of the powders was evaluated by BET method (Flowsorb II 2300, micromeritics model).

The ground powders were granulated by adding poly(vinyl) alcohol (PVA) solution, and then the granules were pressed into cylinders: 12 mm in diameter and 10 mm in height for the hot-pressed samples, 9 mm in diameter and 8.5 or 1 mm in height for the conventionally fired samples.

Sintering properties were investigated by measuring the density of the sintered samples with the Archimede's method and by using Thermo Mechanical Analysis (Setaram TMA 92).

Then after conventional sintering and hot-pressing, the samples were machined or directly metallized to make resonators or capacitors to perform the electromagnetic measurements.

Regarding the conventional method, all samples were sintered at 1000 °C for 2 h.

Hot-pressing was used to enhance the densification at a lower temperature than the usual sintering temperature. It was performed in air during 1 h by applying simultaneously a pressure of 100 MPa and a temperature of 1000 °C. ANT22 Cylinders were coated with alumina powder and placed into a dense alumina matrix.

Microstructures were examined using Scanning Electron Microscope for imagery (SEM S4000, Hitachi model) and Energy-Dispersive X-ray Spectroscopy for mapping (ABT/TOPCON 150F model using Noran EDS system). Sections were prepared by grinding the sintered samples on SiC sandpaper and polished using diamond paste. The polished samples were thermally etched for 10 min at the sintering temperature and then furnace-cooled to room temperature.

Low-frequency dielectric properties were measured using an impedance analyzer (4294A, Agilent model) from 40 Hz to 10 kHz. Dielectric properties in the microwave range were determined by the dielectric resonator method[4] using a network analyser (HP 85-10, Agilent model) in the transmission mode. Temperature dependence of dielectric constant was measured between −25 and +150 °C at 100 kHz by measuring the capacitance of a metallized disk.

3. Results and discussion

3.1. Physico-chemical characterizations

First, the microstructures of raw materials were examined using SEM. Their mean grain size and their specific area are reported in Table 1.

Phase formation was explored by TDA/TGA on raw materials mixture calcined up to 900 °C in air (see Fig. 1a).

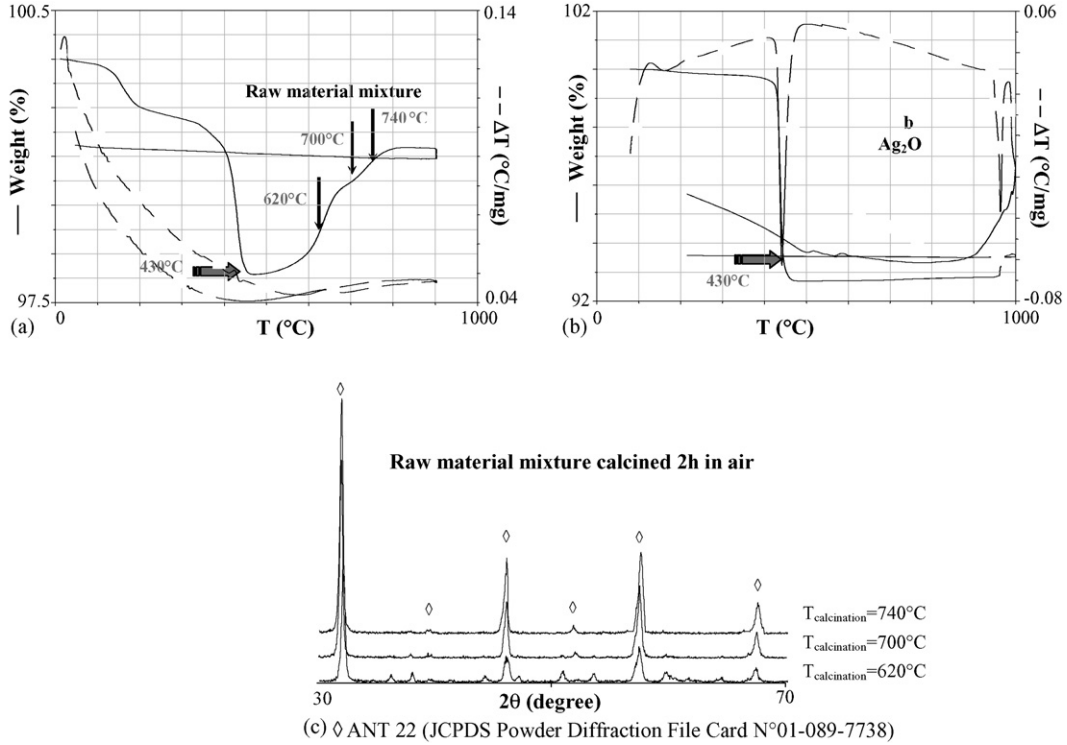

Fig. 1. Study of ANT22 phase formation using Nb_2O_5 HJD: (a) TGA/DTA on raw materials – firing rate 20 °C/h; (b) TGA/DTA on Ag_2O; (c) XRD analysis on raw materials after calcination 2 h in air.

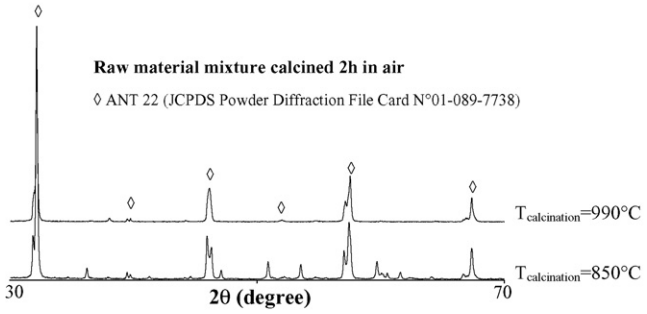

Fig. 2. Study of ANT22 phase formation using Nb_2O_5 alfa.

For Nb_2O_5 HJD, the mass loss observed at 200 and 400 °C are related respectively to H_2O loss and Ag_2O reduction (see Fig. 1b). Once metallic silver is appeared, the ANT phase formation begins at about 410 °C and finishes around 800 °C.

After calcination at 620 °C, XRD analysis revealed the presence of raw materials with ANT phase. At 700 °C, ANT phase is predominant with a few impurities whereas at 740 °C, only ANT phase was observed (see Fig. 1c).

When raw materials mixture is made with Nb_2O_5 alfa, the phase formation finishes around 1000 °C. XRD analysis revealed the presence of impurities at 850 °C whereas at 990 °C, only ANT phase was detected (Fig. 2).

The sintering of ANT22 (using Nb_2O_5 HJD) in air and in O_2 was examined by TMA: the results are shown in Fig. 3. Whatever the atmosphere, the sintering began near 770 °C but was faster in air. However, the final shrinkage was more important in O_2. With Nb_2O_5 alfa, the same phenomena were observed except that the sintering began later at 870 °C due to the larger grain size.

So, using conventional sintering, densification is impossible at temperature lower than 1000 °C (Table 2).

Table 2
ANT22 density using conventional sintering and hot-pressing

Theoretical[a]	Conventional sintering, $T_s = 1000$ °C air	Hot-pressing, $T_s = 1000$ °C air
ANT22 density (g/cm^3)		
8.02	4.2	7.7

[a] cf. JCPDS Powder Diffraction File Card No. 01-089-7738.

Table 3
Dielectric properties at 1.6 GHz of ANT22 vs. sintering conditions

	Hot-pressed ANT22, $T_s = 1000$ °C	ANT22–CuO, $T_s = 880$ °C	ANT22–CuO, Kim et al., $T_s = 900$ °C[3]
Density (g/cm^3)	7.7	7.35	7.27
K (1.6 GHz)	330	390	400
$Q \times f$ (GHz)	405	405	400

To decrease firing temperature and prevent silver evaporation, hot-pressing was performed at 1000 °C. Using this technique, 96% of the theoretical density was achieved.

3.2. Electromagnetic characterizations

Permittivity and dielectric losses for hot-pressed ANT22 in comparison with copper oxide addition are reported in Table 3. The results were very similar to those obtained by Kim et al.[3] No difference was observed concerning the quality factor of the two samples. So, copper oxide doesn't deteriorate ANT22 dielectric properties. However, the low permittivity of hot-pressed ANT22 is very surprising and contradictory with a good densification. This could be due to a smaller grain size and a higher grain boundary density.

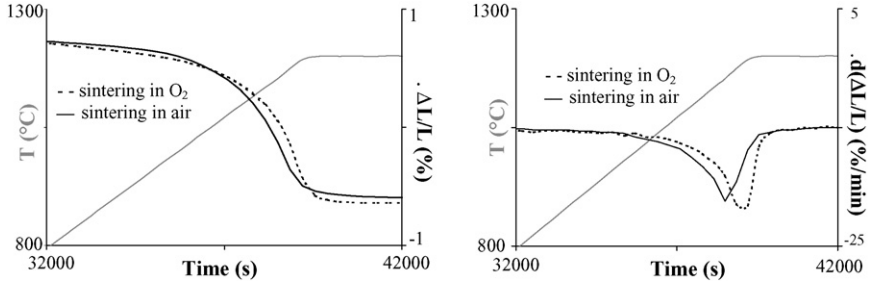

Fig. 3. Effect of the sintering atmosphere on the shrinkage.

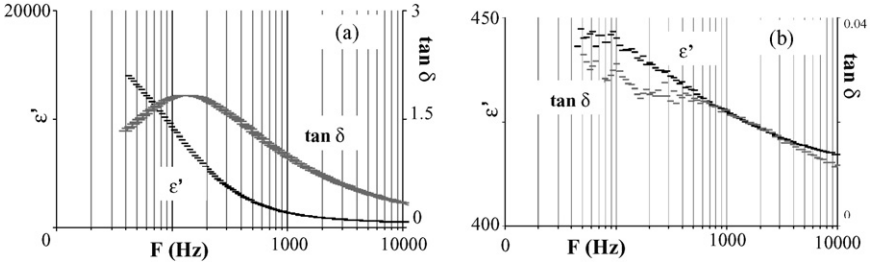

Fig. 4. Dielectric properties from 40 Hz to 10 kHz for: (a) hot-pressed ANT22; (b) ANT22–CuO.

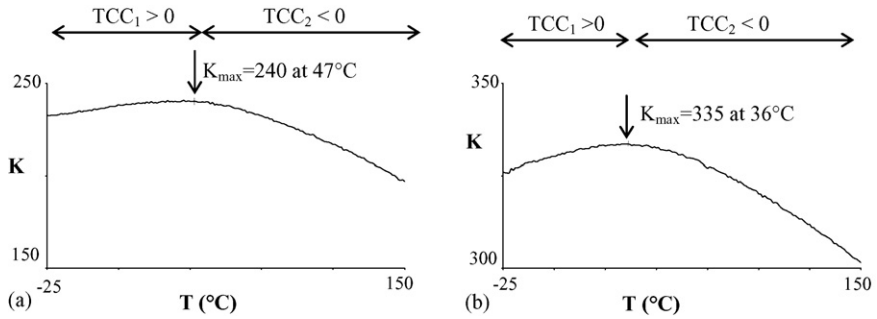

Fig. 5. TCC plots between −25 and 150 °C for: (a) hot-pressed ANT22 T_s = 1000 °C; (b) ANT22–CuO T_s = 900 °C CO_2.

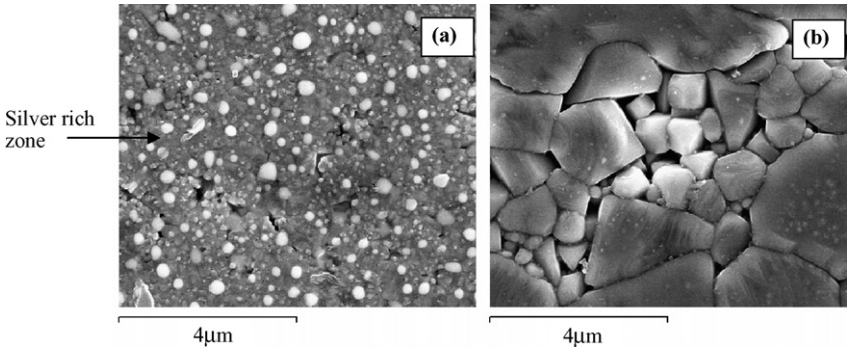

Fig. 6. Microstructures of: (a) hot-pressed ANT22 (T_s = 1000 °C); (b) ANT22–CuO (T_s = 900 °C).

Low frequency dielectric properties were measured from 40 Hz to 10 kHz (Fig. 4). A dielectric relaxation was observed at low frequency for the hot-pressed samples only and whatever the Nb_2O_5 used. Permittivity and losses for copper oxide addition are constant at low frequency and the resulting values are in agreement with the measurements at microwave frequency.

Table 4 gives the temperature coefficient of capacitance (TCC) of samples measured at 100 kHz from −25 to +150 °C. For all samples, K increases from −25 °C to T corresponding to K_{max} and goes down from T to +150 °C. So, the temperature coefficient was defined by the following relation: $TCC = \Delta K/K_{RT}\Delta T$, where $\Delta K = K(T_{max}$ or $T_{min}) - K_{max}$, $\Delta T = (T_{max}$ or $T_{min}) - T(K_{max})$, and K_{RT} is the dielectric constant at room temperature.

TCC of hot-pressed ANT22 and CuO–ANT22 sintered at 900 °C in O_2 are similar. Fig. 5 presents TCC plots for these two samples. For CuO–ANT22 sintered at 880 °C in air, TCC are the lowest.

Table 4
TCC of hot-pressed and conventionally sintered ANT22 measured at 100 kHz between −25 and 150 °C (samples made from Nb_2O_5 HJD)

	TCC_1 (ppm/°C)	TCC_2 (ppm/°C)	K_{max}	T (°C)
Hot pressed ANT22				
T_s = 1000 °C	445	−1455	240	47
ANT22–CuO				
T_s = 880 °C air	370	−845	335	36
T_s = 900 °C O_2	810	−1430	300	48

Table 5
Energy dispersive spectroscopy analysis on a silver rich zone for the hot-pressed ANT22 (T_s = 1000 °C)

Compound formula	Compound wt.% (measured)	Compound wt.% (theoretical)
Ag_2O	50.5	39.5
Nb_2O_5	23.5	23.0
Ta_2O_5	26.0	37.5

We observe that K_{max} obtained for hot-pressed ANT22 remains lower than for CuO-ANT22 samples. This result is in accordance with microwave results.

3.3. Relationship between microstructure and dielectric properties

To understand these results, SEM analysis was performed. Copper oxide addition presents an heterogeneous microstructure, with a grain size from 0.5 to 4 µm. Hot-pressed ANT present a finer and more homogeneous microstructure (Fig. 6) with several white dots. EDS analysis revealed that these dots were silver rich zones (cf. Table 5). This secondary phase could be responsible for the relaxation at low frequency.

4. Conclusions

Hot-pressing at 1000 °C allows the densification of ANT without sintering aids.

A strong dielectric relaxation is observed at low frequency for the hot-pressed samples. This could be related to the presence of nanosized metallic silver.

Dielectric losses of the hot-pressed and copper oxide added ANT are very similar at high frequency (from 1 MHz to 2 GHz), indicating that copper oxide does not degrade the ANT properties. So, CuO can be used with ANT to decrease the sintering temperature as Kim et al. proposed.[3]

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