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Electrical Properties of Magnesium Titanate Ceramics Post-Sintered by Hot Isostatic Pressing

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Abstract:

Post-sintering of magnesium titanate ceramics by hot isostatic pressing (HIP) in an oxygen-free atmosphere significantly alters various electrical properties of the product. In particular, the sintered material becomes a semiconductor. The aims of this paper are: to extend our investigations of the electrical properties of this material by expanding the frequency range of measurements, to design interpolation formulas for the frequency dependence of the complex relative permittivity, and to propose HIP-sintered magnesium titanate as a material for thermistors that have a negative-temperature-coefficient resistance (NTCR), as well as for varistors.

Keywords: Magnesium titanate; Hot isostatic pressing; Complex permittivity; Thermistors; Varistors.

1. Introduction

Magnesium titanate (MgTiO_3) ceramic material has been used in electrical engineering for a long time as an insulating material [1]. Properties of the product depend on the sintering process [2, 3]. Usually, the color of the product is white and the ceramics have a moderate relative permittivity (dielectric constant) and a moderately low loss tangent. The permittivity has a positive temperature coefficient (PTC). In order to compensate the temperature variations of the permittivity, it is mixed with other materials with a negative temperature coefficient (NTC) [4]. The stabilized materials are used in electrical engineering in the production of multilayer capacitors and as carriers for various microwave devices [5].

However, if the material is sintered in air first and then post-sintered by hot isostatic pressing (HIP), the product becomes quite different: its color is dark, almost black, and it behaves as a semiconductor, exhibiting significant variations of electrical parameters as a function of frequency and temperature [2, 3]. Such a behavior can be explained by the lack of oxygen during the HIP in an inert argon atmosphere and by a high concentration of defects [3].

The present paper has several purposes. The first goal is to assemble and compare all our measured results for the electrical properties of the HIP-sintered samples. The second aim is to extend measurements to very low frequencies, in the sub-Hertz range, and also to the

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direct current (DC), in order to obtain a complete picture of the material behavior. The third objective is to design interpolation formulas for the behavior of electrical parameters of the HIP-sintered samples in an ultra wide band of frequencies, from DC up to 10 GHz. The fourth intent is to promote possible applications of HIP-sintered ceramics in electrical engineering.

2. Experimental procedure

Tablets of HIP-sintered magnesium titanate were produced from mixtures of MgO and TiO₂ powders. The powder mixtures were activated by ball milling for 10, 40, 80, and 160 minutes. The resulting compacts were sintered at 1400°C for 30 minutes in the air. Samples without open porosity were post-sintered by the HIP sintering at 1200°C for 2 h in an argon atmosphere at a pressure of 200 MPa. These samples are used here for electrical characterization. They are denoted as HIP-10, HIP-40, HIP-80, and HIP-160, according to the duration of the ball milling.

The tablets were metalized on their bases using liquid silver (Electrolube). Thus, each tablet forms a parallel-plate capacitor, sketched in Fig. 1. The tablet diameters (d) are in the range 9.6–10.8 mm, and their thicknesses (h) are in the range 2.76–3.59 mm.

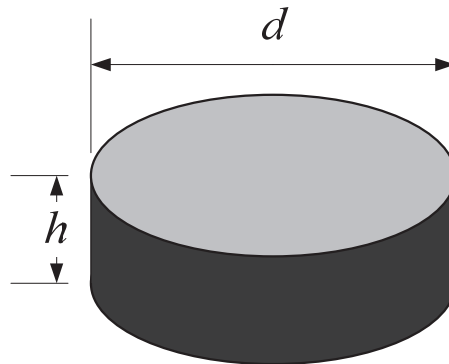


Fig. 1. Sketch of a tablet with silver-coated bases.

In [3], the electrical properties of the HIP-sintered samples were measured in the frequency range from 200 Hz to 1 MHz using an Agilent 4284A LCR meter, for various temperatures in the interval from 20°C to 180°C. In [2], the electrical properties of the same samples were measured at the room temperature in a very wide frequency range, using an HP4192A impedance analyzer for the frequency range between 10 kHz and 10 MHz, an Agilent E5061A network analyzer for the frequency range between 300 kHz and 3 GHz, and an Agilent N5227A network analyzer for the frequency range between 10 MHz and 10 GHz.

At lower frequencies, the complex impedance (\underline{Z}) or admittance ($\underline{Y} = \frac{1}{\underline{Z}}$) of the samples was directly measured (using the LCR meter, viz. the impedance analyzer). At higher frequencies, where network analyzers were used, the reflection coefficient with respect to 50 Ω was measured first, and the complex admittance was calculated from this coefficient. We extend the measurements here to very low frequencies, in the range from 0.1 Hz to 1 MHz, as well as to the stationary case (DC).

The tablets behave as nonlinear loads: their static voltage-current characteristics are nonlinear, as shown in Fig. 2. These characteristics were obtained using the setup from [6], with two Mastech M92A multimeters, one serving as a voltmeter, and another as an ammeter. It was verified by similar tests with fast variations of the voltage, using a Hameg HM303-6

oscilloscope as a component tracer, that the nonlinearities are not primarily due to heating effects, but are inherent to the bulk material. Note that the static characteristics also exhibit small asymmetries that can be seen in Fig. 2b.

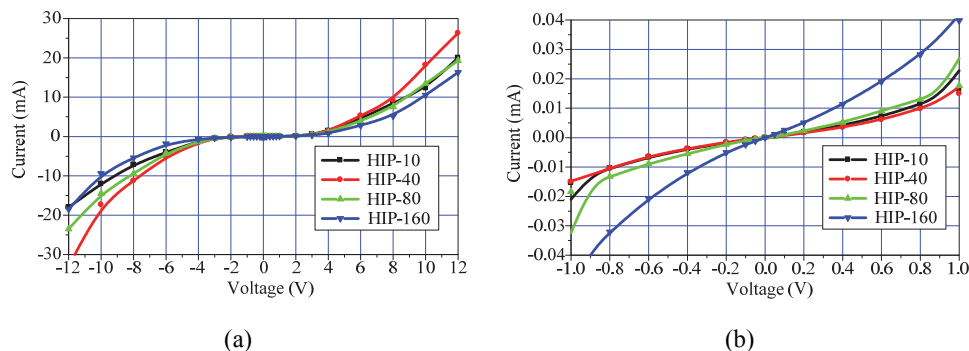


Fig. 2. Static voltage-current characteristics of the tablets: (a) full measured range and (b) zoom-in for voltages between -1 V and 1 V.

It is only for smaller voltages, whose magnitude is well below 1 V, that the tablets can crudely be assumed to be linear and, hence, described by their DC resistances. As an illustration, when a Mastech M92A multimeter is used as an ohmmeter, the voltage of the measured tablet is several hundred mV and it depends on the range. Changing the range affects the measured resistance for 10 – 20 %.

To investigate the temperature behavior of the material, we inserted the tablets into a custom-made fixture, made of temperature-resistant materials, and cooled them in a freezer or heated in a thermostatically controlled oven. The temperature of the tablets was measured using a contactless IR thermometer PeakTech P4980.

For AC measurements at very low frequencies, we used a simple setup, described in [7], with a Hameg HM8030 signal generator and a dual-channel USB oscilloscope Owon VDS1022i (up to 1 kHz) or a Hameg HM2005 (up to 10 MHz). The signal generator was used to create a time-harmonic (sinusoidal) signal. A resistor was connected in series with the tablet in order to sample the current. The resistance was selected to be much smaller than the impedance of the tablet: 1 k Ω for frequencies below 100 Hz, 10 Ω for frequencies above 10 kHz, and 100 Ω for intermediate frequencies. One channel of the oscilloscope measured the instantaneous voltage of the tablet. The other channel measured the voltage of the resistor. When divided by the resistance, this voltage yields the instantaneous current of the tablet.

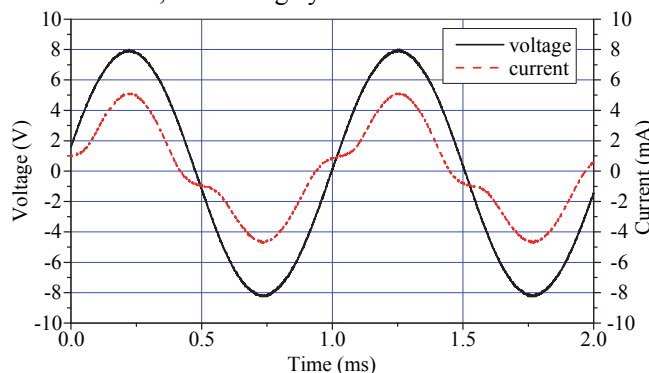


Fig. 3. Instantaneous voltage and current of a tablet for a large excitation.

A typical plot of the tablet voltage and current is shown in Fig. 3: the voltage is practically sinusoidal, but the current is rich in harmonics. Furthermore, due to the nonlinearities, the ratio of the amplitudes of the current and voltage increases as the voltage increases. In the measurements, we have tried to keep the peak voltage below 1 V (when the peak intensity of the electric field in the tablet is below, approximately, 300 V/m) to reduce the effect of nonlinearities. Nevertheless, in such a situation, when the state in the circuit is not time-harmonic, the complex impedance and admittance of the sample should be interpreted with care.

By taking the ratio of the amplitudes of the measured current and voltage, we estimate the modulus of the complex admittance. From the time delay between the zero-crossing points, we evaluate the phase difference between the voltage and the current, i.e., the argument of the complex admittance.

The magnitude of the relative complex permittivity (dielectric constant) of the material ($\underline{\epsilon}_r$) is very large. Hence, at frequencies up to about 100 MHz, the tablet can be analyzed as a parallel-plate capacitor with negligible fringing effects. Therefore, the complex capacitance of the tablet is, approximately, $\underline{C} = \frac{\epsilon_r \epsilon_0 A}{h}$, where $A = \frac{\pi d^2}{4}$ is the surface area of the electrodes and ϵ_0 is the permittivity of a vacuum. The complex admittance is $\underline{Y} = j\omega \underline{C}$, where j is the imaginary unit, $\omega = 2\pi f$ is the angular frequency, and f is the frequency. Hence, the complex permittivity is simply evaluated as $\underline{\epsilon}_r = \frac{h \underline{Y}}{j\omega \epsilon_0 A}$.

At very high (microwave) frequencies, we employ more sophisticated models to extract the complex permittivity from the measured data [8], where we take into account the parasitic influences of the test fixtures. For frequencies in the range from 1 MHz to approximately 200 MHz we use a 3-D quasi-static model. For higher frequencies, up to 10 GHz, we use a 3-D dynamic model in the software WIPL-D Pro.

The complex relative permittivity of a lossy dielectric can be written in various forms: $\underline{\epsilon}_r = \epsilon'_r - j\epsilon''_r = \epsilon'_r(1 - j \tan \delta) = \epsilon'_r - j \frac{\sigma}{\omega \epsilon_0}$. Here, ϵ'_r is the real part of the complex

relative permittivity, whereas the imaginary part is $-\epsilon''_r$. Further, $\tan \delta = \frac{\epsilon''_r}{\epsilon'_r}$ is the loss tangent and $\sigma = \omega \epsilon_0 \epsilon''_r$ is the equivalent conductivity of the material.

By investigating the frequency dependence of $\underline{\epsilon}_r$ in a wide frequency range, it is possible to identify various polarization and loss mechanisms in the material. One option is to use Cole-Cole diagrams [9], which are shown in [3] for the HIP-sintered magnesium titanate. In engineering applications, it is desirable to know the variations of $\underline{\epsilon}_r$ as a function of frequency. However, in the Cole-Cole diagrams, it is not easy to trace the frequency. Plots showing ϵ'_r and ϵ''_r , $\tan \delta$, or σ as a function of frequency are of a greater practical value.

Furthermore, for engineering applications, $\underline{\epsilon}_r$ can be fitted using various functions of frequency. In order to provide a causal response in the time domain, $\underline{\epsilon}_r$ should be fitted by an analytic function of the complex frequency \underline{s} ($\underline{s} = j\omega$ on the imaginary axis) [10].

For all four samples of the HIP-sintered magnesium titanate ceramics, we approximated the relative complex permittivity by

$$\epsilon_r(\underline{s}) = \epsilon_{r\infty} + \sum_{i=1}^3 \frac{\Delta\epsilon_{ri}}{\left(1 + \left(\frac{s}{2\pi f_i}\right)^{\alpha_i}\right)^{\beta_i}} + \frac{\sigma_0}{\epsilon_0 \underline{s}}, \quad (1)$$

where $\epsilon_{r\infty}$ is the asymptotic relative permittivity at very high frequencies (in the microwave region, well beyond 1 GHz). It is followed by three Havriliak-Negami terms [11], whose magnitudes are $\Delta\epsilon_{ri}$, onset frequencies are f_i , whereas α_i and β_i are exponents ($i = 1, 2, 3$). The last term contains the DC conductivity σ_0 , which is extrapolated from the measurements at the sub-Hertz frequencies and verified by the DC measurements.

The temperature dependence of the DC conductivity (σ_0) was approximated by a modification of the Steinhart-Hart equation [12]. In our modification, we use the conductivity instead of the resistance to obtain

$$\frac{1}{T} = \frac{1}{T_{\text{ref}}} + \frac{1}{a} \ln \frac{\sigma_0}{\sigma_{\text{ref}}}, \quad (2)$$

where T is the temperature (in Kelvins), $T_{\text{ref}} = 298 \text{ K}$ is the room temperature in the experiments, σ_{ref} is the conductivity at the room temperature, whereas a is a coefficient to be determined.

3. Results and discussion

The results obtained for all four samples were qualitatively very similar. Subtle differences are important for the study of the structure of the sintered ceramics, but they do not seem to be essential for the applications.

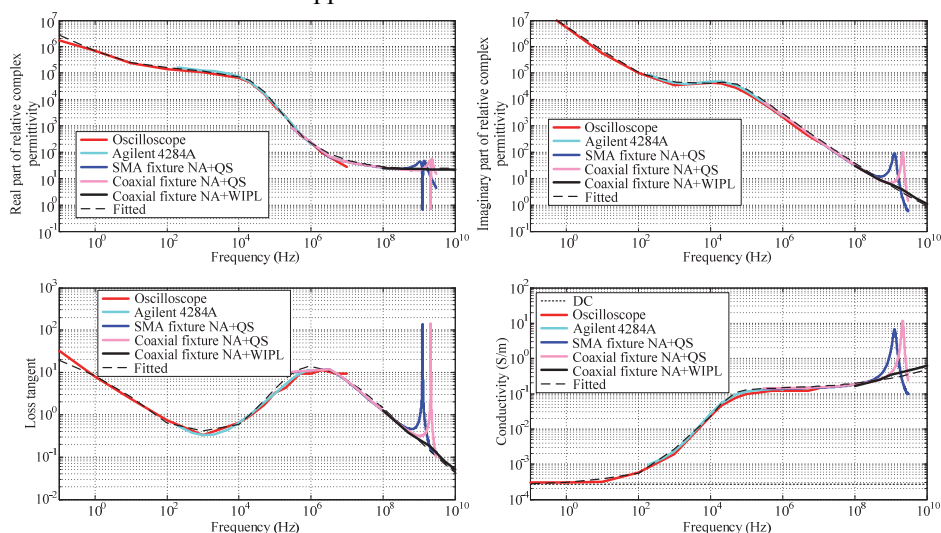


Fig. 4. The real part and the imaginary part of the relative complex permittivity, the loss tangent, and the conductivity of the sample HIP-80 obtained from various sets of measurements (explained in the text), along with fitted values calculated from Eq. (1).

Hence, we show in Fig. 4 the complex permittivity for only one sample, HIP-80. The first two plots show the real part and the imaginary part of the complex relative permittivity, respectively. The third plot shows the loss tangent and the fourth plot shows the conductivity. Various results are overlapped: results obtained from high-frequency measurements using the coaxial and the SMA test fixtures at the room temperature (25°C) and processed by the quasi-static model (labeled “Coaxial fixture NA+QS” and “SMA fixture NA+QS”, respectively), results obtained from high-frequency measurements using the coaxial test fixture at the room temperature (25°C) and processed by the WIPL-D Pro model (“Coaxial fixture NA+WIPL”), results obtained by the Agilent 4284A LCR meter at the temperature of 35°C (“Agilent 4284A”), results obtained using the simple setup for voltage-current measurements using an oscilloscope (“Oscilloscope”) at the room temperature (25°C), and the fitting results obtained from Eq. (1). The coefficients of the fitting formula, for all four samples, are given in Tab. I. For the conductivity, the result of the DC measurements is also shown in Fig. 4.

Tab. I Parameters in Eq. (1) for the four sintered samples.

	HIP-10	HIP-40	HIP-80	HIP-160
$\epsilon_{r\infty}$	19	18	18	16
$\Delta\epsilon_{r1}$	$9.8 \cdot 10^6$	$2.9 \cdot 10^6$	$4.7 \cdot 10^6$	$3.9 \cdot 10^6$
f_1 (Hz)	0.026	0.073	0.043	0.16
α_1	1	0.60	0.64	0.73
β_1	0.60	0.97	0.94	0.83
$\Delta\epsilon_{r2}$	$2.0 \cdot 10^4$	$2.8 \cdot 10^4$	$4.2 \cdot 10^4$	$4.9 \cdot 10^3$
f_2 (Hz)	$7.1 \cdot 10^2$	$6.5 \cdot 10^2$	$6.4 \cdot 10^2$	$2.2 \cdot 10^3$
α_2	1	0.81	1	1
β_2	1	1	0.86	1
$\Delta\epsilon_{r3}$	$8.7 \cdot 10^4$	$7.0 \cdot 10^4$	$8.4 \cdot 10^4$	$4.9 \cdot 10^4$
f_3 (Hz)	$2.3 \cdot 10^4$	$2.6 \cdot 10^4$	$2.5 \cdot 10^4$	$4.9 \cdot 10^4$
α_3	0.98	0.97	0.98	1
β_3	1	1	1	0.99
σ_0 (S/m)	$6.3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$

The high-frequency results obtained using the quasi-static model are inaccurate at frequencies above, approximately, 200 MHz because the model theoretically fails at those frequencies due to the propagation effects. In contrast to it, the full-wave model gives good results even up to 10 GHz. Note, however, that the full-wave model has to be run for each frequency and the relative complex permittivity adjusted by an optimization procedure in order to fit the measured data. The required run time is very long (several hours per tablet), compared to just a few seconds required for the quasi-static model.

The results obtained from the measurements using the impedance analyzer and the LCR meter differ primarily due to the different temperatures of the sample. The differences are also partly due to the different voltages of the tablets. Nevertheless, the data fitted using Eq. (1) follow reasonably well the measured data.

We note that with the HIP-160 sample there were problems with the adherence of silver to the ceramic material: the galvanic contact was gradually lost after several weeks of experimenting. Thereafter, the contact was established again after heating the tablet to 250°C.

Fig. 5 shows the temperature variations of the conductivity for all four samples and Tab. II shows the coefficients in Eq. (2). For each sample, the coefficient a in Eq. (2) was found by the least-squares fitting. The samples show similar behavior. The temperature variations are very large: the conductivity increases approximately 20 times when the temperature of the tablets is increased from -20°C to 250°C . Equivalently, the resistance of a tablet decreases 20 times when the temperature of the tablet is changed. Such a characteristic is typical for a thermistor with a negative temperature coefficient of the resistance (NTCR). Hence, the HIP-sintered magnesium titanate ceramic materials can be used for the production of thermistors for a wide range of temperatures. In addition, the highly nonlinear behavior of the HIP-sintered material makes it convenient for the production of varistors.

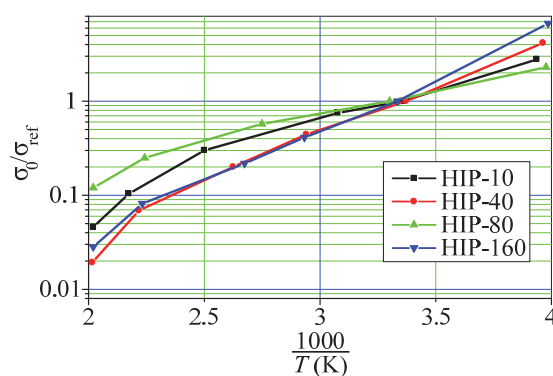


Fig. 5. The normalized DC conductivity of the samples as a function of the reciprocal of the absolute temperature.

Tab. II Parameter in Eq. (2) for the four sintered samples.

	HIP-10	HIP-40	HIP-80	HIP-160
a (K)	1754	2357	1337	2929

4. Conclusions

We have investigated electrical properties of magnesium titanate ceramics post-sintered by the hot isostatic pressing (HIP) in an oxygen-free atmosphere. The sintered material becomes a semiconductor, exhibiting strong nonlinearities and temperature variations of the electric parameters.

We have considered the small-signal relative complex permittivity of the material, along with quantities derived from it (the loss tangent and the equivalent conductivity), in an extremely wide range of frequencies: from DC up to 10 GHz. We have used various measurement techniques and compared the results. We have also designed interpolation formulas for the frequency dependence of the relative complex permittivity. Various results are difficult to be compared due to the nonlinearities and the temperature effects. Nevertheless, we obtained a satisfactory agreement among the results.

The distinct properties of the material make it suitable for applications in electrical engineering: for production of NTCR thermistors, as well as for varistors.

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Садржај: Накнадна обрада магнезијум титаната (после синтеровања) изостатичким пресовањем на високој температури, у атмосфери без кисеоника, значајно утиче на особине материјала. Синтеровани материјал постаје полупроводан. У раду настављамо истраживање електричних особина тог материјала проширивањем фреквенцијског опсега мерења, приказујемо формуле за интерполацију зависности комплексне релативне пермитивности од учестаности и предлажемо примену магнезијум титаната као материјала за термисторе са негативним температурским сачиниоцем отпорности, као и за варисторе.

Кључне речи: Магнезијум титанат; Изостатичко пресовање при високој температури; Комплексна пермитивност; Термистори; Варистори.

