Dielectric investigations of La-doped barium titanate

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Abstract

In the present paper results of the dielectric investigation of barium titanate (BaTiO$_3$) doped with different concentrations of lanthanum are presented. Ceramic samples were prepared by the Pechini process. With increased doping the grain size of ceramics decreases from 2.5 μm in pure samples down to 0.2 μm in 0.5 mol% La - doped BaTiO$_3$. Ceramics showed maximally enhanced dielectric permittivity around low-, room and high-temperature phase transitions, which are the phase transitions of the pure BaTiO$_3$. The Curie temperature, T_C, is lowered by 30 K with increase of doping concentration to 0.5 mol% La. Dielectric spectra revealed three parts: low frequency part which is caused by conductivity process, middle frequency relaxational process part and high frequency relaxational/polar modes contribution.

Keywords: barium titanate, lanthanum, dielectric spectroscopy, dielectric dispersion

I. Introduction

Barium titanate (BaTiO$_3$) is versatile composition that exhibits high permittivity (ε') making it desirable material for multilayer capacitors, ferroelectric thin-film memories, piezoelectric transducers, etc. [1–3]. On heating, it undergoes a ferroelectric/paraelectric phase transition to the cubic polymorph at Curie temperature T_c of ~130°C, at which ε' passes through a maximum ε'_{max} and typically reaches values of ~10000 in undoped ceramic samples. The phase transition is of the first order, and the peak in ε' is correspondingly sharp [4].

BaTiO$_3$, (BT) which is a typical ABO$_3$ perovskite, has five kinds of crystal systems: hexagonal, cubic, tetragonal, orthorhombic and rhombohedral, which changes with the temperature. Interesting changes can be observed with partial substitution of A site ion with suitable impurities. Multiple ion occupation of A and/or B sites in ABO$_3$ compounds is expected to bring in changes in the Curie temperature and other physical properties. This kind of substitution can affect the lattice parameters, tetragonal distortion (c/a), polarization, ferroelectric transition and electro mechanical con-version characteristics of the samples. The aim of the present investigation is to apply the variable- frequency techniques of impedance/admittance spectroscopy to lanthanum doped BaTiO$_3$ to probe some of the above aspects. For example, isovalent dopants are commonly used to alter T_c and the lower temperature orthorhombic/tetragonal and rhombohedral/orthorhombic phase transition temperatures. In this way, the temperature of ε'_{max} may be modified and in some cases lead to diffuse phase transition-type behaviour.

So we prepared La-doped BaTiO$_3$ samples with different concentration of lanthanum. In the present study, the real (ε') and imaginary (ε'') parts of dielectric permittivity were investigated in the frequency ranges of 20 Hz to 1.0 MHz and of 2 MHz to 200 MHz, and temperature range of 120 K to 460 K.

II. Experimental

Barium titanate doped with lanthanum was prepared by the Pechini procedure. First, titanium citrate and barium citrate solutions were prepared using titanium isopropoxide and barium acetate, respectively. Solutions of titanium citrate and barium citrate were mixed, with constant stirring. For doping barium titanate, lanthanum nitrate hexahydrate solution was added for 0.3 and 0.5 mol% La (BTL3 and BTL5). Temperature was raised up

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to 120–140°C, when the solution becomes solidified into a dark -brown glassy resin. Decomposition of the organic part was performed in an oven with special caution, because temperature can rise very quickly. The temperature was maintained at 200°C for 4 h. When the resin was incinerated (reduced to ashes), and became black solid mass, material was pulverized. Material was thermally treated in couple of steps: at 500°C for 4 h, 700°C for 4 h and 800°C for 4 h. The heating rate was 2 C°/min. After cooling to room temperature the barium titanate powders were obtained. The powders were isostatically pressed into pellets of 8 mm in diameter and average thickness of about 2.5 mm using pressure of 98.1 MPa. Sintering was performed at 1300°C for 8 h (in the tube furnace "Lenton", UK) and the heating rate was 10 °C/min with nature cooling in air,which means that sample was cooled down in air, without particular cooling rate.

The grain size of ceramics, which was measured using SEM micrographs of BTL5 shown in Fig. 1, is reported in Table 1 [5].

Table 1. Grain size of barium titanate ceramics

Ceramics	Grain size [μm]
Pure BT	1.0–2.5
BT with 0.3 mol% La	0.75–1.0
BT with 0.5 mol% La	0.2–0.4

Samples where cut for the dielectric spectroscopy in the shape of 2 mm cubes. Silver paste was used for electrical contacts. Dielectric permittivity was measured in the frequency range of 20 Hz to 1 MHz with a HP4284A
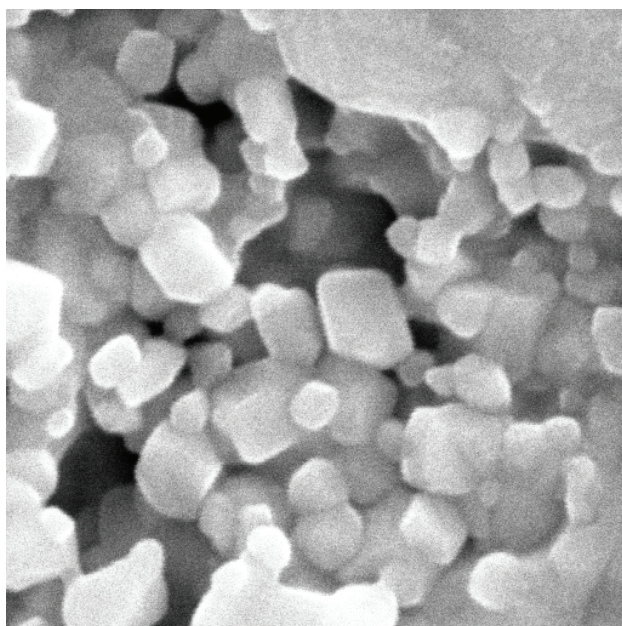

Figure 1. SEM photographs of barium titanate with 0.5 mol% (BTL5) lanthanum

bridge and from 2 MHz to 200 MHz with a vector network analyzer Agilent 8714ET in a temperature range between 120 K and 450 K.

At the beginning, samples were heated up to 450 K to eliminate water observed at the surfaces. Then they were cooled-down about at 1 K/min speed and whole spectrum was measured at constant temperature. Nitrogen was used to lower the temperature down to 120 K.

III. Results and discussion

The temperature dependencies of the real part of dielectric permittivity and loss tangents of pure and doped samples are presented in Figs. 2 and 3, respectively.

Fig. 2 shows that real part of the dielectric permittivity drastically increases with the increase of lanthanum doping. Pure barium titanate (BT) has three dielectric anomalies at typical phase transitions temperatures (200 K, 287 K and 393 K. The increase of the La content leads to an apparent decrease of all the transition temperatures observed, accompanied by a
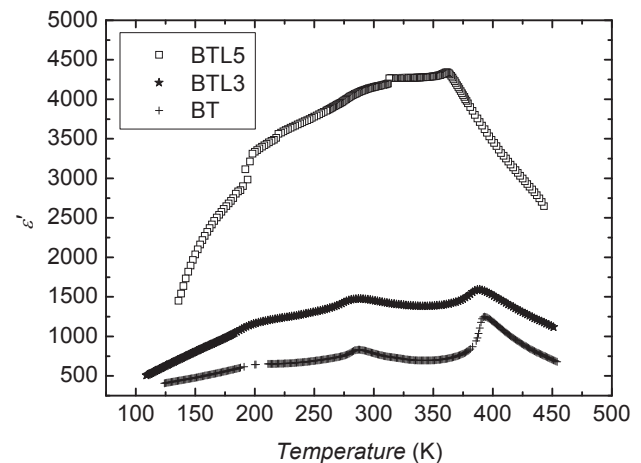

Figure 2. Temperature dependence of the real part of dielectric permittivity of pure barium titanate (BT), barium titanate with 0.3 mol% (BTL3) and 0.5 mol% (BTL5) lanthanum at 1 MHz
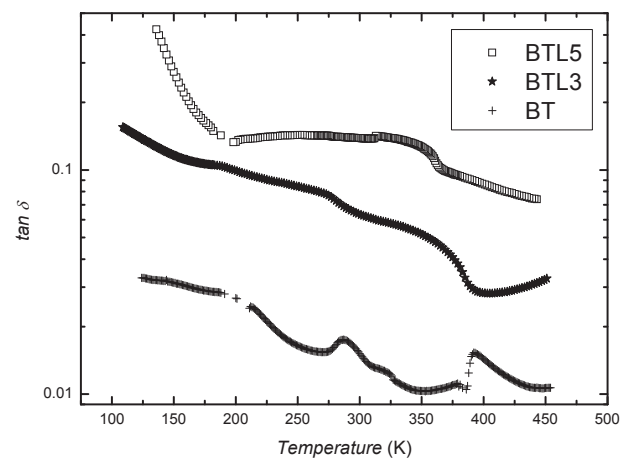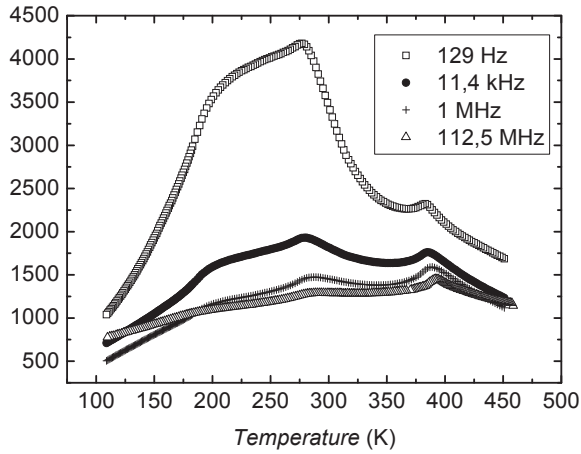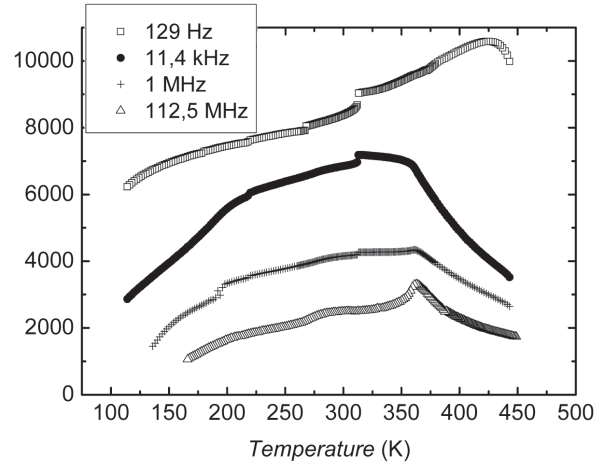

Figure 3. Temperature dependence of the loss tangent of pure barium titanate (BT), barium titanate with 0.3 mol% (BTL3) and 0.5 mol% (BTL5) lanthanum at 1 MHz

broadening of the corresponding peaks. The change of the Curie temperatures is: T_c = 393 K for BT, 388 K for barium titanate with 0.3 mol% lanthanum (BTL3) and 364 K for barium titanate with 0.5 mol% lanthanum (BTL5).

These temperature shifts may be related with the observed grain size changes with La-doping concentration having an influence on grain size (Table 1) [6–12]. The dielectric loss factor tgδ also was increased with doping.
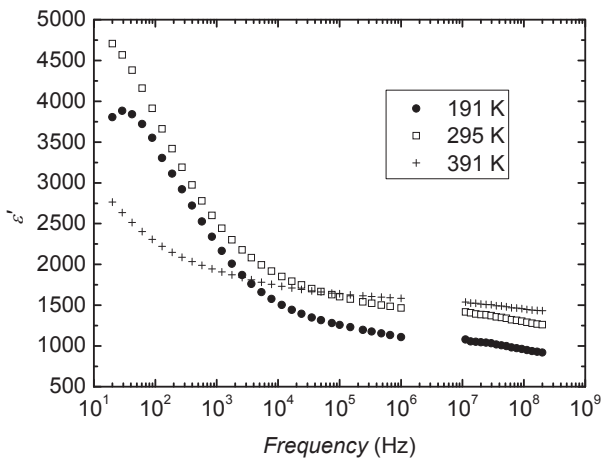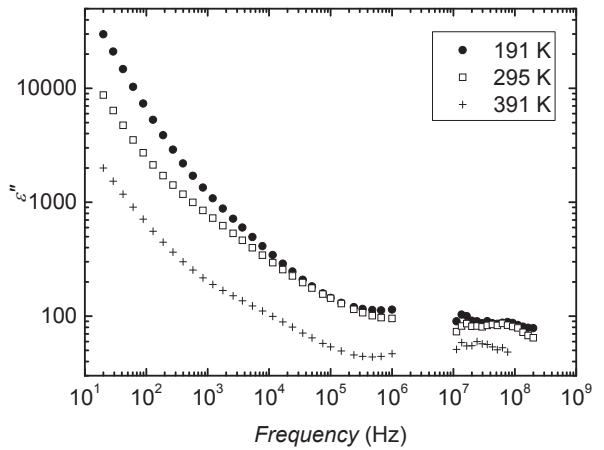

Figure 4. Temperature dependence of the real part of dielectric permittivity of barium titanate with 0.3 mol% (a) and 0.5 mol% (b) lanthanum at different frequencies
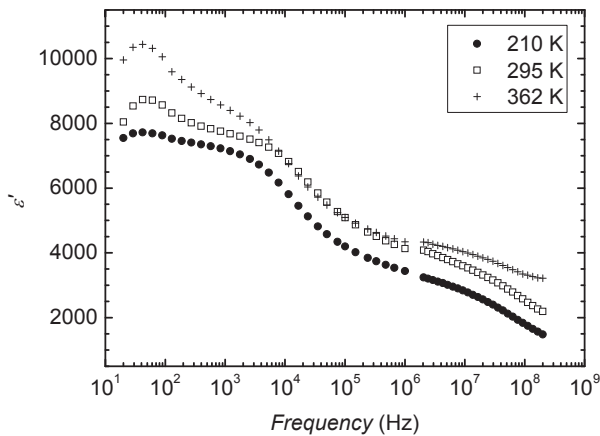

Figure 5. Frequency dependence of the real (a) and imaginary (b) parts of dielectric permittivity of barium titanate with 0.3 mol% lanthanum at different temperatures

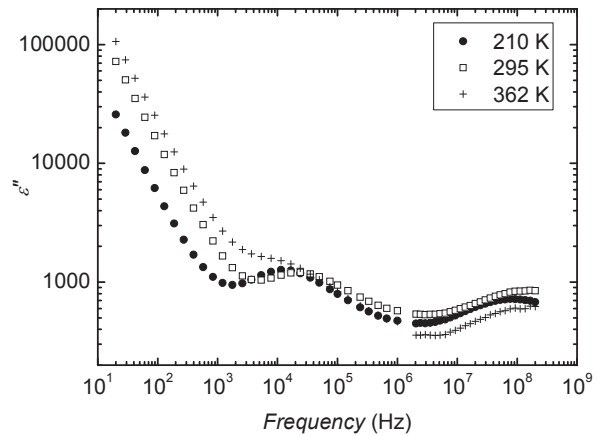**Figure 6. Frequency dependence of the real (a) and imaginary (b) parts of dielectric permittivity of barium titanate with 0.5 mol% lanthanum at different temperatures**

If we look at the temperature dependence of 0.3 mol%-La doped BT at frequencies below 1MHz, the dynamic conductivity affects dielectric spectra around low- and room temperature phase transitions (Fig. 4a). In the temperature dependences of BLT5 ceramics at low frequencies we can clearly see just one anomaly, which becomes apparent by the appearance of a maximum of the real part of dielectric permittivity at temperatures above 400 K and an increase at higher temperatures due to the conduction effects (Fig. 4b).

All other phase transitions cannot be observed in the dielectric curve. With the increase of the frequency, the high temperature tail goes down - this is the manifestation of quite large conductivity at higher temperatures, which becomes suppressed in the measurements at larger frequencies, and at frequencies above 1 MHz this conductivity does not play any significant role in the values of the dielectric permittivity at higher temperatures. In the high frequency range we obtained he real dielectric permittivity caused by the polar modes and dipolar relaxation.

In the middle range of temperatures, we have the same contribution of conductivity - with increase of the frequency the value of dielectric permittivity decreases from more than 8000 to less than 3000. Such huge changes also can be explained only by grain conductivity, which can be attributed to La doping. So, we can state, that in $BaTiO_3$ doped with La we have a significant conductivity and only at higher frequencies it is possible to see the real dielectric permittivity, which is caused by the crystal soft modes (Fig. 4b, 112.5 MHz). This is the general feature of all semiconducting feroelecrics.

It is also possible to see from the Fig. 4b that only at higher frequencies, where the conductivity is suppressed, we have the exact indication of the phase transitions at 213 K, 284 K and 376 K. But even at microwaves, we still have quite big dielectric losses (Fig. 4) (the imaginary part of dielectric permittivity is still the same order of magnitude as the real part).

This is confirmed by the frequency dependence of the real and imaginary parts of dielectric permittivity (Figs. 5 and 6). At lower frequencies in both real and imaginary parts of dielectric permittivity we see tails caused by sample conductivity: with the decrease of the frequency both parts of dielectric permittivity increase.

A much more interesting behaviour appears if we look at frequencies above 10^3 Hz. In the frequency range up to 10^6 Hz in BTL5 we see a dispersion region, and at higher frequencies we have another dispersion region. In BTL3, the low frequency conductivity related dielectric permittivity tail ends at 10^4 Hz, while the imaginary part of the dielectric permittivity flattens at 10^5 Hz. If we attribute the conductivity tail to the bulk conductivity a different source for conductivity must be sought to explain the dielectric dispersion regions in the samples investigated. It can be argued that part of the dielectric dispersion in BTL5 is caused by intergranular ceramics conductivity.

BTL5 ceramic grains are smaller and one can expect that intergranular contributions to dielectric spectrum reveal themselves at higher frequencies than the bulk contributions (increase of the surface to volume ratio of the grains). As we have said before, BTL5 has two dielectric dispersion regions at higher frequencies, where the contribution of the bulk conductivity of the sample is in principle not significant. This may be caused by intergranular ceramics conductivity, together with higher frequency dispersion already caused by soft modes, whose frequency decreases due to the influence of lanthanum doping.

The larger grain size of this ceramic makes the contribution of intergranular conductivity (or conductivity through grain boundaries) not significant.

IV. Conclusions

Ceramics of barium titanate with different concentration of lanthanum were prepared. Lanthanum concentration influences the dielectric behavior. On increasing lanthanum concentration, dielectric spectra become more complicated. Dielectric spectra of barium titanate with 0.5 mol% lanthanum consist of three parts: low frequency part which is caused by conductivity process, middle frequency part presumably related to intergrain relaxation and high frequency part, which is caused by the higher frequency crystalline relaxation and polar modes contribution. La substitute Ba ions in the lattice and due to that changes the inner fields and dynamics of the phase transitions and conductivity of the samples.

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