

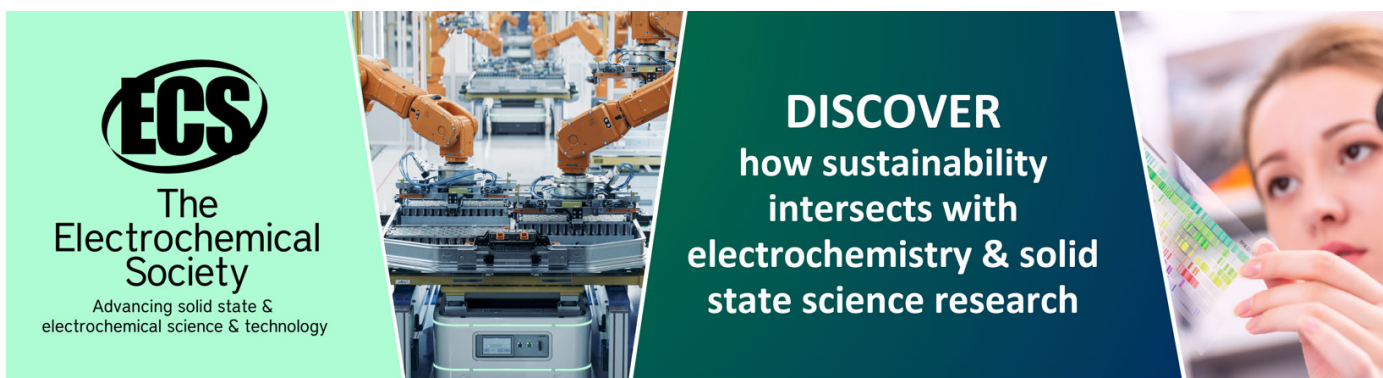
THz and IR dielectric response of BaTiO₃ core-shell composites: evidence for interdiffusion

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THz and IR dielectric response of BaTiO₃ core–shell composites: evidence for interdiffusion

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Abstract

Time-domain THz transmission and FTIR reflectivity spectra of dense core–shell composites of the BaZr_{0.2}Ti_{0.8}O₃, BaZr_{0.4}Ti_{0.6}O₃, Ba_{0.66}Sr_{0.34}TiO₃ and Ba_{0.45}Sr_{0.55}TiO₃ compositions were studied in a broad temperature range of 10–900 K. The spectra were evaluated to obtain the complex dielectric functions and at room temperature they were compared with the prediction of the generalized brick-wall model based on the effective medium approximation. The model was analysed concerning the dielectric losses and electric-field tunability below the polar phonon frequency range. Whereas the predicted losses are much reduced compared with those of the cores, the observed enhanced losses in the THz range give evidence of an interdiffusion of the BaTiO₃ cores into the shells.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, increased attention has been paid to the processing of novel core–shell type composites containing high-permittivity cores, particularly BaTiO₃ [1, 2]. The idea is to prepare functional materials with improved dielectric properties, mainly reduced dielectric losses and/or increased tunability of the permittivity for multilayer capacitors and various microwave applications. The possibilities for improving these properties in composites compared with homogeneous materials were discussed by Tagantsev *et al* [3]. However, in their paper only limited types of composite geometries were considered and the core–shell composite geometry was not discussed at all. To the authors' knowledge, no other theoretical discussion of the dielectric losses and tunability of permittivity in composite materials have appeared in the literature so far.

In this paper we would first like to discuss the appropriate models based on effective medium approximation (EMA) for the core–shell composites and predict the theoretically ideal behaviour of dielectric losses and expected tunability in such composites, based on the EMA models. As it is well known [4–6], the EMA is also valid for ac response

as long as the probing external electric field is uniform within the individual dielectrically uniform components and the boundaries among them are ideally sharp. The former condition for the ac response of dielectric composites limits their applicable frequency range from low frequencies up to the infrared (IR) as long as the radiation wavelength stays much longer than the size of the individual components (grains). Here we shall report on our time-domain terahertz (THz) and Fourier-transform (FT) IR measurements on BaTiO₃–SrTiO₃ (BTO@STO) and BaTiO₃–BaZrO₃ (BTO@BZO) core–shell composites and compare the results with their recently published low-frequency dielectric behaviour [1]. The reason for such a study is to obtain the effective polar phonon response in the IR–THz range of such composites and compare it with the prediction of appropriate EMA models. It is known that in all the pure components (in the case of BTO at least in the paraelectric phase) the whole static dielectric response is determined by their polar phonon contribution and no substantial dielectric dispersion exists below the THz range [7, 8]. However, we shall show that in our core–shell composites a complex dielectric dispersion in the THz and lower frequency range appears in all the samples which is not present in pure components and is not expected from the

EMA models. It brings evidence for an interdiffusion of BTO into the shells, which forms a structure with gradient BTO concentration.

2. EMA Models for the core-shell composites

When applying the long wavelength electric field, it is legitimate to regard composites as effectively homogeneous systems so that their dielectric response could be well described in the quasistatic limit using the EMA approach. The core-shell composites are considered as being constructed from the closely packed grains with the cores possessing the bulk complex permittivity ε_a and the shells with a lower permittivity ε_b . Even if the volume fraction x of the shell component is small ($x < 0.1$), it is well percolated through the sample, while the core material with high concentration $(1 - x) > 0.9$ is not percolated at all. Depending on the particular shape of the grains, the effective complex permittivity can be reasonably described by the brick-wall (brick-layer) model (e.g. with cubic shape of the bricks) [9] or by the Hashin-Shtrikman formula (coated spheres) [10]. Using the Bergman representation [4], the generalized brick model was proposed [5], which includes the above-mentioned special cases, and allows more general shapes of the grains to be considered [5, 6]. The effective complex permittivity is expressed as

$$\varepsilon = \varepsilon_b V_b + (1 - V_b) \frac{\varepsilon_a \varepsilon_b}{(1 - n)\varepsilon_b + n\varepsilon_a} \approx (1 - V_b) \frac{\varepsilon_a \varepsilon_b}{(1 - n)\varepsilon_b + n\varepsilon_a}, \quad (1)$$

where V_b is the volume fraction of the shell component with the zero internal electric field: $0 \leq V_b = ((x - n)/1 - n) < x$ and the depolarizing factor $n = gx$, $0 \leq g \leq 1$, where the geometrical factor g characterizes parallel ellipsoids. Assuming $x < 0.1$, $|\varepsilon_b| < 10$ and $|\varepsilon_b| \ll |\varepsilon_a|$, the first term in (1) $|\varepsilon_b V_b| < 1$ can be neglected in comparison with the much higher second term (~ 100). Further, let us also assume that the square of the loss tangent is $\tan^2 \delta_a \ll 1$, $\tan^2 \delta_b \ll 1$, (e.g. smaller than ~ 0.01). Then the real part of the effective permittivity is

$$\begin{aligned} \varepsilon' &= (1 - V_b) [\varepsilon'_a \varepsilon_b'^2 (1 + \tan^2 \delta_b) (1 - n) + \varepsilon'_b \varepsilon_a'^2 (1 + \tan^2 \delta_a) n] \\ &\quad \times [\varepsilon_b'^2 (1 + \tan^2 \delta_b) (1 - n)^2 + 2\varepsilon'_b \varepsilon'_a (1 + \tan \delta_a \tan \delta_b) (1 - n)n + \varepsilon_a'^2 (1 + \tan^2 \delta_a) n^2]^{-1} \\ &\approx (1 - V_b) \frac{\varepsilon'_a \varepsilon'_b}{\varepsilon_b' (1 - n) + \varepsilon'_a n} \\ &= \varepsilon'_a \frac{1 - x}{1 - n} \frac{1}{1 - n + (\varepsilon'_a / \varepsilon'_b) n}. \end{aligned} \quad (2)$$

The effective loss tangent is

$$\begin{aligned} \tan \delta &= \frac{\varepsilon'_b \tan \delta_a (1 + \tan^2 \delta_b) (1 - n) + \varepsilon'_a \tan \delta_b (1 + \tan^2 \delta_a) n}{\varepsilon_b' (1 + \tan^2 \delta_b) (1 - n) + \varepsilon'_a (1 + \tan^2 \delta_a) n} \\ &\approx \frac{\varepsilon'_b \tan \delta_a (1 - n) + \varepsilon'_a \tan \delta_b n}{\varepsilon_b' (1 - n) + \varepsilon'_a n}. \end{aligned} \quad (3)$$

The quality of the composite can be reflected by the ratio of the effective loss tangent and the real part of the permittivity:

$$\frac{\tan \delta}{\varepsilon'} = \left(\frac{\tan \delta_a}{\varepsilon'_a} (1 - n) + \frac{\tan \delta_b}{\varepsilon'_b} n \right) \frac{1 - n}{1 - x}. \quad (4)$$

Further, assuming that $\tan \delta_b \approx 0$,

$$\begin{aligned} \tan \delta &= \tan \delta_a \frac{(1 - n)}{(1 - n) + n\varepsilon'_a / \varepsilon'_b}, \\ \frac{\tan \delta}{\varepsilon'} &= \frac{\tan \delta_a}{\varepsilon'_a} \frac{(1 - n)^2}{(1 - x)}. \end{aligned} \quad (5)$$

For example, for the spherical or cubic grains $g = 1/3$, and for $x = 0.1$ it is $\tan \delta / \varepsilon' = 1.07 (\tan \delta_a / \varepsilon'_a)$. Assuming small x , it is approximately

$$\frac{\tan \delta}{\varepsilon'} \approx \frac{\tan \delta_a}{\varepsilon'_a}, \quad (6)$$

i.e. the effective loss factor in the core-shell composite decreases roughly proportionally to its effective permittivity. So, both the permittivity and the loss tangent become strongly reduced, but their ratio remains approximately constant.

In order to discuss the tunability of the permittivity [3], we assume that the external electric field affects the permittivity of the core material (dielectrically non-linear material), but not the shells (linear dielectric). Considering low frequencies, the real part of susceptibility is nearly frequency independent (static). Starting from the simple Landau free energy

$$f = \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 - EP \quad (7)$$

the dependence of the polarization on the electric field is given by the equation

$$\alpha P + \beta P^3 = E \quad (8)$$

and the field dependent susceptibility is

$$\chi'_a(E) = \frac{1}{\varepsilon_0} \frac{1}{\alpha + 3\beta P^2} = \frac{\chi'_a(0)}{1 + 3\beta \chi'_a(0) \varepsilon_0 P(E)^2} = \frac{\chi'_a(0)}{t}, \quad (9)$$

where t is the tunability [3]:

$$t = 1 + 3\beta \chi'_a(0) \varepsilon_0 P(E)^2 \approx 1 + 3\beta (\chi'_a(0) \varepsilon_0)^3 E^2. \quad (10)$$

Due to the high values of permittivity $\varepsilon'_a = 1 + \chi'_a \approx \chi'_a$ the susceptibility in expressions (9) and (10) can be replaced by ε'_a . The effective permittivity (for small x) is

$$\varepsilon'(E) = \varepsilon'(0) \frac{1}{t} \frac{\left(1 - n + \frac{\varepsilon'_a(0)}{\varepsilon'_b} n\right)}{\left(1 - n + \frac{\varepsilon'_a(0)}{t \varepsilon'_b} n\right)} \approx \varepsilon'(0) \frac{1}{t} \frac{\left(1 + \frac{\varepsilon'_a(0)}{\varepsilon'_b} n\right)}{\left(1 + \frac{\varepsilon'_a(0)}{t \varepsilon'_b} n\right)}, \quad (11)$$

where the tunability of the effective permittivity

$$t_e = t \left(1 + \frac{\varepsilon'_a(0)}{t \varepsilon'_b} n\right) \left(1 + \frac{\varepsilon'_a(0)}{\varepsilon'_b} n\right)^{-1} < t.$$

So, one can see that the effective tunability of a core-shell composite could be reduced compared with that of the core.

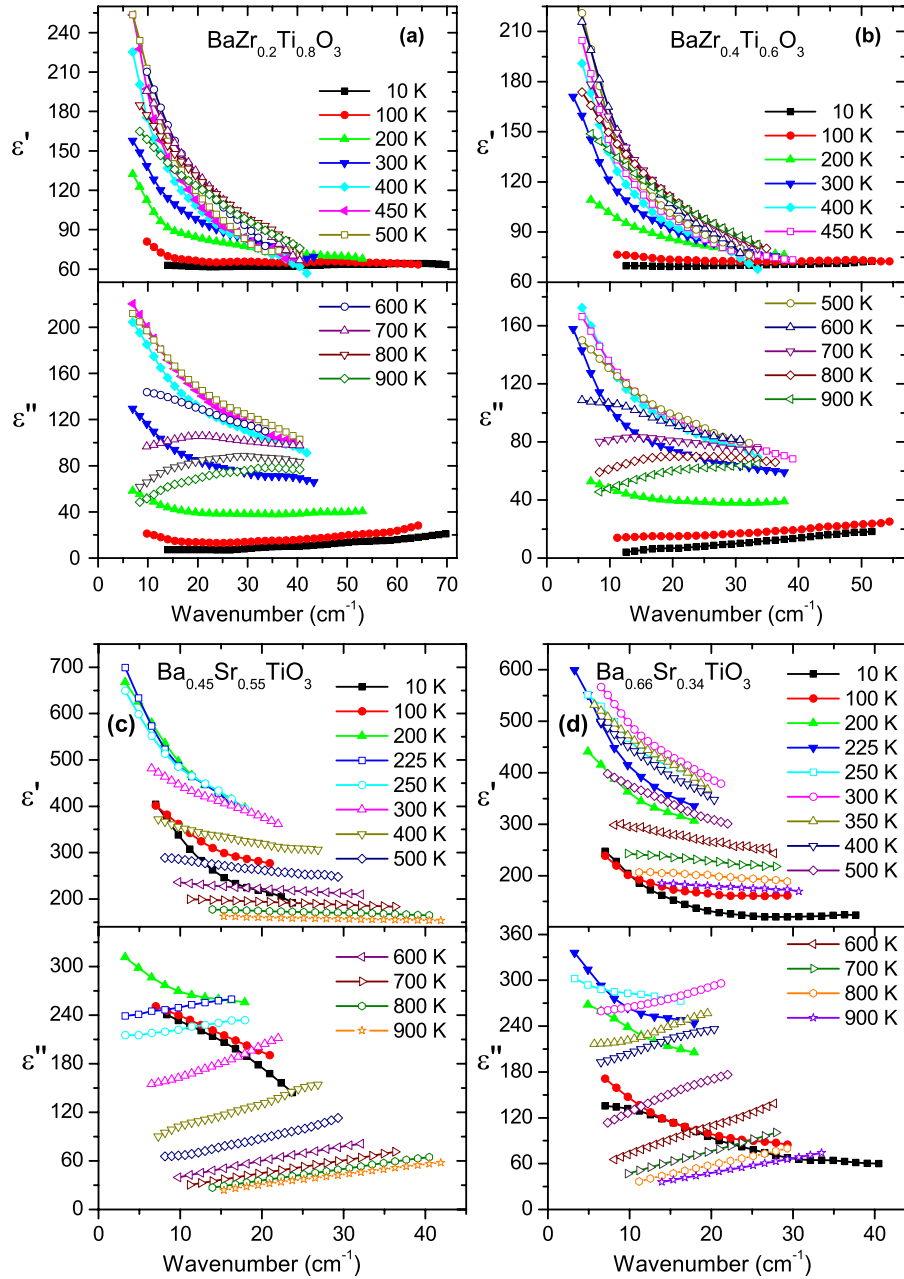


Figure 1. Temperature dependent complex dielectric response of the BTO@BZO and BTO@STO composites obtained from the THz transmission measurements.

Considering the microwave range, where mostly ε_a'' linearly increases with frequency, the dependence of the loss tangent on the tunability can also be calculated:

$$\tan \delta_a(E) = \frac{\varepsilon_a''(E)}{\varepsilon_a'(E)} \approx \frac{\varepsilon_a''(0)}{\varepsilon_a'(0)} t = t \tan \delta_a(0), \quad (12)$$

$$\tan \delta(E) \approx t \frac{\left(1 + n \frac{\varepsilon_a'(0)}{\varepsilon_b'}\right)}{\left(1 + n \frac{\varepsilon_a'(0)}{t \varepsilon_b'}\right)} \tan \delta(0), \quad (13)$$

$$\frac{\tan \delta(E)}{\varepsilon'(E)} = \frac{\tan \delta(0)}{\varepsilon'(0)} t^2. \quad (14)$$

Comparing (12) with (13), it can be concluded that the field tunability of the loss tangent is stronger in the core-shell composite than that of the core material.

3. Experimental

Dense BTO@STO (97–98% theoretical density) and BTO@BZO (95% theoretical density) core-shell ceramics were prepared using spark plasma and conventional sintering, respectively. The following compositions were processed [1]: $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$, $\text{BaZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$, $\text{Ba}_{0.66}\text{Sr}_{0.34}\text{TiO}_3$ and $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$. The STO (BZO) shell was grown on BTO spherical particles by means of a precipitation process making use of inorganic precursors. For the details of synthesis

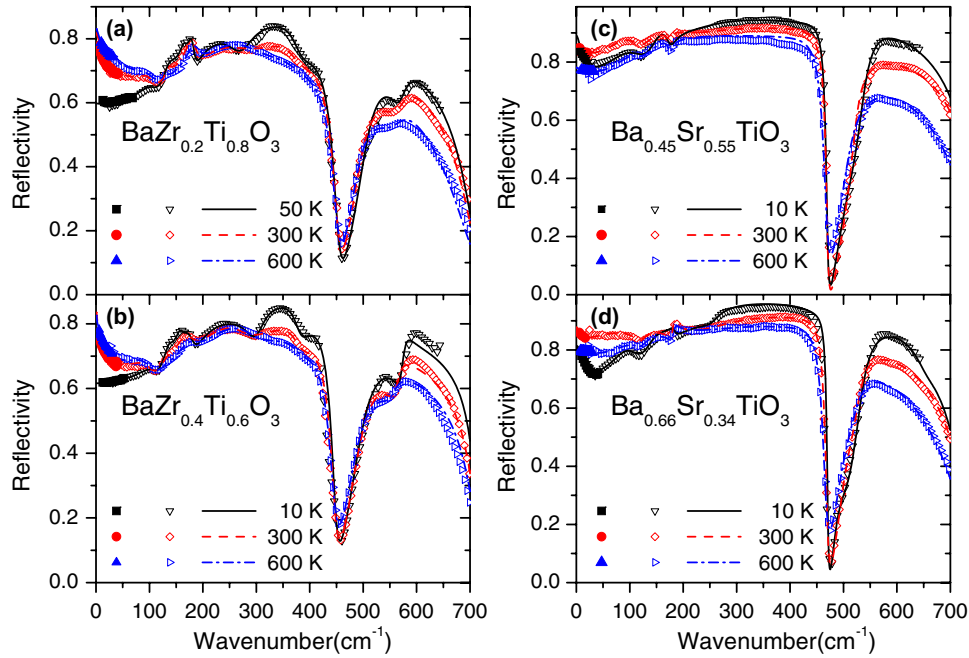


Figure 2. IR reflectivity spectra of the BTO@BZO and BTO@STO composites at selected temperatures together with the fitted spectra and THz reflectivity calculated from the THz transmission measurements.

of the BTO core-shell particles and sintering process see [1]. Ceramic discs with thicknesses of ~ 1 mm and diameters of ~ 8 mm were polished and used for IR reflection measurements. Afterwards, the same samples were polished down to ~ 59 μm and used for time-domain THz transmission studies.

The IR reflectivity measurements under near-normal incidence were performed using an FTIR Bruker IFS 113v spectrometer equipped with pyroelectric deuterated triglycine sulfate detectors and a He-cooled (1.5 K) Si bolometer which were used for high temperatures (300–600 K) and low temperatures (10–300 K), respectively. For high-temperature IR reflection measurements the samples were placed in a commercial high-temperature cell (Specac P/N 5850) and spectra were recorded in the range 30–3000 cm^{-1} . An Optistat CF cryostat (Oxford Instruments) with polyethylene windows was used for low-temperature measurements in the frequency range 30–650 cm^{-1} .

A custom-made time-domain THz spectrometer, based on a femtosecond Ti:sapphire laser and using an interdigitated photoconducting switch for generation of THz pulses and an electro-optic sampling scheme with [1 1 0] ZnTe crystal as the THz detector, was used to measure the complex transmission and calculate directly the complex dielectric response of the samples in the range 5–70 cm^{-1} . An Optistat CF cryostat with mylar windows and a high-temperature cell (Specac P/N 5850) were used for low- and high-temperature measurements, respectively.

4. Results and evaluation

The dielectric spectra calculated (without any model fitting) from the time-domain THz transmission measurements as a function of temperature for all the four core-shell ceramics

are plotted in figures 1(a)–(d). Surprisingly, the spectra are quite complex, show rather high losses and their temperature dependence is non-monotonic. IR reflectivity spectra for selected temperatures, complemented by the reflectivity data calculated from the THz transmission data, are shown in figures 2(a)–(d). The reflectivity spectra were fitted with the standard factorized multi-oscillator formula for the complex permittivity and the Fresnel formula for the normal-incidence reflectivity [11] and the fitted spectra are also shown in figure 2. The complex dielectric spectra calculated from these fits together with those calculated from the THz data for selected temperatures are shown in a log frequency scale in figures 3(a)–(d). Almost all the spectra are dominated by a strong overdamped response at the low-frequency end, i.e. in the 10–100 GHz range, which is absent in pure components [7, 8]. Considering also the low-frequency permittivity data [1], which are still somewhat higher than our fitted low-frequency permittivity limit, it shows that the microwave dispersion due to this excitation is actually even somewhat broader than that following from our fits. Figures 4(a)–(d) show the temperature dependence of the permittivity at 10 and 15 cm^{-1} (300 and 450 GHz) compared with that at 1 kHz [1] for all the samples. One can see that the temperatures of the permittivity maxima at different frequencies do not coincide. This clearly means that some dielectric dispersion exists even below our measured frequency range and the low-frequency dielectric maxima can hardly indicate any ferroelectric transition temperature.

To analyse the dielectric spectra of our composites using the EMA models, we need to know the dielectric spectra of pure BTO, STO and BZO. For BTO and STO the dielectric function of ceramic samples was thoroughly discussed including their dependence on the grain size [7, 8, 12, 13]. The observed giant dielectric size effect was explained by the presence of

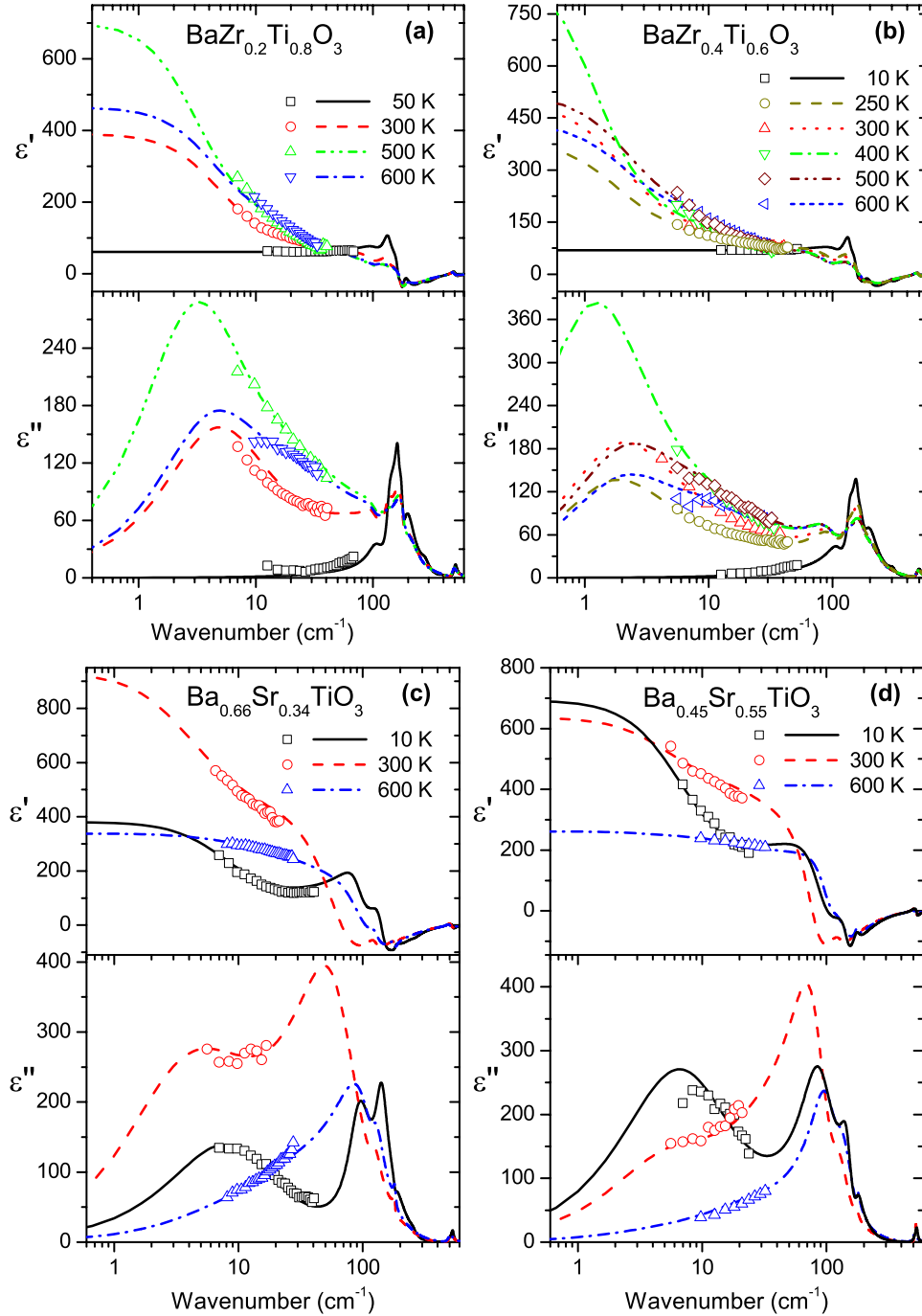


Figure 3. Complex dielectric spectra of the BTO@BZO and BTO@STO composites at selected temperatures as calculated from the IR-reflectivity fits. Note the log wavenumber scale to emphasize the dominating low-frequency response. The THz data are indicated by open symbols.

thin low-permittivity layers at the grain boundaries, which is, however, not so relevant for this discussion. Therefore for the BTO and STO parameters describing the dielectric spectra we took the data for single crystals (in the case of STO and paraelectric BTO) or coarse-grain ceramics (in the case of ferroelectric BTO, since in the ferroelectric phase we have to average out the dielectric anisotropy to simplify our discussion [7]). The dielectric function of BZO has not yet been published to our knowledge. Therefore we measured and fitted the room-temperature IR reflectivity of BZO ceramics

and plotted the corresponding complex dielectric spectrum in figures 5(a) and (b). The extrapolated low-frequency permittivity value from our fit is in perfect agreement with the measured value of 37.5 [14] so that also in this ceramics, no appreciable dielectric dispersion can be expected below the IR phonon frequency range. For comparison with the core-shell BTO@BZO samples, we also measured and fitted the room-temperature reflectivity of ceramic solid solutions of the same composition. The corresponding data are added in figure 5. The temperature dependences of the corresponding dielectric

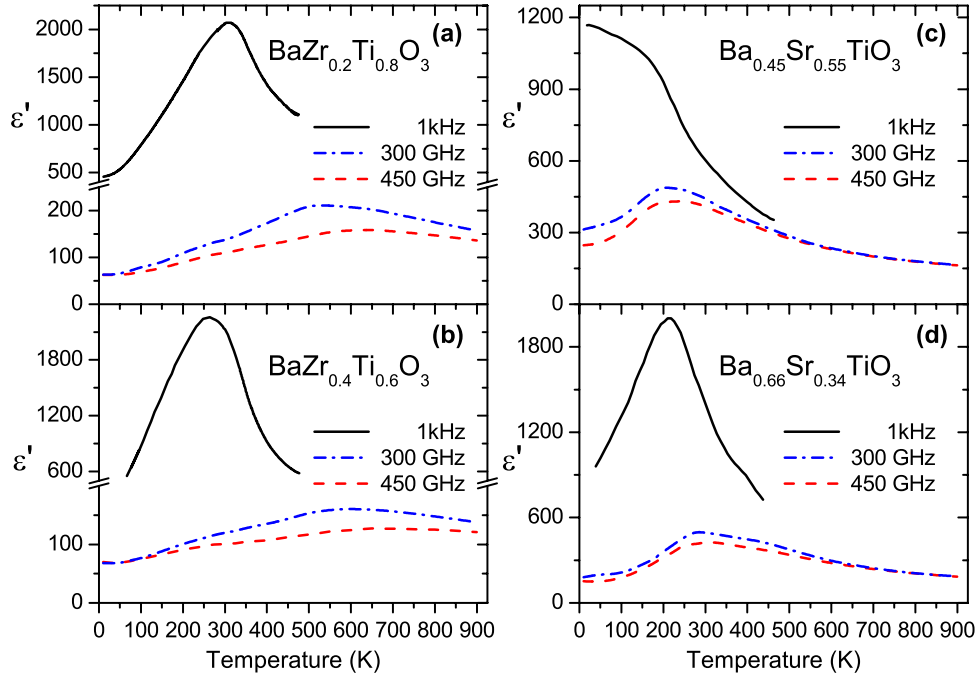


Figure 4. Temperature dependence of the THz permittivity compared with the low-frequency data at 1 kHz from [1].

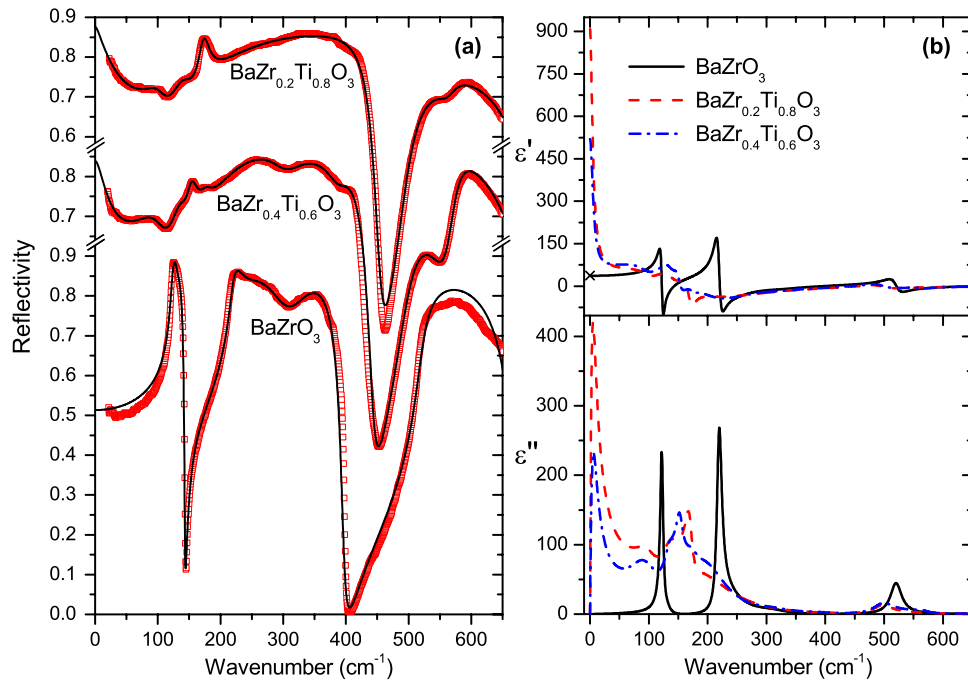


Figure 5. (a) Room-temperature IR reflectivity of pure BZO ceramics and Ba(Zr,Ti)O₃ solid solutions of the same nominal compositions as those of core-shell BTO@BZO composites, together with their fits and (b) calculated complex dielectric response.

spectra and their discussion will be published elsewhere. IR reflectivity and the corresponding dielectric spectra of the BTO–STO solid solutions in the whole composition range were published recently [15].

Using the discussed dielectric function data of the pure compounds (figures 6(a) and (c)), we can calculate the effective dielectric functions for all our composites. Figures 6(b) and (d) show the calculated room-temperature effective dielectric functions using the coated-spheres model compared with our directly fitted experimental data from figure 3.

5. Discussion

The common rather unexpected feature in all our core-shell samples is a rather strong THz absorption which is absent in the pure shell materials. It tends even into the lower frequency (microwave) range than in the pure BTO core spectra [7]. This indicates a broad relaxation which at high temperatures appears in the THz range and on cooling slows down. This recalls a similar behaviour in relaxor ferroelectrics [11]. Let us compare it with the results expected from the coated-spheres

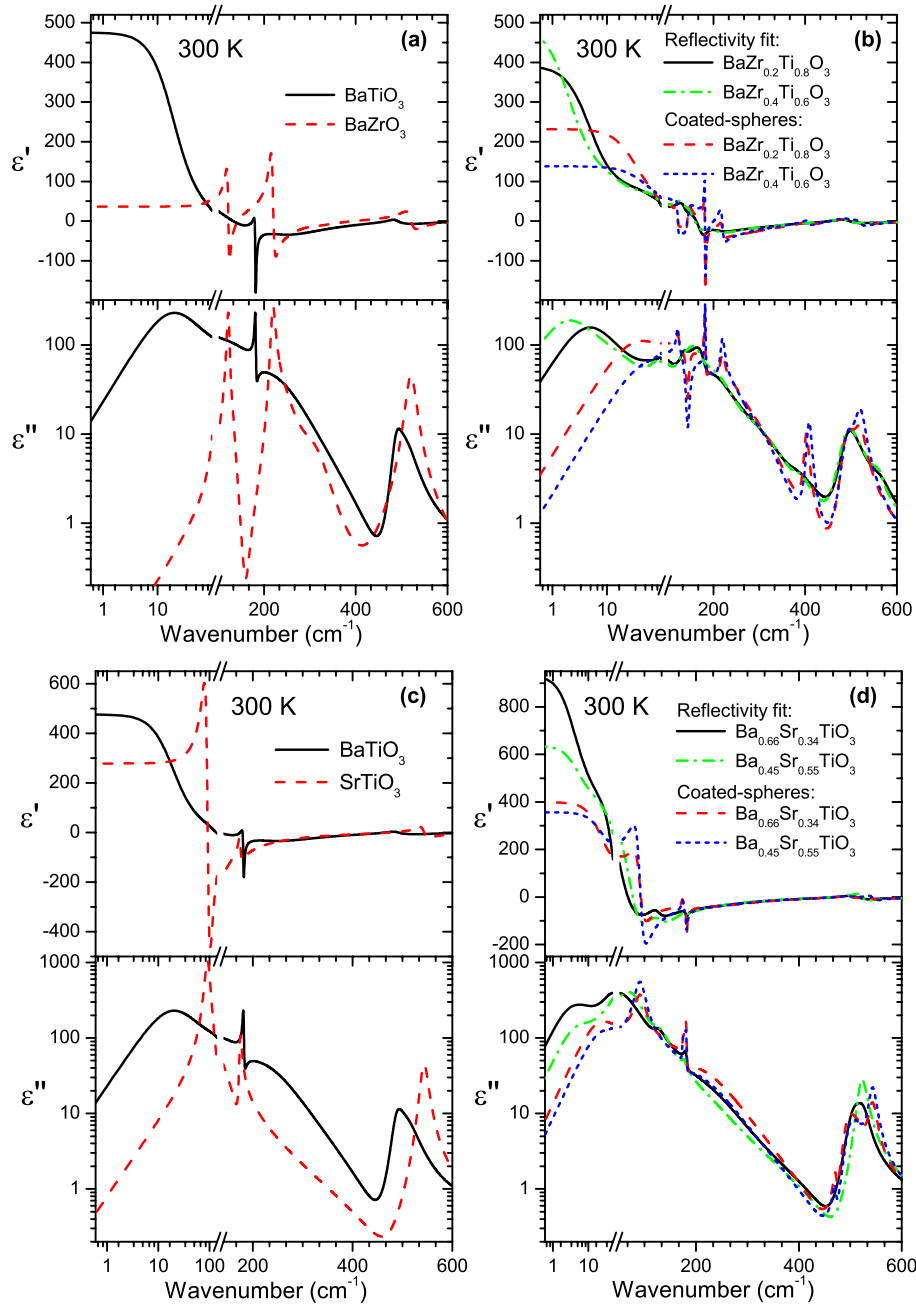


Figure 6. Room-temperature complex dielectric functions of (a) pure BTO and BZO ceramics, (c) pure BTO and STO ceramics, and similar effective spectra calculated from the coated-spheres model (equation (1) for $n = 1/3$) for (b) BTO@BZO composites and (d) BTO@STO composites, as compared with the fitted experimental results. Note the partial log wavenumber and log ϵ'' scale.

model (figure 6). According to this model, the effective low-frequency losses as well as the permittivity in the core-shell composites should be strongly reduced compared with the pure BTO core, see also equation (6). The EMA models assume that the boundaries among the individual components (cores and shells in our case) are ideally sharp. Our results show that this is not the case in our samples and one has to accept a partial interdiffusion from the BTO cores into shells, which was suggested also from the microstructure analysis by electron microscopy [1]. It appears that such nano-inhomogeneities can produce quite strong absorption features below the polar phonon response due to the interfacial

polarization effects caused by the gradient of the composition, but a more quantitative theory of such effects is presently not available. Some percolation among the BTO cores is also evident from the effective response in the phonon range, which shows somewhat lower and broader peaks compared with what is predicted from our model (figure 6).

Such effects could be taken into account (at least qualitatively) within the core-shell model by considering dispersion of the shell permittivity ϵ_b . Assuming an increase in ϵ_b at low frequencies, it follows from equation (2) that the effective permittivity increases, and, as can be shown, the effective losses increase as well (compared with the non-dispersive ϵ_b).

6. Conclusions

The effective complex dielectric function of our four examples of dense core-shell composites with the high-permittivity BTO cores was for the first time studied using the THz and IR spectroscopy in a broad temperature range and compared with the model calculations at room temperature based on the EMA coated-spheres model. The results show appreciably enhanced THz and microwave absorption compared with what was expected from the model calculations, which can be qualitatively understood by an interdiffusion of BTO cores into the shells. On the other hand, the EMA models with sharp boundaries among the cores and shells yield reduced dielectric losses in this low-frequency range compared with those of the BTO cores, and the suppression of the effective loss tangent approximately equals the suppression of the effective permittivity. The theoretical electric-field tunability is reduced compared with the core-material tunability.

For practical applications it could be of interest to compare the core-shell composites with ceramic solid solutions of the same composition. However, our models cannot conclude in this respect since the dielectric properties of solid solutions are not easily predictable from those of the pure end materials.

Acknowledgments

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