

# Plačiajuostė dielektrinė kobalto ferito ir švino cirkonio titanato kompozitų spektroskopija

## Broadband dielectric spectroscopy of cobalt ferrite and lead zirconium titanate composites

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Multiferroics belongs to class of materials in which the ferroelectric and ferromagnetic ordering occurs simultaneously in the same temperature range. Some of them can exhibit also a coupling between these orders, i.e. possess a magnetoelectric effect. It is not surprising that multiferroics are promising as multifunctional materials for various sensors, actuators, transducers, four state memory devices, etc [1] and are being intensively studied at the present. The most interesting multiferroic materials at the moment are so-called two-phase multiferroic composites due to the possibility to realize the “product property” referring to effects present in the composites but not in the individual phases. Lead zirconate titanate  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  is the well known ferroelectric perovskite with excellent electromechanical properties while cobalt ferrite  $\text{CoFe}_2\text{O}_4$  exhibit good ferromagnetic and magnetostrictive properties. These above mentioned properties allow combining them together to form composite exhibiting multiferroic behaviour. Due to the lack of high frequency dielectric investigations the applicability of such multiferroics in GHz and THz range is still limited and the present work is dedicated to the broadband dielectric spectroscopy results of  $\text{Pb}_{0.988}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}\text{O}_3$  (PZTN) and  $\text{CoFe}_2\text{O}_4$  (CF) composite ceramics.

CF-PZTN composite ceramics with CF ratio of 10%, 20 % and 30% were prepared were prepared in situ by citrate–nitrate combustion by using PZTN-based template powders as described in [2]. Various devices and broadband dielectric spectroscopy methods were used in experiments to cover the wide range of temperatures and frequencies, spanning from 100 K to 500 K and from 20 Hz up to 50 GHz. Transmission mode time domain THz spectroscopy was employed in measurements of complex dielectric response in the range of 5 – 50  $\text{cm}^{-1}$  with a resolution of 0.5  $\text{cm}^{-1}$  at 20 – 800 K. In order to investigate phonon properties of composites, IR reflectivity and Raman spectra were collected of optically polished samples. Bruker IFS 113v Fourier-transform IR spectrometer was used in the range of 30 – 3000  $\text{cm}^{-1}$  at the room temperature, and up to ~700  $\text{cm}^{-1}$  in cooling and heating regimes with the resolution of 2  $\text{cm}^{-1}$ . For Raman measurements, RENISHAW RM-1000 micro-Raman spectrometer was used in back-scattering geometry in the range of 20 – 1200  $\text{cm}^{-1}$  with the spectral resolution below 2  $\text{cm}^{-1}$ .

The obtained results show a broad dielectric anomaly around the temperature of 630 K, whereas steady increase of dielectric loss above this temperature is

observed as well. The peak of permittivity in the temperature dependencies can be associated with the paraelectric-ferroelectric phase transition in the morphotropic phase boundary (MPB) PZT material, in accordance to the phase diagram of lead zirconate-lead titanate system [3]. Comparing  $\epsilon'$  and  $\epsilon''$  temperature dependencies at a fixed frequency one can conclude that permittivity values decrease with an increase of cobalt ferrite concentration, as can be explained by a sum rule.

Dielectric spectra of (1-x)PZTN-xCF composites can be divided into three regions, where characteristic differences exist in each of them between soft and hard doped PZT.

At low frequencies dielectric spectra are governed by electrical conductivity phenomena while in the midrange, they show monotonic increase of dielectric permittivity upon decreasing the frequency. Generally, such dispersion is called *Universal Dielectric Response*, or *Logarithmic Dispersion* law and it is believed that it is the reason of the existence of disorder in the materials. The origin of the dielectric relaxation in GHz range is of piezoelectric nature and possibly is caused by grain or domain wall resonance.

In IR spectra characteristic phonons of ferroelectric morphotropic phase boundary PZT are dominated in all (1-x)PZTN-xCF composites. While it is known that phonon mode close to 80  $\text{cm}^{-1}$  is related to the ferroelectric behavior, the softening of central mode around 45  $\text{cm}^{-1}$  is observed in our case. Furthermore, this softening is disturbed by the increasing concentration of CF. It seems that cobalt ferrite effectively disturbs the softening of ferroelectric IR phonon modes.

### References

- [1] W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* 442 (2006).
- [2] A.R. Jordan, M. Airimioaei, M.N. Palamaru, C. Galassi, A.V. Sandu, C.E. Ciomaga, F. Prihor, L. Mitoseriu, A. Ianculescu, *J. Eur. Ceram. Soc.* 29, 2807 (2009).
- [3] B. Noheda, D.E. Cox, G. Shirane, R. Guo, B. Jones, and L.E. Cross, *Phys. Rev. B* 63, (2000).