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FABRICATION AND DIELECTRIC PROPERTIES OF 0-3 CONNECTIVITY CERAMIC-POLYMER COMPOSITES

WYTWARZANIE I WŁAŚCIWOŚCI DIELEKTRYCZNE KOMPOZYTÓW CERAMICZNO-POLIMEROWYCH O SPOSOBIE ŁĄCZENIA FAZ 0-3

In the present study BST//PVC composites with 0-3 connectivity were prepared from $(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$ (BST60/40) ceramic powder and polyvinyl chloride (PVC) polymer powder by hot pressing method for different concentration of the ceramics phase. The morphology of BST60/40//PVC composites powder was observed by transmission electron microscopy, crystalline structure was studied by X-ray diffraction method. Temperature dependence of dielectric permittivity of BST60/40//PVC composites was measured in the frequency range of $f=10\times 10^3-1\times 10^6\text{Hz}$. Influence of the ferroelectric ceramic phase on dielectric properties of ceramic-polymer composite has been studied for volume fraction of the active phase in the composite from $c_V=1.47\%$ up to $c_V=60\%$. It was found, that properties of the ceramic-polymer composite are not a simple sum of properties of the phases constituting the composite but they depend on both the way of connectivity and mutual influence of the phases on each other.

Keywords: composite, BST, PCV

Prezentowane kompozyty BST//PCV o sposobie łączenia faz 0-3 wytwarzane były z proszku ceramicznego $(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$ (BST60/40) oraz z proszku poli(chlorku winylu) (PCV) metodą prasowania na gorąco z różną zawartością fazy ceramicznej. Określono morfologię otrzymanych próbek kompozytowych przy użyciu transmisyjnego mikroskopu elektronowego oraz ich strukturę krystaliczną metodą dyfrakcji rentgenowskiej. Wyznaczono temperaturową zależność przenikalności elektrycznej kompozytów, w zakresie częstotliwości pola pomiarowego $f=10\times 10^3-1\times 10^6\text{Hz}$ oraz wpływ ferroelektrycznej fazy ceramicznej na właściwości dielektryczne tych kompozytów w zakresie objętościowej zawartości procentowej fazy aktywnej równej $c_V=1.47\%-60\%$. Stwierdzono, że właściwości kompozytu ceramiczno-polimerowego nie są prostą sumą właściwości poszczególnych faz składowych, ale stanowią efekt oddziaływania faz składowych i sposobu ich wzajemnego połączenia.

1. Introduction

Composite technology in general sets out to combine materials in such a way that the properties of the composite are the optimum for a particular application. The property, whether mechanical, thermal, electrical etc., is determined by the choice of component and their relative amounts and, most importantly, the 'connectivity', that is the manner in which the components are interconnected [1].

The concept of 'connectivity' is useful in classifying different types of mixture [2, 3]. The basis of this concept is that any phase in a mixture may be self-connected in zero, one, two or three dimensions. Thus randomly dispersed and separated particles have a connectivity of 0 while the medium surrounding them has a connectivity of 3. A disc containing a rod-shaped phase extending

between its major surfaces has a connectivity of 1 with respect to the rods and of 3 with respect to the intervening phase.

There are 10 different ways of connecting the phases in a two-phase composite, each described by two numbers $m-n$ (0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, 3-3). The first number m defines how the active phase (e.g. piezoelectric ceramic) is connected and the second number n -how the passive phase (e.g. polymer) is connected. In the present context, a 0-3 composite consists of discrete ceramic particles dispersed in a polymer, whereas a mixture consisting of a stack of plates of two different phases extending over the entire area of the body exhibits a connectivity of 2-2 [1].

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Composites made of ferroelectric ceramics and polymer are very attractive for applications since they combine properties, which are typical for polymers, like good flexibility and the capability of forming with high electroactivity (piezo- and pyroelectric) responses of electroceramics. As a result, one may be able to develop a new material exhibiting properties tailored to various requirements. As the dielectric permittivity is involved in figures of merit (FOM) of various physical quantities important for applications (e.g. hydrostatic piezoelectric strain coefficient, electromechanical coupling factor) the knowledge of the dielectric response of the composites is essential [4, 5].

In the present study attention is confined to one of the most commonly encountered connectivity 0-3. The ceramic-polymer composite exhibiting the 0-3 connectivity, with different concentration of ceramics phase, has been fabricated on the base of sol-gel derived barium strontium titanate electroceramic powder $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$

(BST60/40) and poly(vinyl chloride) (PVC) polymer, by hot pressing method. Influence of the ferroelectric ceramic phase on dielectric properties of ceramic-polymer composite has been studied for volume fraction of the active phase in the composite from $c_V=1.47\%$ up to $c_V=60\%$.

2. Experimental

In the present work the BST60/40/PVC ceramic-polymer composites of volumetric content $c_V=1.47\%$, 3.04%, 4.75%, 6.60%, 10%, 20%, 50% and 60% and 0-3 connectivity were prepared in form of disks. $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ powder was obtained by sol-gel technique from barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$, 99%), strontium acetate ($\text{Sr}(\text{CH}_3\text{COO})_2$, 99%), and tetra-butyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, 97%) as starting materials according to the method described elsewhere [6]. The sol-gel process used is shown schematically in Fig.1.

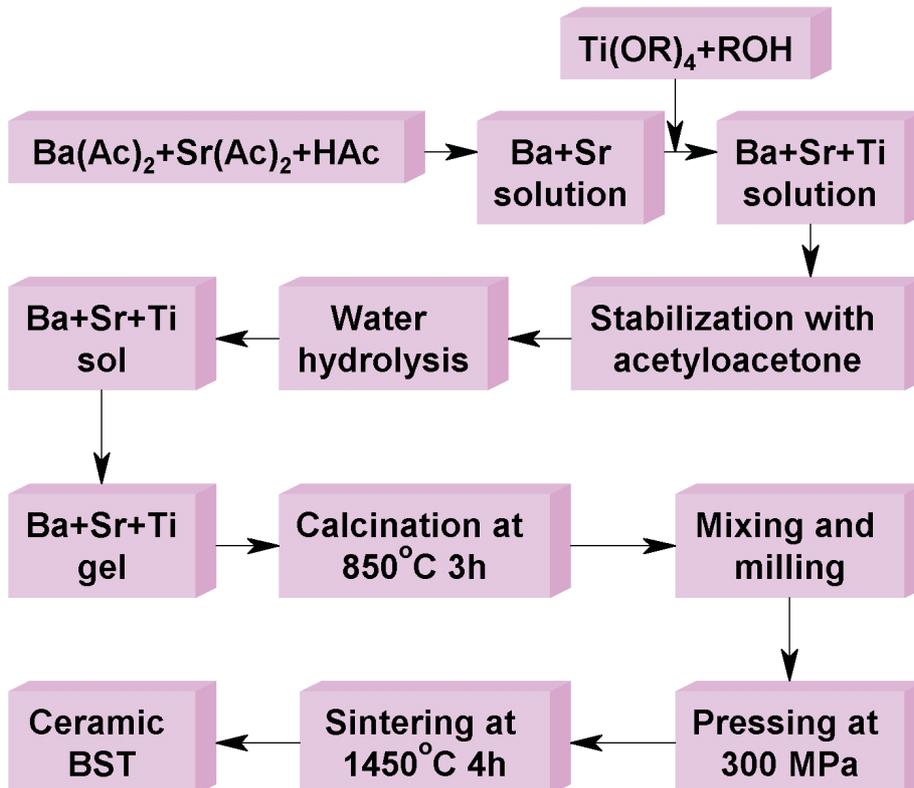


Fig. 1. Flow diagram of the synthesis of BST 60/40 powders by the sol-gel method

Differential thermal analysis (DTA) and thermogravimetric analysis (TG/DTG) were used to determine the thermochemical properties of BST60/40 dried gel both before and after calcinations. Simultaneous measurements were executed by heating the dried powders

in air at $10^\circ\text{C}/\text{min}$, to 1300°C Netzsh STA-409 thermal analyzer was utilized for the studies.

Distribution of grain sizes of calcinated BST60/40 ceramic powder was characterized by Dynamic Light Scattering method.

The BST60/40 ceramic powder was carefully mixed with PVC powder and hot pressed at $T=145^{\circ}\text{C}$, $p=120\text{MPa}$. Fig.2 shows basic steps for fabrication of

BST60/40//PCV by hot pressing technique. The inset shows a view of ceramic powder, polymer powder and ceramic-polymer composite samples.

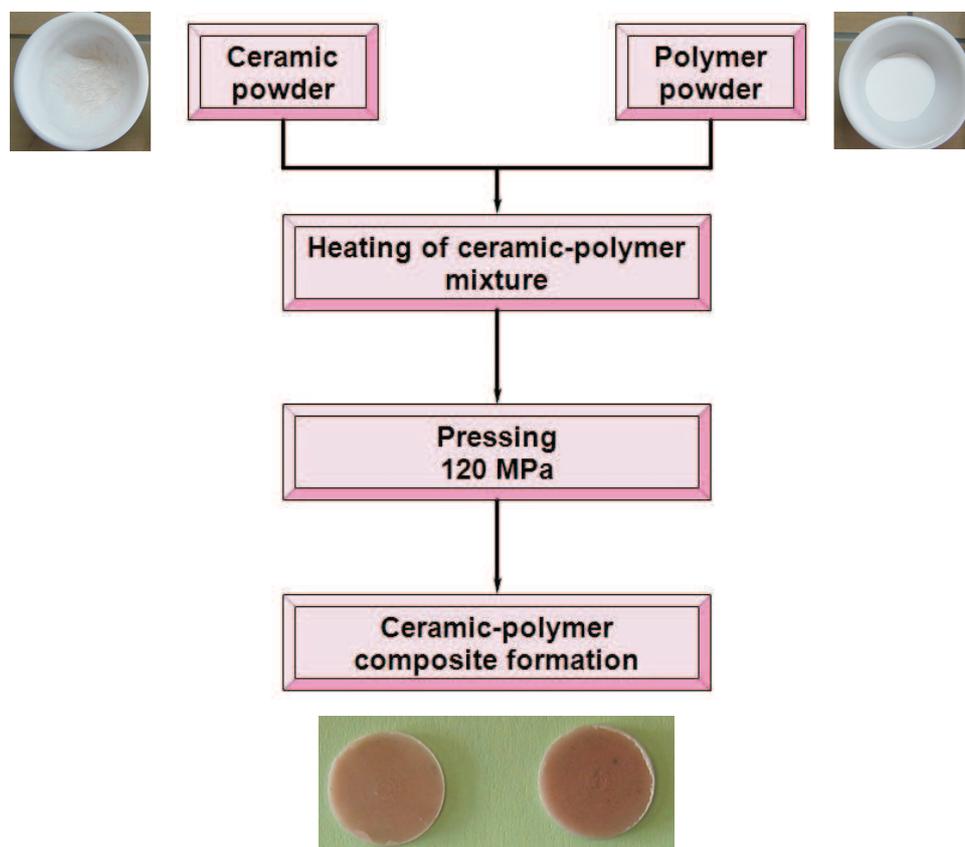


Fig. 2. Basic steps for fabrication of BST60/40//PCV by hot pressing technique

For electric measurements composite samples of 1mm thick and 20mm in diameter were covered with silver paste electrodes. To compare the properties of the composites with those of the component phases PVC samples were prepared at the same conditions as the composites and BST60/40 ceramic samples were fabricated by free sintering.

The crystal structure was examined by X-ray diffraction with CoK_{α} radiation (θ - 2θ method, scan step size $\Delta\theta = 0.02$ deg, scan type continuous, scan step time $t=4\text{s}$) at room temperature. The morphology of BST60/40//PVC composites powder was observed by transmission electron microscopy.

The dielectric properties of BST60/40 ceramic sam-

ple, PVC polymer, and ceramic- polymer composites were studied with the impedance gain/phase analyser HP4192A in the frequency range from $f=10\text{kHz}$ to $f=1\text{MHz}$. The measurements were performed on heating from $T=-50^{\circ}\text{C}$ to $T=200^{\circ}\text{C}$ at a rate of $1\text{deg}/\text{min}$.

3. Results and discussion

Results of thermal analysis of BST60/40 dry gel before and after calcination are given in Fig.3a and 3b, respectively. One can see from Fig.3a that all dried gel powders exhibited a large total weight loss $\Delta m \approx 47\%$. The analyses show three stages of weight loss.

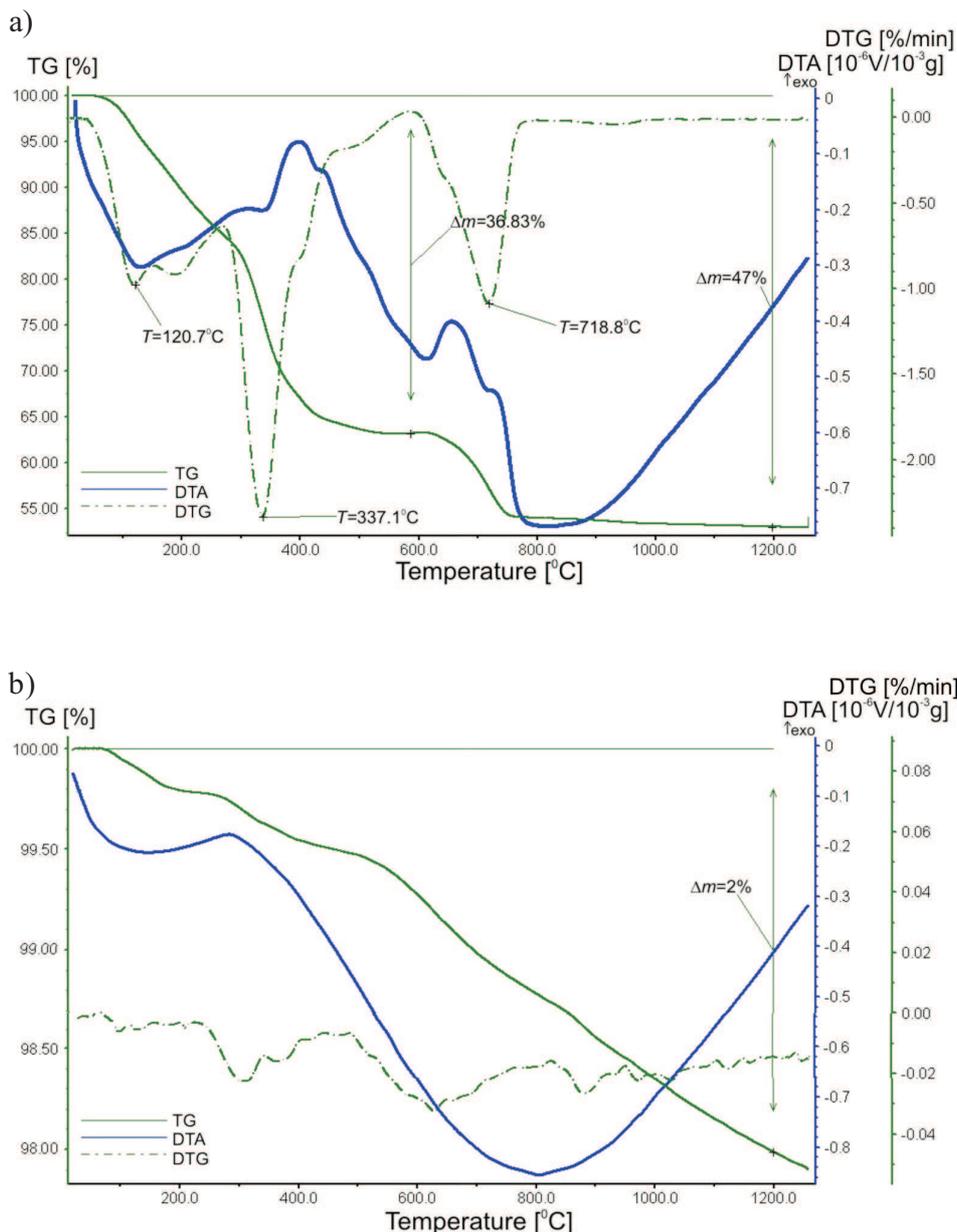


Fig. 3. a) Curves thermal analysis of dry gel BST60/40 before calcinations, b) curves thermal analysis of dry gel BST60/40 after calcinations

The endothermic peak at around 120°C and corresponding weight loss $\Delta m_1 \approx 15\%$ on the TG curve are due to the evaporation of solvents. Below 300°C, the first drop corresponds to the evaporation of the solvent.

The second notable weight loss $\Delta m_2 \approx 21\%$ was detected at $\sim 337^\circ\text{C}$, which matched a large exothermic peak in the DTA curve. Since no crystallization takes place below 500°C, the weight loss is probably due to the decomposition of organic additives in the gel.

The exothermic peak around 400°C and relatively broad exothermic features at 650°C could be due to crystallization of various intermediate phases. It is

known that for sol-gel derived barium titanate several intermediate phases for prior to the transformation of the amorphous phase into the perovskite phase. The nature of these intermediate phases and the crystallization sequence depends upon the precursors used [7].

The third notable drop between 600°C and 800°C corresponds to an exothermic peak of the DTA curve at about 718.5°C. The weight loss originates from the release of various side products during alcoxolation and oxolation.

Fig.3b shows that after calcination no thermal effects take place in BST60/40 powder.

On the basis of thermal analysis, the temperature calcination was chosen $T = 850^{\circ}\text{C}$.

The grain size distribution of BST60/40 ceramic powder obtained by 24h milling of sintered ceramic sam-

ples is given in Fig.4. One can see that median of the powder distribution is $2.97\ \mu\text{m}$. Some grains are agglomerated into clusters of mean size amounting to $\sim 100\text{nm}$.

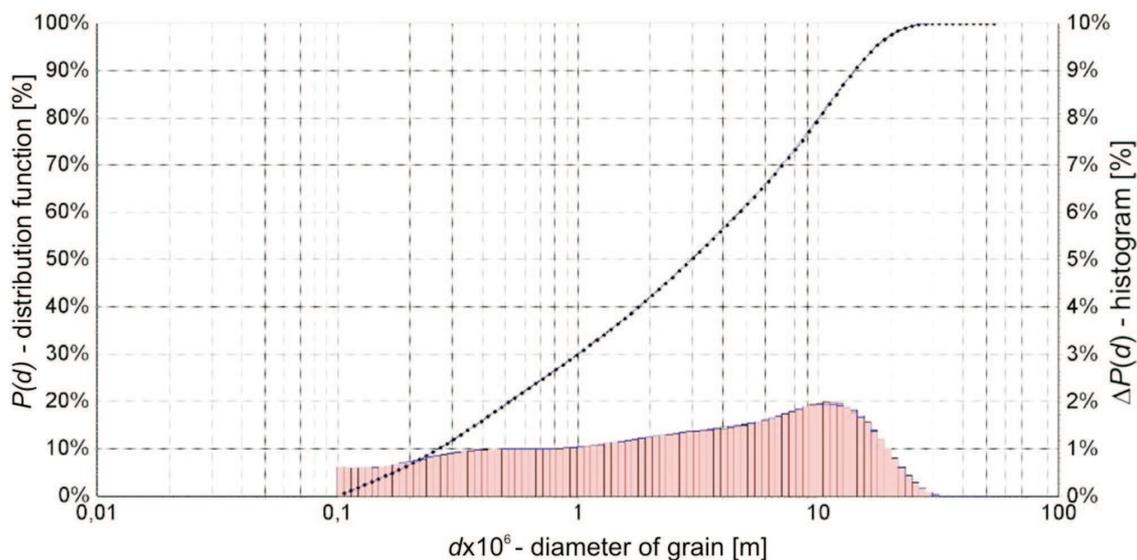


Fig. 4. Grain size distribution of BST60/40 ceramic powder

The dependence of density on concentration of ceramic phase for BST60/40/PCV composite is given in

Fig.5. As ceramic content increases, an increase of density occurs.

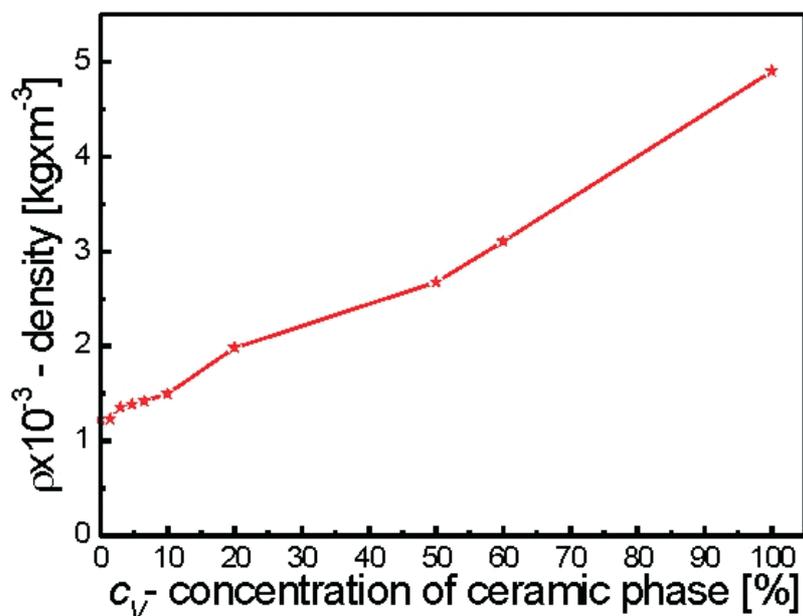


Fig. 5. Dependence of density of BST60/40/PCV composite on concentration of ceramic phase

It is worth noting that in the present research values of X-ray intensities and dielectric constants are given in dimensionless numbers and are denoted as [1] in figures 6-9 and 13-15.

X-ray diffraction spectrum (XRD) recorded at room temperature for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic powder is shown

in Fig.6. Structural analysis was performed for the X-ray spectrum of the ceramic powder, whereas the phase analysis was performed for both polymer and composite spectra with the help of Match! computer programme [8].

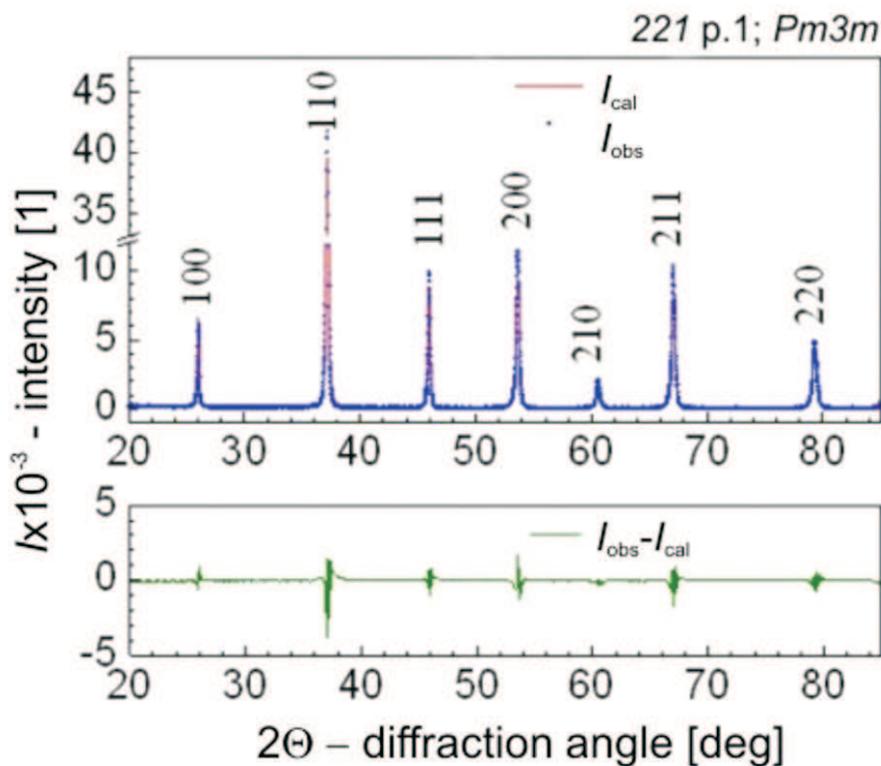


Fig. 6. X-ray diffraction spectrum recorded at room temperature for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic powder

It was found that at room temperature BST60/40 ceramic powder exhibited cubic symmetry described by $Pm3m$ (position 1) space group. The lattice parameters for sol-gel derived BST60/40 ceramic specimens were calculated using Rietveld refinement, embedded into the computer program PowderCell 2.4 [9]. Fitting of the XRD spectrum profile was performed for Pseudo-Voigt function. The following R -parameters were obtained: $R_p=13.72\%$, $R_{wp}=19.44\%$, $R_e=3.67\%$. Calculated ele-

mentary cell parameter of the cubic crystalline structure was $a=0.396(2)\text{nm}$.

X-ray diffraction spectra (XRD) for ceramic powder BST60/40 (a), polymer (c) and 6.60%BST60/40//PVC composite (b) are given in Fig.7. X-ray phase analysis for 6.60%BST60/40//PVC composite is shown in Fig.8 and X-ray diffraction spectrum for 6.60%BST60/40//PVC composite with lines for barium strontium titanate and polyvinyl chloride are shown in Fig.9.

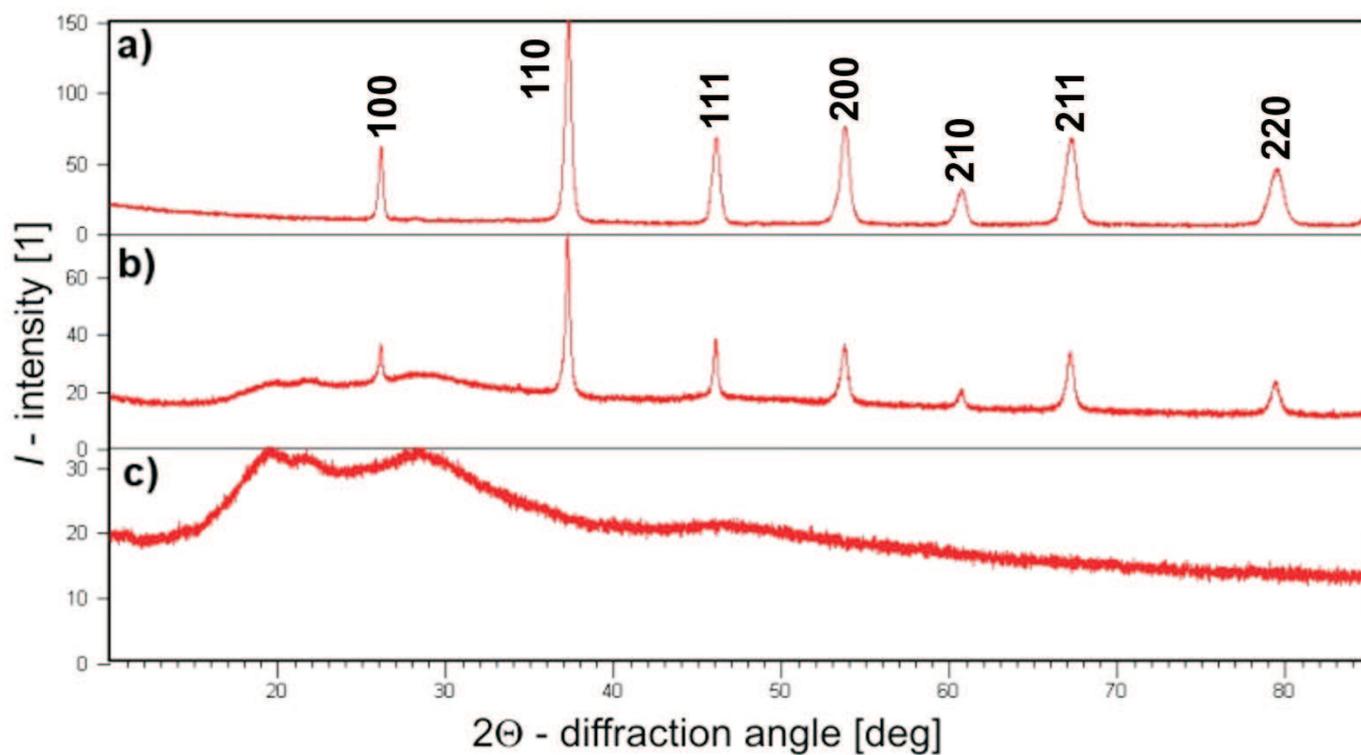


Fig. 7. X-ray diffraction patterns for ceramic powder BST60/40 (a), polymer (c) and 6.60%BST60/40//PVC composite (b)

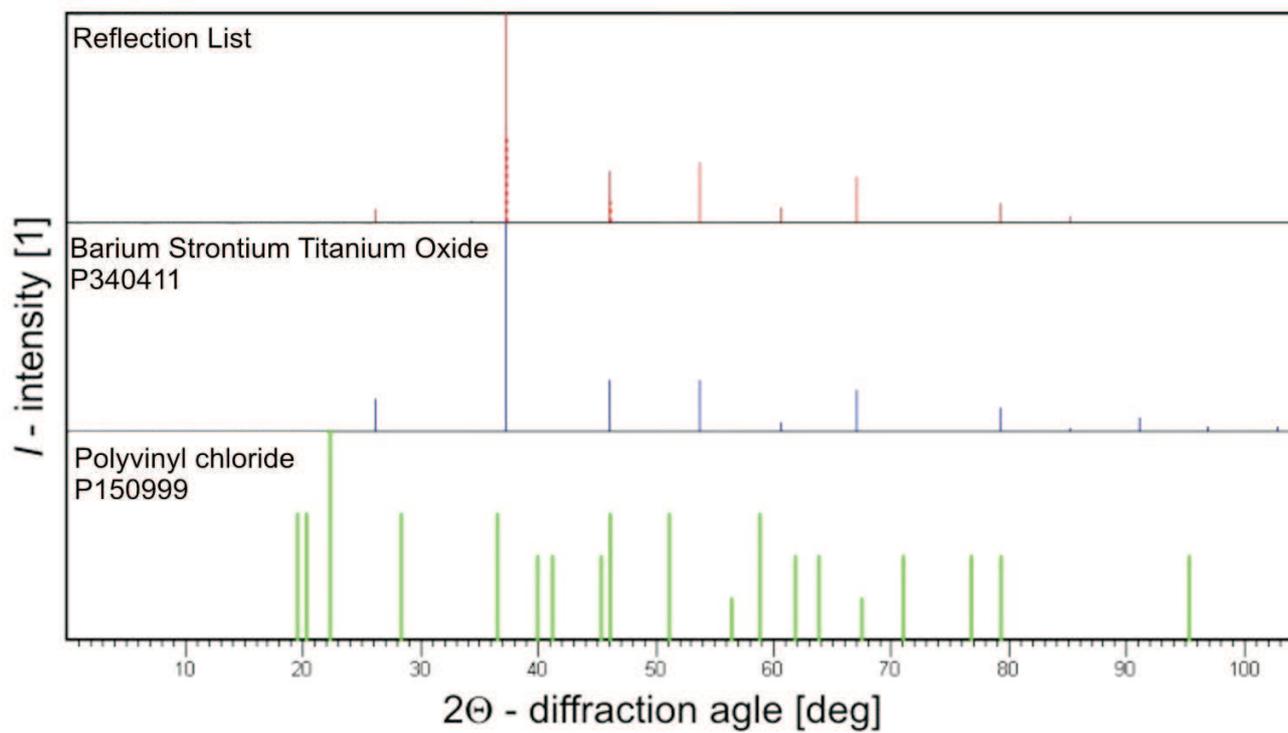


Fig. 8. X-ray phase analysis for 6.60%BST60/40//PVC composite

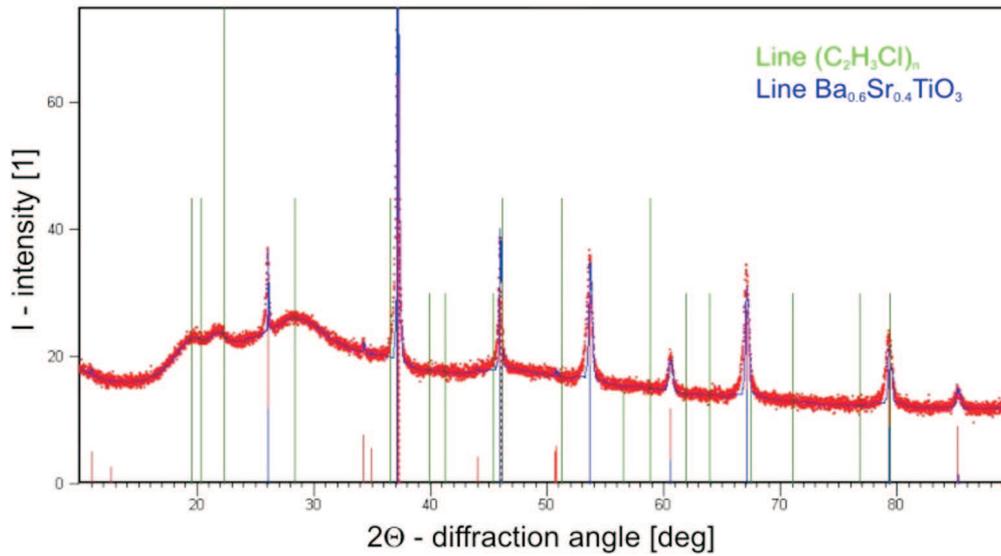


Fig. 9. X-ray diffraction spectrum for 6.60%BST60/40//PVC composite with lines for barium strontium titanate and polyvinyl chloride

Identification of the phases constituting the composite have shown good agreement of positions of the diffraction lines of the ceramic phase ($\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ – PDF card No 340411) and polymer phase ($(\text{C}_2\text{H}_3\text{Cl})_n$ – PDF card No 150999) with the experimental spectrum of the BST60/40//PCV ceramic-polymer composite.

Transmission electron micrographs of BST60/40

powder, PCV polymer powder and 6.60%BST60/40//PVC composites powder are presented in Fig.10, Fig.11, Fig.12, respectively. One can see that polymer grains are arrange around ceramics grain. The BST60/40 powder is well dispersed in the PVC polymer matrix without serious powder agglomeration.

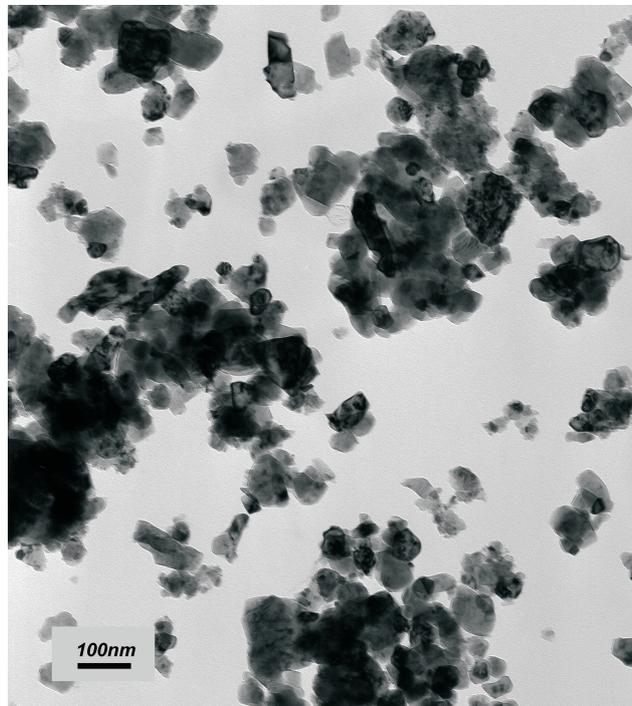


Fig. 10. TEM micrographs of BST60/40 ceramic powder

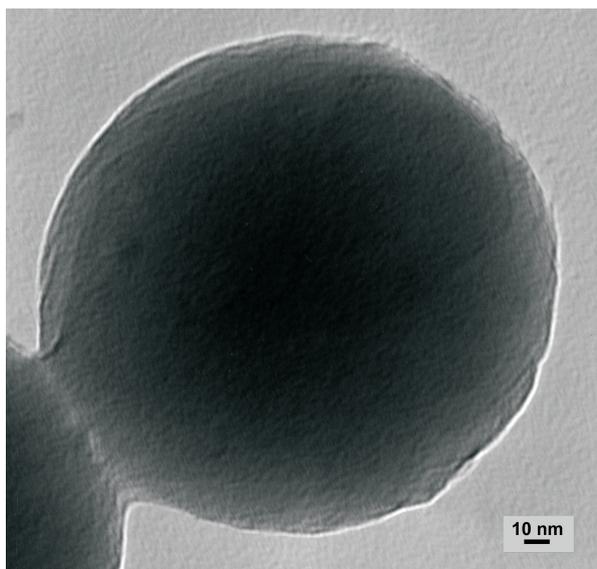


Fig. 11. TEM micrographs of PVC polymer powder

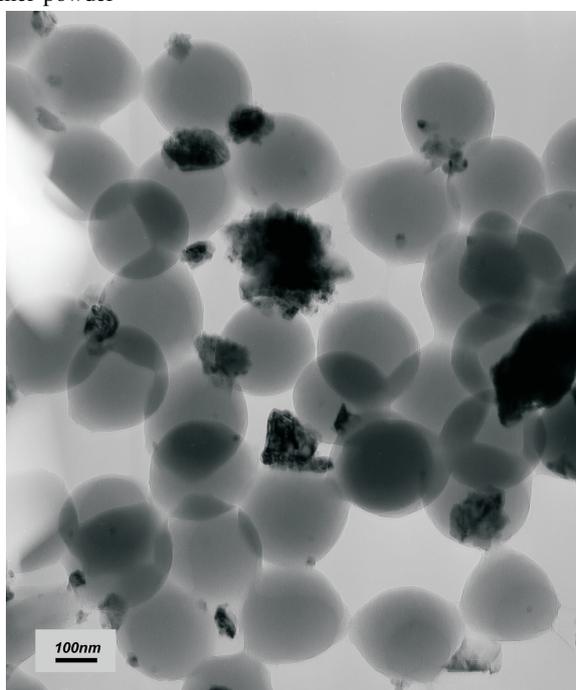
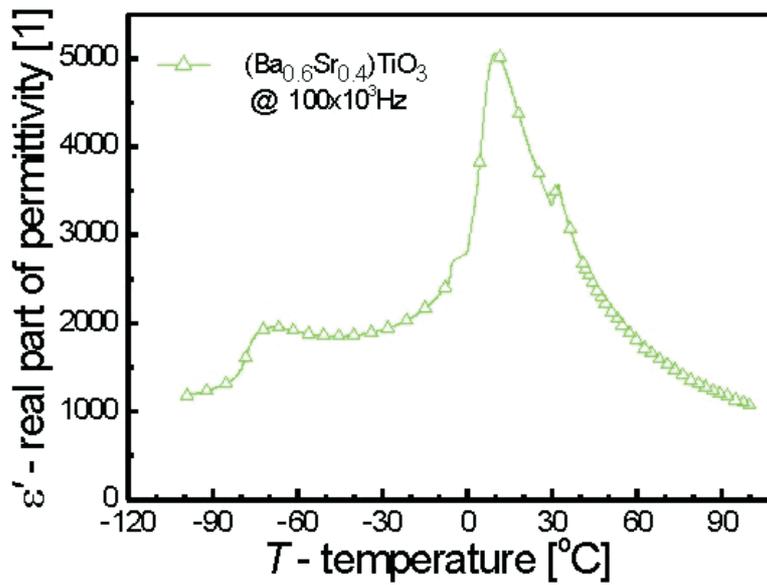


Fig. 12. TEM micrographs of 6.60%BST60/40/PVC composite

The knowledge of dielectric response of the composites is essential because the permittivity is involved in FOM of the physical quantities important for applications [3, 4]. Dependence of the real ϵ' (a) and imaginary ϵ'' (b) part of dielectric permittivity on temperature for BST60/40 electroceramic powder

used for composite fabrication is given in Fig.13. It can be seen from Fig.13 that the three peaks originated from cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedral phase transition can be seen.

a)



b)

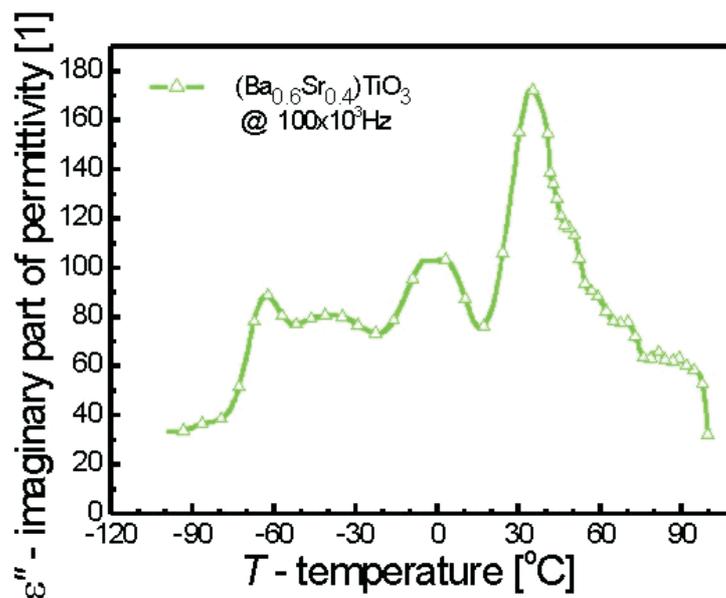


Fig. 13. a) Temperature dependence of the real part permittivity ϵ' for BST60/40 ceramic, b) temperature dependence of imaginary part permittivity ϵ'' for BST60/40 ceramic

Dielectric dispersion (ϵ') and absorption (ϵ'') of polyvinyl chloride (PVC) are shown in Fig.14a and 14b, respectively. It is known that PVC has two relaxation processes: the most intense one, called α , is attributed to the segmental molecular motions occurring above the

glass transition temperature (T_g) and the less intense one, called β , taking place at temperatures lower than T_g , is due to local motions of small groups in the chain [10]. These processes are manifested in form of broad peaks in Fig.14.

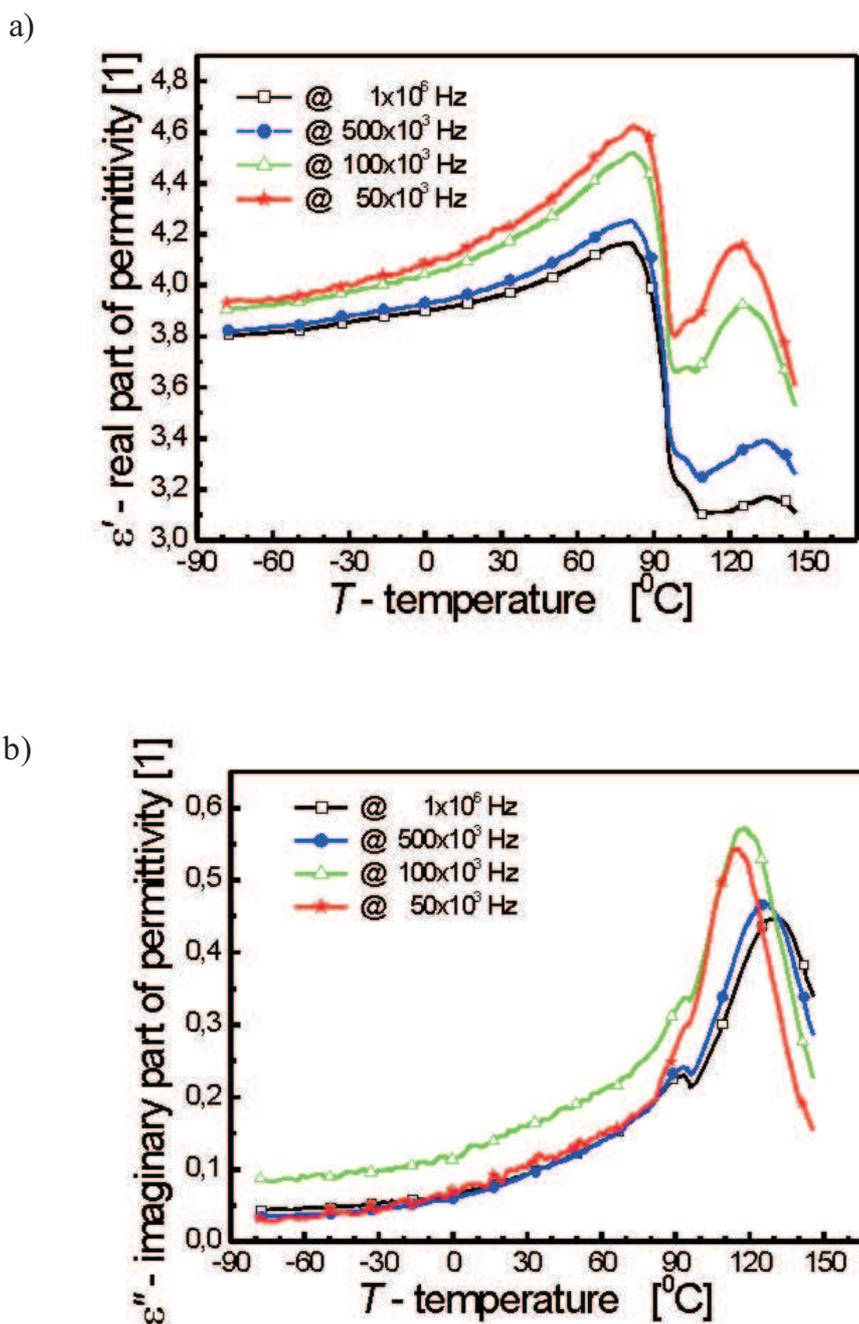


Fig. 14. a) Temperature dependence of the real part permittivity ϵ' for polyvinyl chloride PVC, b) temperature dependence of the imaginary part permittivity ϵ'' for polyvinyl chloride PVC

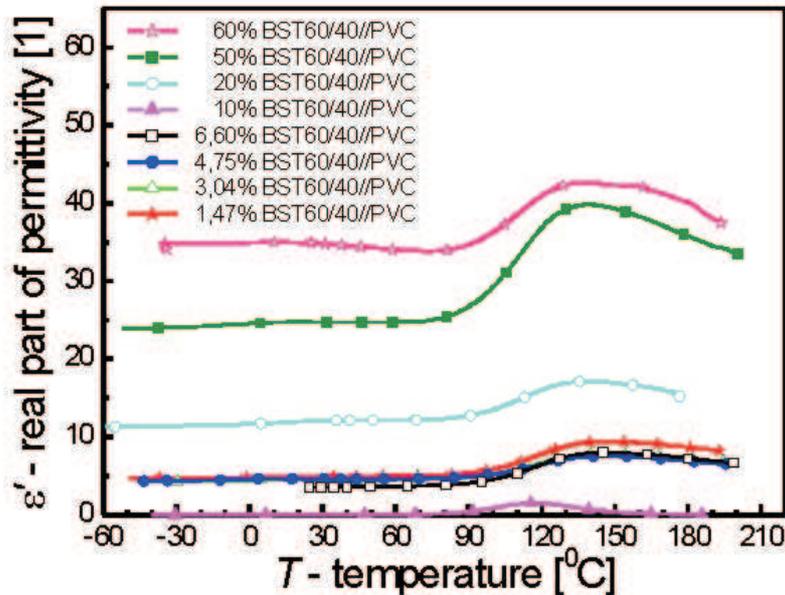
Temperature dependence of the real part permittivity ϵ' (a) and the imaginary part permittivity ϵ'' (b) of BST60/40//PVC composites with different concentration of ceramics phase, for frequency $f=100\text{kHz}$ is shown in Fig.15. The permittivity ϵ' is higher in comparison with that of the polymer (Fig.14) due to the high permittivity value of BST (Fig.13). The relative permittivity of the

composites increases with the increase of ceramic volume fraction. It should be observed that the temperature dependence of the dielectric response of the polymer determines the response of the composites. In the low temperature range the dielectric response of the composites is determined by the anomaly characteristic of the glass transition of the polymer, whereas in the high tempera-

ture range the relaxation related to wide angle oscillation of the polymer polar groups followed by their rotation with main chain co-operation is dominant. The addition of the ceramics only slightly changes the dynamics of

the process in the polymer. The addition of the ceramics result in increase of thermal strength of composites.

a)



b)

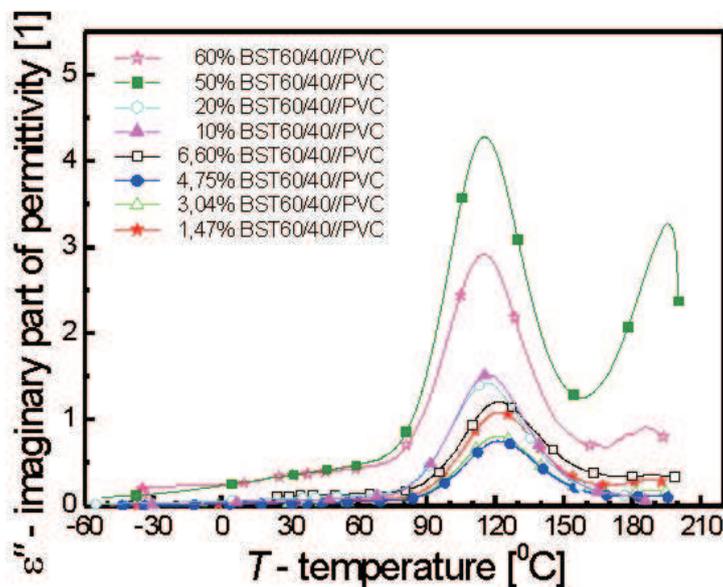


Fig. 15. a) Temperature dependence of the real part permittivity ϵ' of BST60/40/PVC composites for $f=100\text{kHz}$, b) temperature dependence of the imaginary part permittivity ϵ'' of BST60/40/PVC composites for $f=100\text{kHz}$

4. Conclusions

In the present study we have fabricated the electroactive ceramic-polymer composites of 0-3 connec-

tivity using sol-gel derived barium strontium titanate $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ fine powder of grain size less than 100nm. The BST solid solution used is in paraelec-

tric phase at room temperature (cubic $Pm3m$ crystalline structure). Structure, morphology and dielectric measured of BST60/40//PVC composites approve influence of the ceramic phase content on properties of BST//PVC composites. Properties of the ceramic-polymer composite are not a simple sum of properties of the phases constituting the composite but they depend on both the way of connectivity and mutual influence of the phases on each other.

Acknowledgements

The authors wish to acknowledge Polish Ministry of Education and Science for financially supporting the present research from the funds for science in 2006-2009 as a research project N507 098 31/2319.

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