

Dielectric properties of BaTiO₃ based materials with addition of transition metal ions with variable valence

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Abstract. Dielectric properties of BaTiO₃(BT), BaTiO₃+0.1wt.%MnO₂(BTMn) and BaTiO₃+0.1 wt.%Fe₂O₃ (BTFe) solid solution was investigated. The effects of substitution on the microstructure and on the electric properties of BaTiO₃ samples were studied by performing X-ray diffraction and electric measurements. X-ray diffraction analysis of the samples shows the formation of single-phase compound with a tetragonal structure at room temperature. SEM microphotographs exhibit the uniform distribution of grains. The electric properties (a real part of electrical permittivity(ϵ') and an imaginary part of electric modulus (M'')) were investigated in the temperature range from 150K to 600K and in the frequency range from 0.1 Hz to 10 MHz. It was found that a Fe and Mn ions -doping influence the electric properties of the investigated polycrystalline materials.

1. Introduction

Doped ceramics allows the control of electric, electromechanical and electro-optic properties of ferroelectric functional materials such as BaTiO₃. By a proper substitution attractive materials for capacitors and transducers with a wide range of applications from power engineering to medical-device technology [1, 2]. In many recent papers [3, 4] the influence of substitutions on electric properties and the phase transition temperature of BT ceramics have been extensively investigated.

A large number of different dopants can be accommodated in the BaTiO₃ lattice. The ionic radius of dopants is the parameter which mainly determines the substitution site. According to Tsur for ionic radii, $r \leq 0.87\text{\AA}$, the dopants occupy the B-site. For ions of the transition metals such as a Mn³⁺ (0.78Å) and Fe³⁺ (0.64 Å) ions it is well established that they preferentially were substituted on the Ti³⁺(0.74Å) site [5-7]. Additionally, the dopants, event at small concentration, can cause lattice deformations [8-11] as well as changes in the charge balance of the material. The oxygen vacancies are responsible for a charge compensation, involves the creation of a stoichiometric amount of oxygen vacancies, so they behave as acceptors of dopants [12]. The oxygen vacancies could be easily created by a loss of oxygen from a crystal structure during sintering at high temperature. The aim of this work is clarify the influence of Mn and Fe ions on the dielectric properties of BaTiO₃.

2. Experimental procedure

The BaTiO₃+ 0.1 wt.% x (x=MnO₂, Fe₂O₃) polycrystalline samples were prepared by a solid state synthesis [13] in the Institute of Solid State Physics University of Latvia.



The X-ray studies were performed with the use of an X'Pertt PRO (PANalytical) diffractometer using the $\text{CuK}\alpha$ radiation ($\lambda = 0.154178 \text{ nm}$) and a graphite monochromator. The patterns were obtained at the rising temperature. To analyse and fit the spectra, the program FULLPROF based on Rietveld method was used. The investigations of the microstructure of specimens were performed using the Hitachi S4700 SEM (Scanning Electron Microscope) with field emission and the Noran Vantage EDS (Energy-Dispersive X-ray Spectroscopy) system. The X-ray microanalysis EDS was applied to investigate the homogeneity of the composition and the EPMA (Electron Probe Microbeam Analysis) was applied to analyse the distribution of elements on the sample surface. The investigations of chemical composition were performed using the Noran - Vantage microanalyses which is a part of the Hitachi scanning electron microscope. All the electric measurements of the samples were performed with the use of an Alfa – AN modular measurement system with a temperature control system Quatro Krio 4.0 range from 0.1Hz to 10 MHz.

3. Results and discussion

Surface SEM investigations were performed on doped (BTMn, BTFe) and undoped (BT) samples. The parameters of the elementary cell of all samples were calculated. From the obtained results was stated the elementary cell parameters are: $a = b = 3.9943 \text{ \AA}$, $c = 4.0354 \text{ \AA}$, $a = b = 3.9996 \text{ \AA}$, $c = 4.0339 \text{ \AA}$ and $a = b = 3.9995 \text{ \AA}$, $c = 4.0338 \text{ \AA}$ for BT, BTFe and BTMn respectively. The space group of BT, BTFe and BTMn samples at room temperature is $P4mm$. The SEM images of BaTiO_3 show that the microstructure consists of intergranular pores and grains of various size. Moreover, one can observe that substitutions have an inhibiting effect on the grain growth process and, consequently, a relative homogeneous microstructure, which reveals a higher amount of an intergranular porosity and the lower size of grains than those ones in a non-modified sample. This may be due to the nucleating behavior of Mn, Fe ions in the BaTiO_3 ceramics. Figures 1 indicates that the addition of transition metal ions decreases the size of grains. The EDS investigations showed that BTMn and BTFe ceramics contained Ba, Ti, O, Mn and Fe elements near their surfaces and no other impurity elements were detected in the spectrum. The homogeneity of element distribution in the samples was investigated by an EPMA method with use of an X-ray microprobe. The obtained “mappings” confirmed the qualitative composition of the examined samples.

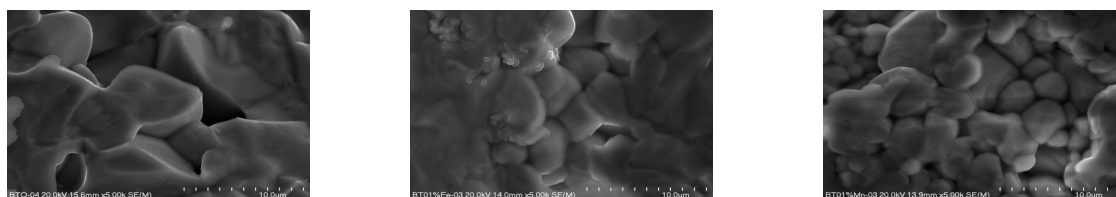


Figure 1. The SEM images of BT, BTFe and BTMn ceramics (magnification 5 000x).

A dielectric spectroscopy is a convenient and widely used method for the electrical properties characterization of ceramic ferroelectrics. In particular, a.c. measurements in a wide frequency range ($10^{-1} \text{ Hz} \div 10^7 \text{ Hz}$) give reliable characteristics of both: a bulk (grain) and a grain boundary dielectric polarization dynamic. The dependence of real part of electric permittivity (ϵ') on temperature at the constant value of the frequency (10 kHz) electric field of applied for the investigated samples was studied. The maxima of electric permittivity ($\epsilon'(T)$) seen in the figure 2 are observed at the temperatures corresponding to the temperatures of phase transitions. In the case of BT – ceramics, these temperatures are well correlated with the temperature obtained by calorimetric measurements (not shown here). For BTMn material, the value of ϵ' is damped down in the whole temperature range but the temperatures of phase transitions are the same as for those BT. For the BTFe material the temperature of the paraelectric – ferroelectric transition is almost the same as for BT. The low temperature transitions posses a diffusion character with the maximum value of ϵ' occurs at a temperature of 253K. The frequency dependencies of real part of electric permittivity ($\epsilon'(v)$) at 600K

for the investigated samples are presented in figure 3. The measured frequency dependence of ϵ' consists of two characteristic regions: one of frequency above and the other below $\sim 10^4$ Hz. For the low frequency region, the ϵ' values of all investigated samples are high values and they are frequency dependent.

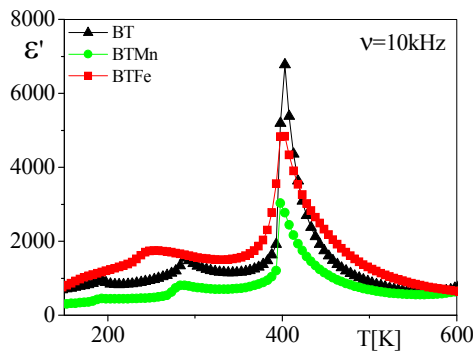


Figure 2. The temperature dependence of ϵ' for BT, BTFe and BTMn.

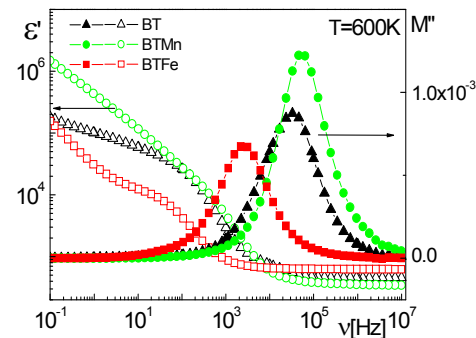
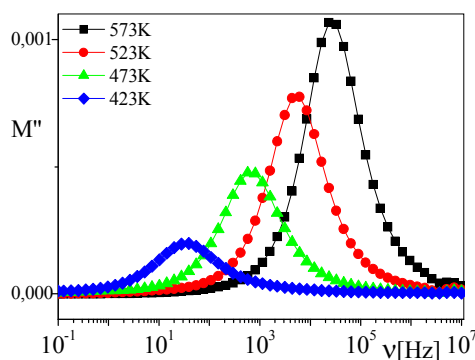
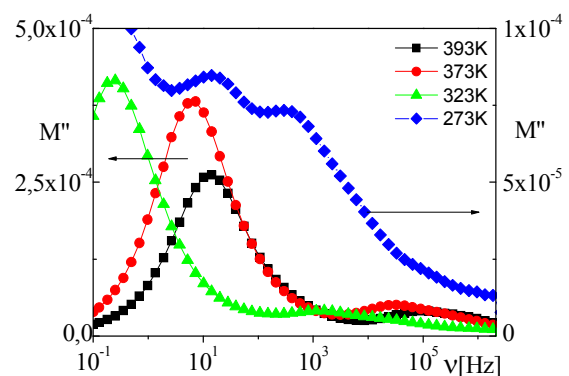


Figure 3. The frequency dependence of ϵ' and M'' for BT, BTFe and BTMn.

For frequencies higher than $\sim 10^4$ Hz, the ϵ' values observed in the same scale show the lack of frequency dependence. The same two frequency regions can be defined also for an electric modulus (imaginary part of M''). The values of M'' indicate the weaker polarization processes which were identified as connected with a bulk polarization. The electric modulus M^* and complex permittivity ϵ^* are related by the following formula: $M^* = 1/\epsilon^* = M' + iM''$. The dependence of imaginary part of the electric modulus (M'') on frequency at selected temperature (423K, 473K, 523K and 573K) is presented in figure 4(a). The increase in temperature cause two effects: the first one is the increase of the M'' peak values up to about 5 times, and the second one the shift of the curves in the figures towards higher frequencies. The characteristics of $M''(\nu, T)$ at temperature: 273K, 323K, 373K and 393K, for the same sample are presented in figure 4(b). At the lower temperatures the M'' behaviour is not a regular function of temperature and frequency and the M'' values are of one order of magnitude smaller than those in figure 4(a). On the basis of the data presented in figure 4 the relaxations times were calculated using the $\omega\tau = 2\pi\nu_m\tau = 1$ equation, where ν_m – value of frequency for the M'' peaks at fixed temperature. The collected results are presented as Arrhenius plots.



(a)



(b)

Figure 4. The frequency dependence of MO for BTMn at the temperature: (a) 423K, 473K, 523K and 573K (b) 273K, 323K, 373K and 393K.

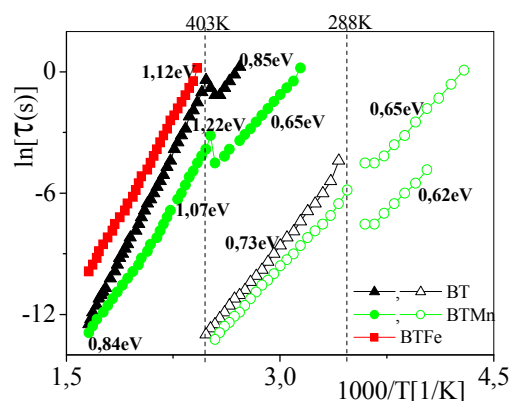


Figure 5. Arrhenius plot of relaxation times for BT, BTFe and BTMn samples (open symbols – grain, solid symbols – grain boundary).

The thermal activation energies for all investigated materials are shown in figure 5. The visible breaks seen in figure 5 occur at the temperature of phase transitions for all samples. The Fe dopant shifts the curves towards higher temperatures compared with the BT sample. The Mn dopant causes opposite shift and appearance of next values of thermal activation energy. These values of the activation energies may be related to the electron excited process from the oxygen vacancy.

4. Conclusions

The structural and electric properties of titanate ceramics prepared by a solid state synthesis were investigated. The space group ($P4mm$) and the lattice parameters were obtained. EDS and EPMA measurements were used for a microstructure and chemical analysis. SEM investigation reveals a fine grain and dense microstructure. No significant impurities were detected in an EDS spectrum and the samples are in good stoichiometric ratio. The obtained dielectric data suggest that, the substitution of transitions metal ions has a significant influence on the value of real part of electric permittivity (ϵ') and character of the electric modulus M^* . The thermal activation energies for investigated samples which characterized the electrical properties of grains and grain boundaries were calculated.

5. References

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