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EFFECT OF SEMICONDUCTOR ELEMENT SUBSTITUTION ON THE ELECTRIC PROPERTIES OF BARIUM TITANATE CERAMICS

The investigated ceramics were prepared by a solid-state reaction from simple oxides and carbonates with the use of a mixed oxide method (MOM). The morphology of $BaTi_{0.96}Si_{0.04}O_3$ (BTSi04) ceramics was characterised by means of a scanning electron microscopy (SEM). It was found that Si^{+4} ion substitution supported the grain growth process in BT-based ceramics. The EDS results confirmed the high purity and expected quantitative composition of the synthesized material. The dielectric properties of the ceramics were also determined within the temperature range (ΔT=130-500K). It was found that the substitution of Si^{+4} ions had a significant influence on temperature behavior of the real (ε') and imaginary (ε'') parts of electric permittivity as well as the temperature dependence of a.c. conductivity. Temperature regions of PTCR effect (positive temperature coefficient of resistivity) were determined for BTSi04 ceramics in the vicinity of structural phase transitions typical for barium titanate. No distinct maximum indicating a low-temperature structural transition to a rhombohedral phase in BTSi04 was found. The activation energy of conductivity was determined from the Arrhenius plots. It was found that substitution of Si ions in amount of 4wt.% caused almost 50% decrease in an activation energy value.

Keywords: barium titanate, ceramics, dielectric permittivity, electric conductivity, phase transitions, PTCR effect

1. Introduction

The perovskite-type $BaTiO_3$ ceramics shows a ferroelectric state below the temperature of 400K, at which the crystal structure changes from a cubic to tetragonal one in a first-order-type structural transition. Moreover, $BaTiO_3$ exhibits two another structural phase transitions at the temperature of about T=285K and T=190K. Pure $BaTiO_3$, doped $BaTiO_3$ and substituted $Ba_{1-y}Ti_{1-x}O_3$ (called $BaTiO_3$-like compounds) that are ceramics, monocrystals or films have many kinds of electrical functional properties [1, 2]. The wide industrial applications of the $BaTiO_3$-like compounds are based mainly on the ease of changing the structural and electrical properties by the doping or substitution of Ba^{2+}or Ti^{4+} ions with other ions. Among the possible modifications, the substitution of Ti^{+4} (R=0.0605 nm) ions by the smaller ions of silicon Si^{+4} (R=0.040 nm) in the B site of ABO_3 structure leads to the $BaTi_{1-x}Si_xO_3$ solid solution (the ionic radii R are taken from Shannon with a six fold coordination [3]). In addition the presence of small amounts of Si^{+4} ions in $BaTiO_3$ should be particularly important for its electrical properties.

Goal of the present paper was to fabricate $BaTiO_3$ and $BaTi_{0.96}Si_{0.04}O_3$ ceramics by MOM method and characterize ceramic materials in terms of electric properties to reveal influence of Si^{+4} ion substitution on electric behavior of $BaTiO_3$-based ceramics within the temperature domain covering the all three phase transitions of barium titanate (ΔT=130-500K).

2. Experimental procedure

2.1. Sample preparation

$BaTi_{0.96}Si_{0.04}O_3$ (BTSi04) ceramic samples were prepared by means of the mixed oxide method. The samples were synthesized from analytically pure titanium oxide TiO_2, silica SiO_2 and barium carbonate $BaCO_3$. The mixture of the raw materials was homogenized and ground in an agate ball mill in ethanol for t=24 hours. The dried material was calcined for t=1.5 hours at temperature T=1580 K. After calcination the powder was ground in ethanol, cold pressed (at p=100 MPa) and sintered for t=2 hours at temperature T=1600 K. After sintering the ceramic samples were covered with silver paste electrodes. Before the experiments, the samples were annealed at temperature T=520K for t=1 hour in order to eliminate internal and near electrode stresses.

2.2. Measurements methodology

SEM investigations were carried out with the use of a field emission Hitachi S4700 scanning electron microscope equipped with an EDS Noran Vantage system. The investigations of microstructure of polycrystalline specimens were performed on polished sections and fractures. Before the measurements the samples were sputtered with carbon in order to carry away the electric charge from the surface.

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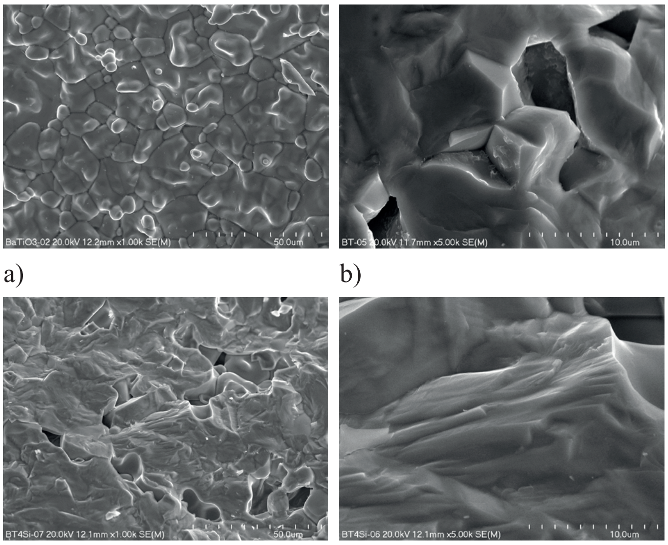
The homogeneity of the composition was investigated by means of an Energy-Dispersive X-Ray Spectroscopy and the analysis of the distribution of elements on the sample surface was performed with the use of an Electron Probe Microbeam Analyses (EPMA) [4, 5]. The electric studies of the ceramic samples were performed by means of an Alpha-A High Performance Frequency Analyzer system combined with a Quatro Cryosystem for the temperature control and WinDETA Novocontrol software. The measurements were carried out at the temperature ranging from T=500K to T=130K on cooling process. The frequency varied from ν=10 Hz to ν=1 MHz.

3. Results and discussions

The SEM images of the $BaTiO_3$ and $BaTi_{0.96}Si_{0.04}O_3$ ceramics made at magnification 1000x and 5000x are shown in Fig.1 a, c and Fig.1 b, d, respectively. In the micrographs one can observed layered structures, plates and irregularly oriented grains. A good homogeneity of the microstructures and a very small degree of porosity was observed. In the investigated ceramics the growth of grains proceeds according to a layer mechanism with a screw dislocation (the growth terraces of grains are clearly seen). The local analysis of the chemical composition of ceramics were carried out with the use of EDS. They confirmed the high purity and the expected qualitative composition. The homogeneity of element distribution in the samples was investigated by means of the EPMA method with the use of an X-ray microprobe. The obtained "mappings" confirmed the qualitative composition of the examined polycrystalline material.

From the obtained results it was stated that the grain size of BTSi04 increased in comparison with pure barium titanate $BaTiO_3$ (BT). Due to the fact that the ionic radii of Ti^{4+} and Si4+ and the covalence degree of the bonds are different, it is expected that the interaction between Ti-O and Si-O bonds exists.



a) b)

c) d)

Fig.1. SEM images of $BaTiO_3$ (a, b) and $BaTi_{0.96}Si_{0.04}O_3$ ceramics (c, d) [mag. 1000x: a and c; mag. 5000x: b and d]

According to the Pauling valence bond theory [6] the structure of investigated compounds with characteristic an oxygen octahedron, depends on the occurrence of a hybridization of d^2sp^3 - type in the cell [7-9]. Silicon ions can easily occupy a B site of oxygen octahedron to form a solid solution and according to the first rule of Pauling, the oxygen octahedron is not stable. In these materials the partial substitution of Ti^{4+} by Si^{4+} takes place, and therefore the new crystalline structures depending on the level of substitution occur.

Dielectric properties of BTSi04 and BT ferroelectric ceramics are described by the temperature dependences (in cooling process) of the real (ε') and imaginary (ε'') parts of dielectric permittivity The plots of $\varepsilon'(T)$ and $\varepsilon''(T)$ for two types of investigated samples for the frequency of measuring electric field ν=1kHz are presented in Fig. 2 and Fig. 3, respectively. It is worth noting that the temperatures corresponding to any maxima of ε' have not changed in the whole measured frequency range. In the case of ferroelectric samples these maxima correspond to their structural phase transitions.

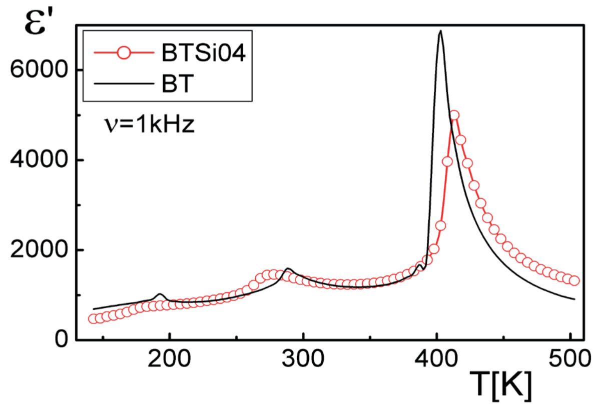


Fig.2. The temperature dependence of the real part of complex dielectric permittivity (ε') for BTSi04 and BT samples

A classic paraelectric - ferroelectric phase transition with a simultaneous change from a cubic to tetragonal structure occurs, at the temperatures of T=403K and T=413K for BT and BTSi04 samples, respectively. With a decrease in temperature, i.e. at T=288K (BT) and T=278K (BTSi04), one can identify other maxima of $\varepsilon'(T)$ which are connected with the structural transition to an orthorhombic phase. The further temperature lowering leads to a weak maximum at temperature of T=193K (BT), which is connected with the structural transition of even the lower symmetry of rhombohedral type. The BTSi04 sample does not exhibit a distinct maximum indicating a low-temperature structural transition to a rhombohedral phase as in the case of BT. One can postulate then, that the diffusive character of phase transitions in BTSi04 sample is a result of Si ions substitution in cationic sublattice.

The dielectric losses for the investigated samples are presented as a $\varepsilon''(T)$ function (Fig.3). For the BT sample, the maxima of these losses are correlated with the maximum of $\varepsilon'(T)$ whereas for the BTSi04 sample there are no sharp maxima visible. One can see in Fig.3 that the values of $\varepsilon''(T)$ increased rapidly in the paraelectric phase for both types of the samples i.e at temperature T>403K and T>413K for BT and BTSi04 ceramics respectively. The character of these changes evidences the dominant contribution of the *d.c.* component of electrical conductivity in dielectric losses. One can see in Fig.3 that dielectric loss factor (*ε”*) for BTSi04 sample is substantially higher as compared with BT.

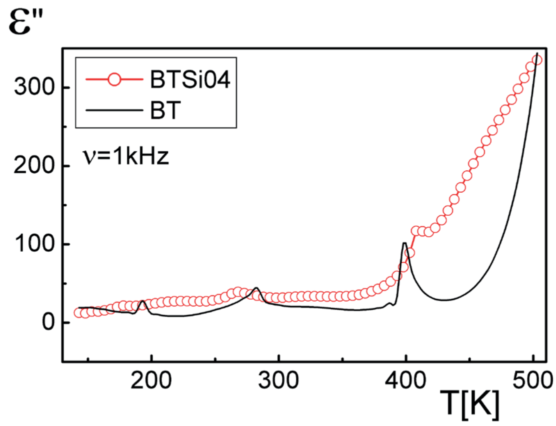


Fig. 3. The temperature dependence of the imaginary part of complex dielectric permittivity (*ε”*) for BTSi04 and BT samples

The dielectric losses of investigated samples are also presented by the dependence of the real part of *a.c.* conductivity (*σ’*) on the inverse absolute temperature (1000/*T*) in the so called Arrhenius system (Fig.4).

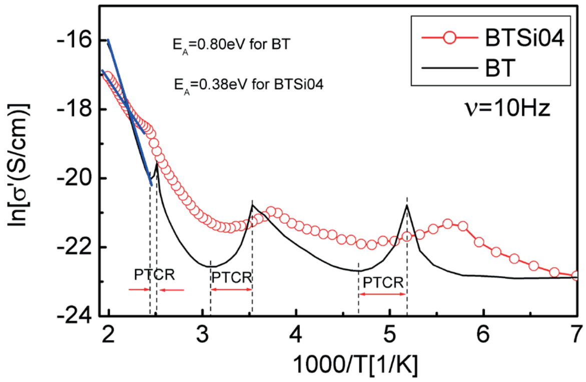


Fig.4. A plot of the a.c. conductivity (σ’) in the Arrhenius system with frequency measurement field of 10 Hz for BTSi04 and BT samples

The character of the *a.c.* conductivity plots indicates a complex mechanism of electric charge transport. In the phase transition regions, where the value of the *σ’* reaches local minima (for both samples) a PTCR (*Positive Temperature Coefficient Resistivity*) effect is observed. This has been explained earlier by Heywang [10, 11] who predicted such a behavior basing on the acceptor state density at the grain boundaries, the charge carrier density and the energy gap between the conduction band and the acceptor levels.

The local minima appearing on a plot of electrical conductivity (Fig.4) are associated with a polaronic transport mechanism [12-14]. The minimum values of this electrical conductivity can be a result of the change in the nature of the conduction mechanism: from the tunnel mechanism into the hopping one, that is the short-range into the long-range mechanism.

In the range of high temperatures (paraelectric phase) the linear straight sections are observed which indicate the activation nature of *a.c.* conductivity. The values of thermal activation energies, determined by means of a linear regression method at the frequency of measuring field ν=10 Hz, are as follows E_a=0.80±0.01eV and E_a= 0.38±0.02eV for BT and BTSi04 samples, respectively. At the high temperature the electrical conductivity can be dominated by an ionic conductivity associated with an oxygen vacancy while the variable range hopping polaron conductivity was assumed to be active at low temperatures. In the small-polaron model the drift mobility increases with decreasing in temperature [12]. The transition temperature between the tunneling and hopping regimes approximately agrees with the minimum on the ln*σ’*(1000/*T*) curve. The observed shape (Fig.4) of ln*σ’*(1000/*T*) function with a distinct minima of conductivity is typical for small polaron mechanism transition from the hopping to the tunneling conductivity.

4. Conclusions

The $BaTi_{0.96}Si_{0.04}O_3$ (BTSi04) solid solution was prepared by means of a solid state synthesis. The SEM results made it possible to determine the stoichiometry of the materials and evaluate their microstructure: grain and pore sizes, shapes and an orientation. It can be concluded, from obtained results, that Si^{4+} ions substitution for Ti^{4+} in barium titanate increases the value of temperature of the paraelectric-ferroelectric phase transition for about 10 K. The change of this temperature can be explained by the differences in ionic radius size of the substituted ions, and the interaction between these ions and the oxygen and barium ions. The diffusive character of the phase transitions in BTSi04 sample was also found as a result of Si ions substitution in the cationic sublattice. As far as hybridization of d2sp3 - type in the BTSi04 elementary cell is highly possible the oxygen octahedron instability and formation of new crystal structure may be responsible for the above mentioned diffusive character of the ferroelectric-paraelectric phase transition as well as lack of a distinct maximum indicating a low-temperature structural transition to a rhombohedral phase as in the case of BT. The low frequency measurements of BTSi04 sample reveal the transport process related to the transition from polaronic to tunneling mechanism.

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