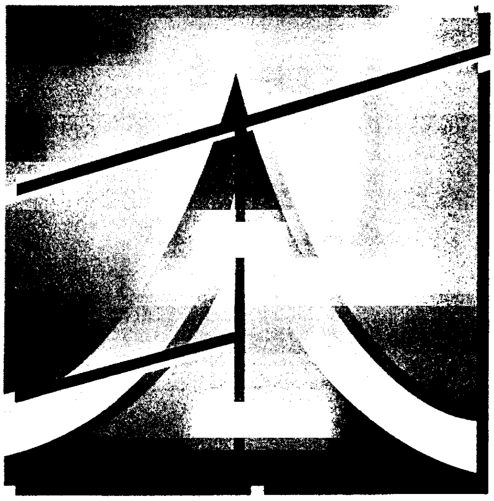
ELECTROCERAMICS V



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EFFECT OF ISO- AND ALIOVALENT SUBSTITUTIONS ON THE PROPERTIES OF $BaTiO_3$ PTCR CERAMICS

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Abstract. Systems based on $BaTiO_3$ with aliovalent substitutions of barium by yttrium, titanium by niobium, tantalum, molybdenum and tungsten and with isovalent substitution of barium by calcium, strontium and lead have been investigated. The effect of substitution on chemical reaction sequence, the microstucture and electrophysical properties of ceramic is shown.

Keywords: posistor, synthesis, substitutions, grain size.

1 Introduction

$BaTiO_3$-based solid solutions are used to prepare posistor materials, of which a considerable increase in electrical resistance on heating is characteristic. Posistor properties can arise in the case of aliovalent substitution in cation sublattices. The main chemical processes responsible for the arising of semiconductor and posistor properties are reduction in the case of high-temperature burning and oxidation in the case of cooling. Taking into account the literature data relating to interaction between equimolar $BaCO_3$-TiO_2 mixtures, it may be stated that there are substantial differences in results relating to the $BaTiO_3$ formation mechanism. The reasons of this are different methods of investigation and different prehistory of TiO_2. The composition of primary product in the case of interaction between $BaCO_3$ and TiO_2 depends on TiO_2 fineness [1]: when the grain size is under 5 µm; the primary interaction product is $BaTiO_3$; and when it is over 20 µm, the primary interaction product is Ba_2TiO_4. The properties of posistor ceramic depend on the presence of the Ba_2TiO_4 phase, which retards reduction processes during synthesis, on what sublattice substitution is performed in and on the content of ions added.

The aim of the present work was to study the effect of iso- and aliovalent substitutions in cation sublattices on the formation and properties of $BaTiO_3$-based PTCR ceramics.

2 Materials Preparation and Experimental Methods

All the samples for this investigation were prepared by a conventional solid-state reaction technique. Super-pure $BaCO_3$, TiO_2, Y_2O_3, Nb_2O_5, SiO_2 and chemically pure

Ta_2O_5, MoO_3, WO_3 were used as starting reagents. The TiO_2 grain size was not over 1.5 µm. Phase changes were studied by the thermogravimetric method using a Q-1000 OD-102 device. The X-ray measurements were carried out on a DRON-3M diffractometer with CuKα radiation. The lattice parameters were determined using $(224)_{\alpha 1}$ and $(422)_{\alpha 1}$ reflection, the determination error being $5 \cdot 10^{-5}$ nm. Samples sintered at 1340-1360°C were used to study the electrophysical properties. Ohmic contacts were produced by the burning aluminum paste applied to posistor surfaces. The granular structure of as-fired surfaces was examined using an electron-probe microanalyzer (EPMA, JEOL JCXA-733, Japan).

3 Results and Discussion

According to the results of thermographic and X-ray phase analysis, barium carbonate decomposed over the range 600-1100°C, barium oxides and titanium oxides interacting to form $BaTiO_3$, $BaTi_3O_7$, Ba_2TiO_4 and $BaTi_4O_9$ whatever the nature of doping ions. The intermediate phases change to barium titanate: $Ba_2TiO_4+TiO_2 \text{--->} 2BaTiO_3$; $BaTi_3O_7+2BaO \text{--->} 3BaTiO_3$; $BaTi_4O_9+3BaO \text{--->} 4BaTiO_3$. The temperature ranges of the existence of intermediate phases are shown in fig.1. Aliovalent substitutions in cation sublattices, which give rise to semiconductor properties in $BaTiO_3$, do not change the sequence of chemical barium metatitanate phase formation reactions; however, a shift of the temperature range of the existence of intermediate phases towards lower values is observed in this case. When the $BaCO_3$-$CaCO_3$-TiO_2 system is treated thermally, the $BaTiO_3$ phase is formed initially, and at higher temperatures the solid solution $(BaCa)TiO_3$ is formed. In the case of the $BaCO_3$-$SrCO_3$-TiO_2 system, the decomposition of barium carbonates and strontium carbonates occurs simultaneously to form $(BaSr)TiO_3$.

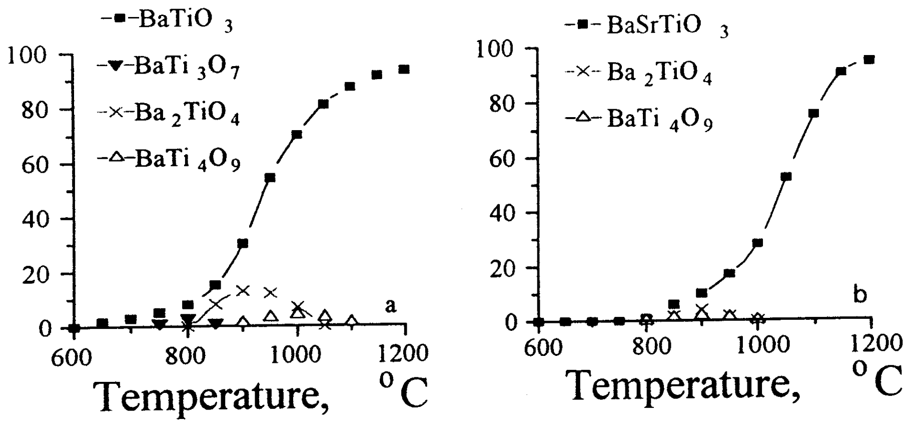

Fig.1 Temperature ranges of existence of phases in the case of synthesis of semiconducting barium titanate in the $BaTiO_3$-TiO_2 system with additives Nb_2O_5 (a), Y_2O_3 + $SrCO_3$ (b).

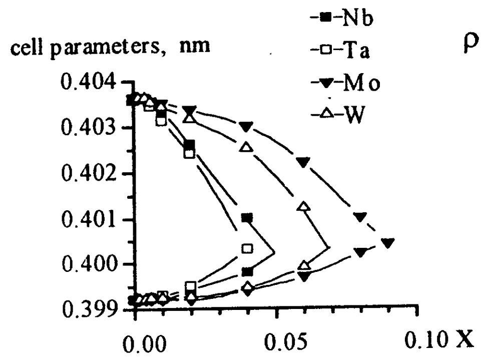

Fig.2 Crystallographic parameters of the $Ba(Ti_{1-x}Me_x)O_3$ ceramic, where Me = Nb, Ta, Mo, W as a function of the degree of aliovalent substitution (x)

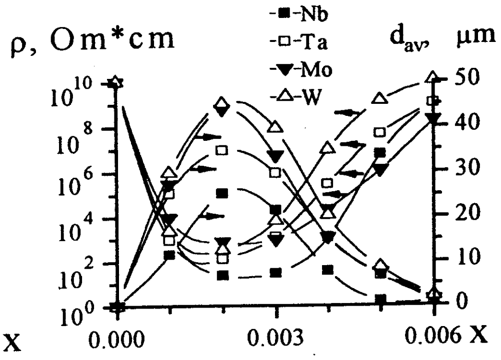

Fig.3 Specific resistance (ρ, 20°C) and average grain size (d_{av}) of the $Ba(Ti_{1-x}Me_x)O_3$ ceramic, where Me = Nb,Ta,Mo,W as a function of the degree of aliovalent substitution (x)

The crystallographic parameters of samples of the $Ba_{1-x}Y_xTiO_3$ system in the range x=0-0.008, the $Ba(Ti_{1-y}Me_y)O_3$ system for Me=Nb, Ta in the range y=0-0.006 and for Me=Mo, W in the range y=0-0.008 are: a=0.3992 nm, c=0.4036 nm, which agrees with data for undoped $BaTiO_3$ [2]. When the dopant content is increased to x,y=0.01, there is a decrease in the splitting of peaks (422) and (224), which is attributed to the presence of a cubic phase along with a tetragonal one in the ceramic. Fig.2 shows plots of the crystal parameters of the samples versus aliovalent substitution concentration in the titanium sublattice. When the niobium, tantalum, molybdenum and tungsten concentration is increased above y=0.05, 0.04, 0.07 and 0.09 respectively, a transition from the tetragonal to the cubic phase takes place. Similar results were obtained in the case of aliovalent substitution of barium by lanthanum [3]. In contrast to the results of ref.[3], no anomaly of the lattice parameters within the concentration range, where a drastic decrease of grain size occurs, was found in the systems under investigation (fig.2).

In the case of isovalent substitution of barium by calcium, a positive deviation from Vegard's law is observed, indicating the presence of microregions with different phase compositions, which are formed during synthesis. Nevertheless, when barium was substituted by strontium, there was no noticeable deviation from Vegard's law.

In the case of aliovalent substitution, the broadest concentration range in which semiconductor properties exist is observed when yttrium is added. The radius and charge value of the aliovalent ions substituting for titanium ions do not affect substantially the ceramic grain size (fig.3). The amount and nature of the temperature dependence of the specific resistance of niobium-, tantalum-, molybdenum- and tungsten-doped ceramic differ only slightly.

When barium is substituted by calcium, strontium or lead, the average grain size decreases. In the case of isovalent substitution of barium ions by ions of smaller radius, compressive strains arise in the crystal lattice, which retard diffusion processes and lead to obtaining a finer grain structure [4].

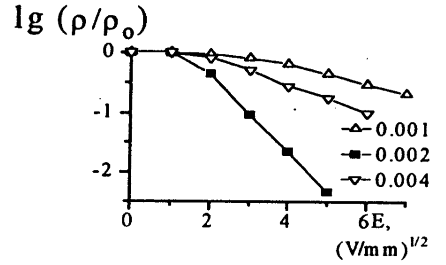

Fig.4 Logarithm of the normalized specific resistance (lg ρ/ρ_o) of the $Ba(Ti_{1-x}Nb_x)O_3$ ceramic as a function of field strength (T=300°C).

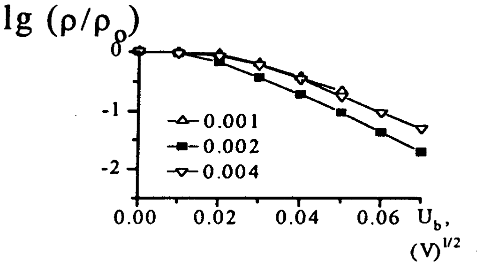

Fig.5 Logarithm of the normalized specific resistance (lg ρ/ρ_o) of the $Ba(Ti_{1-x}Nb_x)O_3$ ceramic as a function of single-boundary voltage (T=300°C).

Investigations of electrophysical properties showed that the strongest varistor effect is observed in ceramic at x=0.006 (yttrium) and at y=0.002 (niobium, tantalum, molybdenum or tungsten) (fig.4). At the same concentrations, the grain size (d_{av}) is a maximum. Fig.5 shows plots of specific resistance normalized with respect to its value at zero voltage versus single-boundary voltage (U_b=E x d_{av}), which were made using data on grain sizes. As can be seen from fig.5, these plots are linear when voltage is over 0.3 V. The dependences of the slope of the linear region of the curve $lg(\rho/\rho_o)=f(U_b)^{1/2}$ on the yttrium, niobium, tantalum, molybdenum and tungsten additive concentration are essentially the same. Similar results were obtained for isovalent-substitution samples. It follows that the ceramic grain size and not the nature of doping ions influences mainly the varistor effect.

4 Conclusion

It was found that aliovalent substitutions in cation sublattices, which give rise to semiconductor properties in $BaTiO_3$, do not change the sequence of barium titanate phase formation reactions and shift the temperature range of existence of intermediate phases towards lower values. Increase in the degree of aliovalent substitution changes the lattice crystal system from tetragonal to cubic one. The radius and charge value of the aliovalent ions substituting for titanium do not affect greatly the ceramic microstructure. In the case of isovalent substitution of barium by calcium, a positive deviation from Vegard's law is observed, indicating the presence of microregions with different phase compositions. Isovalent substitutions hinder the grain growth. The magnitude of varistor effect is mainly determined by the ceramic grain size.

5 References

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