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Phase Transformation in the Synthesis of $Ba(Ti_{1-x}M_x)O_3$-based PTCR Ceramic

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Abstract

Systems based on $BaTiO_3$ with aliovalent substitutions of titanium by niobium, tantalum, molybdenum and tungsten have been investigated. The effect of substitution on the microstructure and electrophysical properties of ceramic is shown. Novel compounds with perovskite structure have been synthesized.

Keywords: powders-solid state reaction, grain growth, grain boundaries, electrical properties, $BaTiO_3$ and titanates.

1 Introduction

Posistor properties, which are coupled with the simultaneous presence of ferroelectric and semiconductive properties, arise on aliovalent substitution in one of the cation sublattices. It was shown earlier that semiconductive properties arise in ferroelectric barium titanate on the aliovalent substitution of barium ions by rare-earth ions as a result of the formation of the solid solution $(Ba^{2+}_{1-x}Ln^{3+}_{x})(Ti^{3+}_{x}Ti^{4+}_{1-x})O_3$ between barium metatitanate ($BaTiO_3$) and rare-earth titanates ($LnTiO_3$).[1] Semiconductive properties can also arise from the aliovalent substitution of titanium by niobium, tantalum, antimony, bismuth, tungsten, molybdenum, rhenium.[2,3] The aliovalent substitution of titanium in barium metatitanate can be deemed to lead to the formation of solid solutions such as $Ba(Ti^{3+}_{x/2}Ti^{4+}_{1-x}M^{5+}_{x/2})O_3$, where M = Nb, Ta, Mo, W. However, there are no data in literature on individual phases, whose formation gives rise to semiconductive properties, and no data on the phases that are formed at grain boundary on oxidation.

Therefore, the aim of the study was to investigate the phases that appear on the aliovalent substitution of titanium and impart semiconductive properties to barium metatitanate and the phases that appear during the oxidation of solid solutions such as $Ba(Ti^{3+}_{x/2}Ti^{4+}_{1-x}M^{5+}_{x/2})O_3$, where M = Nb, Ta, Mo, W.

2 Experimental

All the samples for this investigation were prepared by a conventional solid-state reaction technique. Extra-pure-grade $BaCO_3$, TiO_2, SiO_2 and reagent grade Nb_2O_5, Ta_2O_5, MoO_3, WO_3, titanium metal were used as starting reagents. The samples were sintered in air or in CO/CO_2–nitrogen mixture (extra pure) at 600–1400°C. XRD analysis was carried out on a DRON-3M diffractometer with CuK_α radiation. Ohmic contacts were produced by burning aluminum paste applied to posistor surfaces. The granular structure of as-fired surfaces was examined using a JCXA Superprobe 733 X-ray microanalyzer.

3 Results and Discussion

XRD analysis of $Ba(Ti^{3+}_{x/2}Ti^{4+}_{1-x}M^{5+}_{x/2})O_3$ systems (where M = Nb, Ta, Mo, W) showed that at $x > 0{\cdot}01$ the cubic and tetragonal phases are present in the ceramic at one time. When the concentration of niobium, tantalum, molybdenum and tungsten is increased above $x = 0{\cdot}05$, 0·04, 0·07 and 0·09, respectively, a transition from the mixture of tetragonal and cubic phases to the cubic phase takes place.

The plot of X-ray density against the degree of the aliovalent substitution of titanium by groups V and VI elements has a minimum at $x = 0{\cdot}001$–$0{\cdot}003$ (Fig. 1), which correlates with the maximum of the average grain size of barium metatitanate ceramic

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with aliovalent substitutions of titanium by groups V and VI elements (Fig. 2).

The plots of ceramic resistivity against niobium, tantalum, molybdenum and tungsten concentration pass through a minimum (Fig. 3). The decrease in resistivity in the low impurity concentration region ($x = 0\ldots0{\cdot}002$) is due to an increase in the number of charge carriers; in this case, substitution solid solutions are formed:[2]

$$\mathrm{Ba}((\mathrm{Ti}^{4+}e^-)x\mathrm{Ti}^{4+}_{1-2x}\mathrm{Me}^{5+}_x)\mathrm{O}_3 \equiv \mathrm{Ba}(\mathrm{Ti}^{3+}_x\mathrm{Ti}^{4+}_{1-2x}\mathrm{Me}^{5+}_x)\mathrm{O}_3 \tag{1}$$

The increase in resistance at concentrations above $x = 0{\cdot}002$ is due to the formation of subtraction substitution solid solutions,[2] which lead to a decrease in the number of charge carriers:

$$(\mathrm{Ba}_{1-x/2}\,\square_{x/2})(\mathrm{Ti}_{1-x}\mathrm{Me}^{5+}_x)\mathrm{O}_3,\quad \text{where } \square = \text{barium vacancies} \tag{2}$$

By examining EPR spectra it was found that a large amount of Ti^{3+} ions is present in all solid solutions of the $\mathrm{Ba(Ti_{1\text{-}x}M_{x/2}{}^{5+}{}_x)O_3}$ type (where M = Nb, Ta, Mo, W). It was found that the group VI elements incorporate into perovskite structure in the oxidation state + 5 (Fig. 4).

$\mathrm{Ba}(\mathrm{Ti}^{3+}_{x/2}\mathrm{Ti}^{4+}_{1-x}\mathrm{M}^{5+}_{x/2})\mathrm{O}_3$ solid solutions (where M = Nb, Ta, Mo, W) may be regarded as the result of interaction between compounds with perovskite structure: between barium metatitanate ($\mathrm{BaTiO_3}$), where titanium is in the tetravalent state, and $\mathrm{Ba}(\mathrm{Ti}^{3+}_{1/2}\mathrm{M}^{5+}_{1/2})\mathrm{O}_3$–type compound with trivalent titanium. To ascertain the conditions of existence of individual $\mathrm{Ba}(\mathrm{Ti}^{3+}_{1/2}\mathrm{M}^{5+}_{1/2})\mathrm{O}_3$ compounds

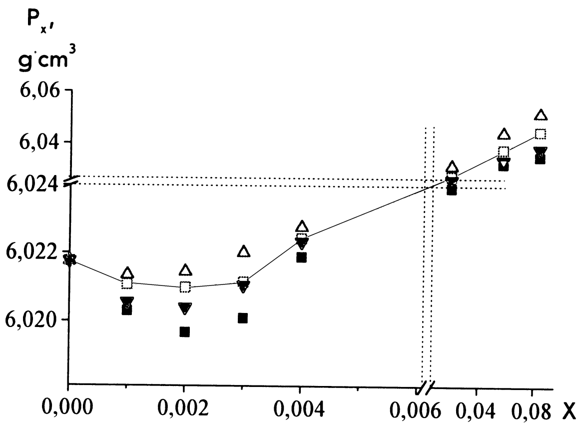

Fig. 1. X-ray density (P_x) of the $\mathrm{Ba(Ti_{1-x}M_x)O_3}$ ceramic as a function of the degree of aliovalent substitution: M = Nb(■); Ta(□); Mo(▼); W(△).

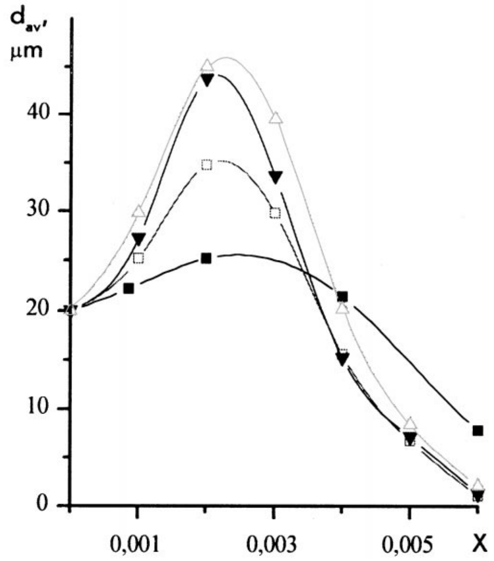

Fig. 2. Average grain size of the $\mathrm{Ba(Ti_{1-x}M_x)O_3}$ ceramic as a function of the degree of aliovalent substitution: M = Nb(■); Ta(□); Mo(▼); W(△).

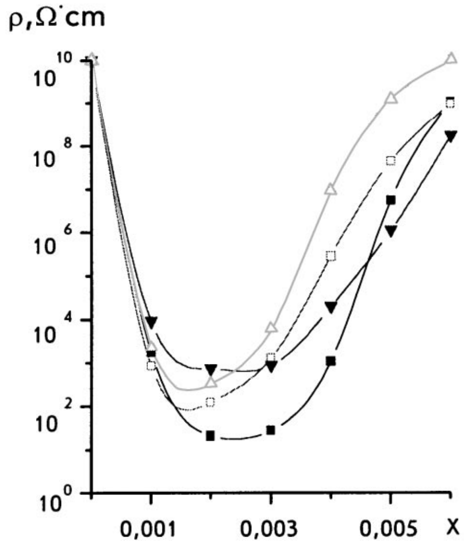

Fig. 3. Resistivity of the $\mathrm{Ba(Ti_{1\text{-}x}M_x)O_3}$ ceramic as a function of the degree of aliovalent substitution: M = Nb(■); Ta(□); Mo(▼); W(△); T = 20°C.

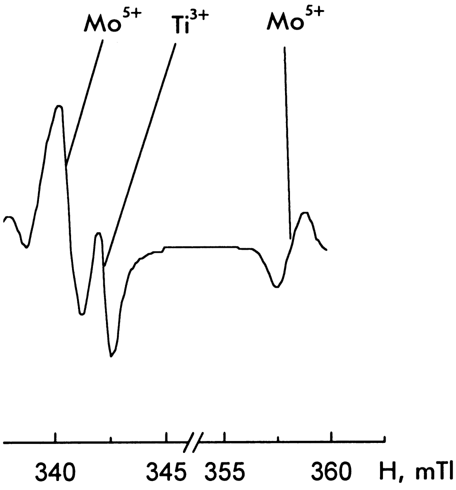

Fig. 4. EPR spectra of the $\mathrm{Ba(Ti_{0{\cdot}999}Mo_{0{\cdot}001})O_3}$ ceramic; $T = 20$°C.

with perovskite structure (where M = V, As, Nb, Ta, Mo, W), steric parameters for complicated perovskite compounds $A(B_x{}',B_{x2}{}''\ldots B_{xL}{}^{(L)})O_3$ (where $\sum_{i=1}^{k} x_i = 1$) were calculated according to Ref. 4. The calculation of steric parameters for individual $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ compounds shows that perovskite structure can only exist when M = Nb, Ta, Mo, W, whereas steric requirements are not met when M = V, As. The results of calculations are in good agreement with experimental data, which indicate that semiconductive properties arise in barium metatitanate only when the formation of $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ perovskites (where M = Nb, Ta, Mo, W) is possible. To corroborate the results of calculations, we carried out synthesis of individual $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ compounds in a CO/CO_2 reducing atmosphere. Niobium, tantalum, molybdenum and tungsten oxides are reduced in a CO/CO_2 atmosphere at temperatures above ~1300, 1500, 600 and 700°C, respectively.[5] Therefore, $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ perovskites (where M = Nb, Ta, Mo, W) can be only synthesized at temperatures below 1300°C (for Nb-containing compounds), 1500°C (for Ta-containing compounds), 600°C (for Mo-containing compounds) and 700°C (for W–containing compounds).

Investigations showed that at about 1200°C, the X-ray diagrams contain only reflections which appertain to the compounds $Ba(Ti_{1/2}Nb_{1/2})O_3$ and $Ba(Ti_{1/2}Ta_{1/2})O_3$ with perovskite structure and cubic crystal system; it was found that the compound $Ba(Ti^{3+}_{1/2}Mo^{5+}_{1/2})O_3$ has a cubic crystal system. Calculated lattice parameters are listed in Table 1.

To elucidate the trivalent titanium oxide formation mechanism, two possible cases were considered:

1. Titanium oxide (TiO_2) is partially reduced, which is accompanied by a weight loss due to oxygen evolution:[6]

$$xTi^{4+}O_2^{2-} \Longleftrightarrow \frac{x}{2}Ti_2^{3+}O_3^{2-} + \frac{x}{4}O_2 \uparrow \qquad (3)$$

2. Partial reduction of barium metatitanate in complex titanium oxides containin barium metatitanate and oxide of groups V and VI elements, which leads to the formation of trivalent titanium oxide (or Magneli phases, Ti_nO_{2n-1}):[7]

$$2BaTiO_3 \rightarrow \frac{1}{2}Ti_2O_3 + \frac{6}{11}Ba_2TiO_4 + \frac{1}{4}O_2 \uparrow \qquad (4)$$

Table 1. Lattice parameters of compounds with perovskite structure and cubic crystal system

Compound	*Lattice parameters (pm)*	*Molecular weight*	$\rho_x (g\,cm^{-3})$
$Ba(Ti_{1/2}Nb_{1/2})O_3$	405·1	255·74	6·39
$Ba(Ti_{1/2}Ta_{1/2})O_3$	406·3	299·76	7·42
$Ba(Ti_{1/2}Mo_{1/2})O_3$	410·3	257·26	6·19

The entropies of reduction reactions (3,4) are positive ($\Delta S > 0$) since these reactions are accompanied by oxygen evolution. The enthalpies of titanium oxide reduction reaction (3) and barium metatitanate reduction reaction (4) are 176 ± 12 and $295 \pm 30\,kJ\,mol^{-1}$ respectively,[6] therefore under equal conditions the reduction of titanium oxideis more probable than that of barium metatitanate. The formation of discrete Magneli phases is only possible at a high degree of reduction ($x \geq 0{\cdot}0278$),[6] which is not the case for the systems under investigation. Thus, the formation of compounds with trivalent titanium involves most probably the reduction of titanium oxide.

The formation of $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$–type perovskite may be represented by the reaction:

$$\begin{aligned} &xBaCO_3 + \frac{x}{4}Ti_2O_3 + \frac{x}{4}M_2O_5 \\ &\quad \rightarrow xBa(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3 + xCO_2 \uparrow \end{aligned} \qquad (5)$$

The phase $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O$, which is unstable in oxidizing atmosphere, is stabilized when it is dissolved in barium titanate according to the reaction:

$$\begin{aligned} &(1 - x)BaTiO_3 + xBaTi^{3+}_{1/2}M^{5+}_{1/2}O_3 \\ &\quad \rightarrow Ba(Ti^{3+}_{x/2} + Ti^{4+}_{1-x}M^{5+}_{x/2})O_3 \end{aligned} \qquad (6)$$

The change to high-resistance ceramic when increasing the groups V and VI elements content can be attributed to vacancy formation in cation lattices:

1. Formation of barium vacancies, which compensate M(V) metal ion excess charge:

$$\begin{aligned} &(1 - \frac{x}{2})BaCO_3 + (1 - x)TiO_2 + \frac{x}{2}M_2O_5 \\ &\rightarrow (Ba^{2+}_{1-x/2}\,\square_{x/2})(Ti^{4+}_{1-x}M^{5+}_{x})O_3 + (1 - \frac{x}{2})CO_2 \uparrow \end{aligned} \qquad (7)$$

This may be represented as follows:[8]
$BaO + M_2O_5 \rightarrow Ba_{Ba} + 2M_{Ti}{}^{\bullet} + 60_O + V_{Ba}{}''$

2. Formation of titanium vacancies, which compensate M (V) metal ion excess charge:

$$\begin{aligned}&BaCO_3+(1-5X)TiO_2+2XM_2O_5\\&\quad\rightarrow Ba(Ti^{4+}_{1-5x}\,\square_x M^{5+}_{4x})O_3+CO_2\uparrow\end{aligned}\qquad(8)$$

This may be represented as follows:[8]

$$5BaO+2M_2O_5\rightarrow 5Ba_{Ba}+4M_{Ti}^{\bullet}+15O_O+V_{Ti}''''$$

The investigations of the ceramic microstructure show a change in grain growth mechanism and corroborate the fact that the character of solid solutions changes as a function of the degree of aliovalent substitution. Examination of EPR spectra of strongly doped specimens shows that barium vacancies are mainly formed. This allows one to conclude that at high degrees of the aliovalent substitution of titanium by groups V and VI elements, conduction electrons are compensated by barium vacancies [eqn (7)], leading to an increase in resistance.

XRD analyses showed that the oxidation of $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ compounds (where M = Nb, Ta) may be represented by the following reaction:

$$\begin{aligned}&Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3+\frac{1}{8}O_2\\&\rightarrow\frac{49}{132}BaTiO_3+\frac{1}{12}Ba_7M_6O_{22}+\frac{1}{132}Ba_6Ti_{17}O_{40}\end{aligned}\qquad(9)$$

XRD analyses showed that the oxidation of the $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$ compounds (where M = Mo, W) to lead to the formation of the phases $BaMO_4$ and $BaTiO_3$, which may be represented by the reaction:

$$Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3+\frac{1}{4}O_2\rightarrow\frac{1}{2}BaTiO_3+\frac{1}{2}BaMO_4\qquad(10)$$

4 Conclusion

Thus, as a result of the investigations carried out it was found that in the case of the aliovalent substitution of titanium by groups V (niobium, tantalum) and VI (molybdenum, tungsten) elements semiconductive properties arise; semiconducting barium metatitanate with the partial substitution of titanium by molybdenum has been obtained for the first time. It was found that the groups V and VI elements incorporate into the solid solution lattice in the oxidation state +5 and that semiconductive properties of barium titanate arise from the formation of a solid solution between barium metatitanate ($BaTiO_3$) and $Ba(Ti^{3+}_{1/2}M^{5+}_{1/2})O_3$–type compound. Novel compounds, $Ba(Ti^{3+}_{1/2}Nb_{1/2})O_3$ and ($Ba(Ti_{1/2}^{3+}Ta_{1/2})O_3$), with perovskite structure and cubic lattice with the parameters $a=405{\cdot}1$ and $406{\cdot}3$ pm, respectively, have been synthesized; there are formed in barium metatitanate on the aliovalent substitution of titanium by group V elements.

It was found that when the solid solution $Ba(Ti^{4+}_{1-2x}Ti^{3+}_xM^{5+}_x)O_3$ is oxidized, barium metatitanate and phases such as $Ba_7M_6O_{22}$, $Ba_6Ti_{17}O_{40}$ (M = Nb, Ta) or $BaMO_4$ (M = Mo, W) are formed at grain boundaries, leading to the appearance of a dielectric interlayer at grain boundaries.

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