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Nb_2O_5-doped $BaTiO_3$ Semiconductor

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Abstract—Semiconducting Nb_2O_5-doped $BaTiO_3$ was prepared and characterized by x-ray diffraction, electron microscopy, thermogravimetry and electrical measurements. The addition of the Nb_2O_5 donor dopant does not affect the sequence of chemical reactions during synthesis of the ceramic material. The effect of microstructure on the semiconducting properties of barium titanate was studied. Electrically stable $(Ba_{1-y}Ca_y)(Ti_{1-x}Nb_x)O_3$ ceramics were prepared.

INTRODUCTION

$BaTiO_3$-based solid solutions are among widely used posistor materials. Posistor properties are known to appear upon heterovalent substitution in one of the cation sublattices. The effect of pentavalent metals (Nb^{5+}, Sb^{5+}, Ta^{5+}), which substitute for titanium in the structure of $BaTiO_3$, was studied in [1–3]. Niobium was found to be an efficient dopant for semiconducting ceramics [1]. The effect of synthesis atmosphere on the grain size of Nb_2O_5-doped ceramics was studied in [2]. Complex impedance analysis [3] showed that only part of the added niobium atoms enter the titanium sublattice and act as donors. Semiconducting properties of Nb_2O_5-doped barium titanate have been studied inadequately. In this work, we synthesized a number of semiconducting materials in the system $(Ba_{1-y}Ca_y)(Ti_{1-x}Nb_x)O_3$ and studied their properties.

EXPERIMENTAL

$BaCO_3$, TiO_2, Nb_2O_5, SiO_2 (all extra-pure-grade) and $CaCO_3$ (reagent grade) were used as starting materials. Synthesis temperature was selected so that the content of free barium oxide after the first thermal treatment was below 1%. Disk-shaped green compacts 10 mm in diameter and 3 mm thick were sintered at 1340–1360°C. Phase transformations were followed thermogravimetrically with a Q-1000 OD-102 device at a heating rate of 10°C/min. Phases were identified by XRD on a DRON-3M diffractometer with CuK_α radiation. To measure lattice parameters, we used the 224 and 422 reflections in the 2θ range from 139° to 144° (accuracy, 0.0005 Å). Electrical properties were measured over a wide range of temperatures and fields. Ohmic contacts were made by firing aluminum paste. Grain size was determined on thermochemically etched surfaces with a JCXA Superprobe 733 x-ray microanalyzer.

RESULTS AND DISCUSSION

The effect of donor dopant (niobium) was studied for the following three systems: $BaCO_3$–TiO_2 (I), $Ba(Ti_{1-x}Nb_x)O_3$ (II) and $(Ba_{1-y}Ca_y)(Ti_{1-x}Nb_x)O_3$ (III), where $x = 0.001$–0.03 and $y = 0.05$–0.2.

TG and XRD data for system I (table) show that $BaCO_3$ decomposes in the temperature range 800–1100°C. Barium oxide reacts with titanium oxide to form $BaTiO_3$, $BaTi_3O_7$, $BaTi_4O_9$, and Ba_2TiO_4. In the range 1000–1100°C, the intermediate phases transform into barium titanate [4, 5]:

$$Ba_2TiO_4 + TiO_2 \longrightarrow 2BaTiO_3,$$

$$BaTi_3O_7 + 2BaO \longrightarrow 3BaTiO_3,$$

$$BaTi_4O_9 + 3BaO \longrightarrow 4BaTiO_3.$$

Doping with Nb_2O_5 (system II) does not change the sequence of chemical reactions during the formation of barium metatitanate and intermediate phases (table) but affects their ratio: the content of barium-rich phase (Ba_2TiO_4) decreases, while that of titanium-rich phases ($BaTi_3O_7$, $BaTi_4O_9$) increases.

The lattice parameters of the material are constant at $a = 3.992$ Å and $c = 4.036$ Å as Nb content rises from 0 to 0.6 mol %, in agreement with earlier [6]. As the Nb content is raised to 1 mol %, the 422 and 224 reflections undergo asymmetrical broadening (Fig. 1), indicating the presence of a cubic phase along with the tetragonal one.

The TG curves of mixtures containing $CaCO_3$ (system III) exhibit endothermic peaks at 850 and 900°C, in accordance with the temperatures of $BaCO_3$ (800–1000°C) and $CaCO_3$ (880–920°C) decomposition.

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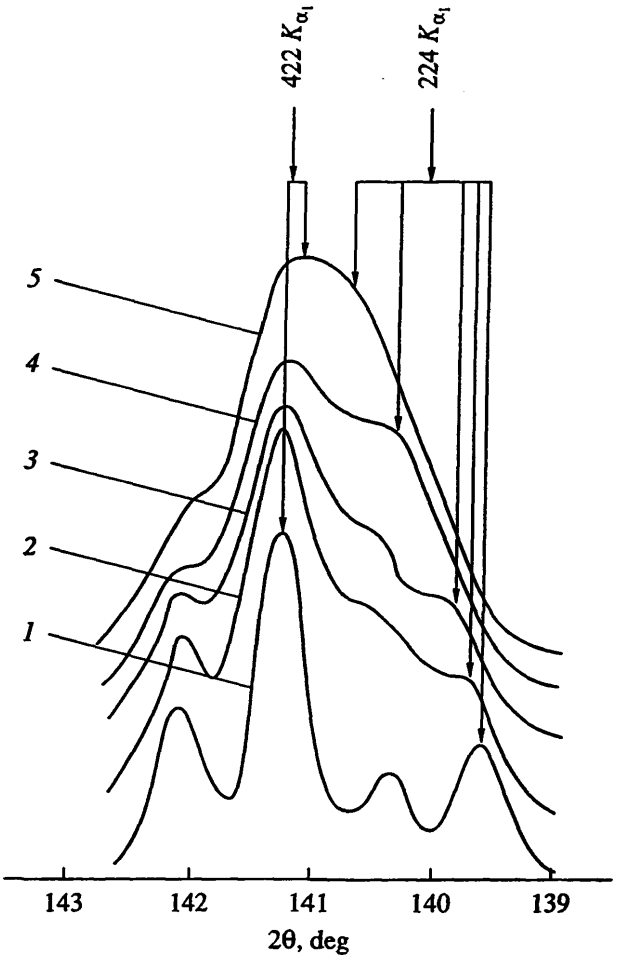

Fig. 1. X-ray diffraction scans of $Ba(Ti_{1-x}Nb_x)O_3$: x = (*1*) 0.001, (*2*) 0.008, (*3*) 0.014, (*4*) 0.02, and (*5*) 0.03.

$(Ba_{1-y}Ca_y)TiO_3$ solid solutions were found to form above 1000°C. The variation of lattice parameters with Ca content (Fig. 2) is similar to that observed in [6]. For all values of y, the measured c parameter is greater than the calculated parameter, indicating the presence of microdomains differing in phase composition [7].

Microstructural studies show that doping with Nb and Ca strongly affects the grain size of the $BaTiO_3$-based

Phase composition of $BaTiO_3$-based materials

t, °C	Phase composition		
	I	II	III*
20–600	$BaCO_3$, TiO_2	$BaCO_3$, TiO_2	$BaCO_3$, $CaCO_3$, TiO_2,
700	$BaCO_3$, TiO_2	$BaCO_3$, TiO_2, $BaTiO_3$	$BaCO_3$, $CaCO_3$, TiO_2, $BaTiO_3$
800	$BaCO_3$, TiO_2, $BaTi_3O_7$	$BaCO_3$, TiO_2, $BaTiO_3$, $BaTi_3O_7$ (tr)	$BaCO_3$, $CaCO_3$, TiO_2, $BaTiO_3$
900	$BaCO_3$, TiO_2, $BaTi_3O_7$	$BaCO_3$, TiO_2, $BaTiO_3$, Ba_2TiO_4, $BaTi_4O_9$	$BaCO_3$, $CaCO_3$, TiO_2, $BaTi_4O_9$ (tr), Ba_2TiO_4, $(BaCa)TiO_3$
1000	$BaTiO_3$, TiO_2, Ba_2TiO_4, $BaTi_4O_9$	$BaCO_3$, TiO_2, $BaTiO_3$, Ba_2TiO_4, $BaTi_4O_9$	$BaCO_3$, TiO_2, $(BaCa)TiO_3$, Ba_2TiO_4, $BaTi_4O_9$
1100	$BaTiO_3$, Ba_2TiO_4 (tr)	$BaTiO_3$	$(BaCa)TiO_3$
1200	$BaTiO_3$	$BaTiO_3$	$(BaCa)TiO_3$

* No Nb was detected by TG and XRD.

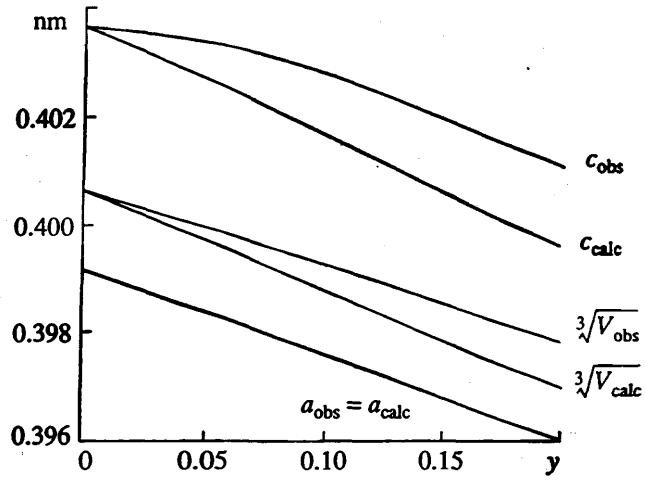

Fig. 2. Lattice parameters vs. Ca content for $(Ba_{1-y}Ca_y)(Ti_{0.998}Nb_{0.002})O_3$ ceramics.

ceramics (Fig. 3). At $x = 0.002$, the electrical resistivity of $Ba(Ti_{1-x}Nb_x)O_3$ $\rho_{20°C}$ exhibits a minimum, while the average grain size d_{av} passes through a maximum (Fig. 4).

Resistivity of the $BaTiO_3$-based semiconducting ceramic is known to be field-dependent (so-called varistor effect) owing to a number of factors, including chemical composition and grain size. The field dependence of electrical resistivity is plotted here in the coordinates $\log(\rho/\rho_0)-\sqrt{E}$ because, for $E > 3$–4 V/mm, it is almost linear [8]. The most prominent varistor effect in $Ba(Ti_{1-x}Nb_x)O_3$ was observed at $x = 0.002$, which corresponds to the maximum grain size (Fig. 5a). At a dopant content fixed at $x = 0.002$, the isovalent substitution of Ca for Ba in $(Ba_{1-y}Ca_y)(Ti_{0.998}Nb_{0.002})O_3$ reduces the varistor effect (Fig. 5b).

The field dependence of resistivity is generally related to the variation in the potential barrier height at grain boundaries [9]. The behavior of such materials in electric fields is determined by the density of grain boundaries, which is inversely related to the average grain size. Our data show (Fig. 6) that the difference between the $\log(\rho/\rho_0) = \varphi(\sqrt{Ed_{av}})$ dependences for $Ba(Ti_{1-x}Nb_x)O_3$ and $(Ba_{1-y}Ca_y)(Ti_{0.998}Nb_{0.002})O_3$ is insignificant; therefore, the influence of doping on the varistor effect is mainly associated with the variation in grain size.

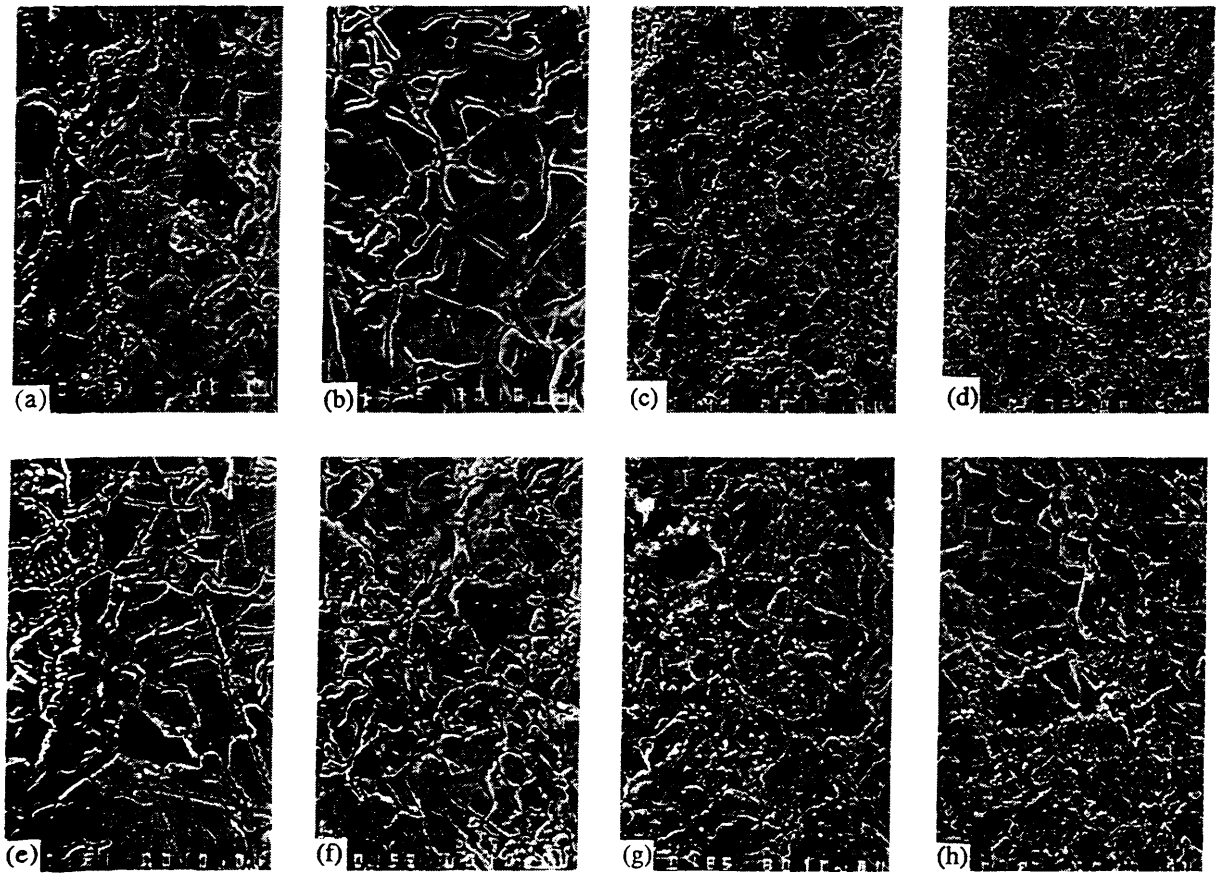

Fig. 3. Microstructure of ceramic materials: (a) $Ba(Ti_{0.999}Nb_{0.001})O_3$, (b) $Ba(Ti_{0.998}Nb_{0.002})O_3$, (c) $Ba(Ti_{0.996}Nb_{0.004})O_3$, (d) $Ba(Ti_{0.994}Nb_{0.006})O_3$, (e) $(Ba_{0.95}Ca_{0.05})(Ti_{0.998}Nb_{0.002})O_3$, (f) $(Ba_{0.9}Ca_{0.1})(Ti_{0.998}Nb_{0.002})O_3$, (g) $(Ba_{0.85}Ca_{0.15})(Ti_{0.998}Nb_{0.002})O_3$, (h) $(Ba_{0.8}Ca_{0.2})(Ti_{0.998}Nb_{0.002})O_3$; ×500.

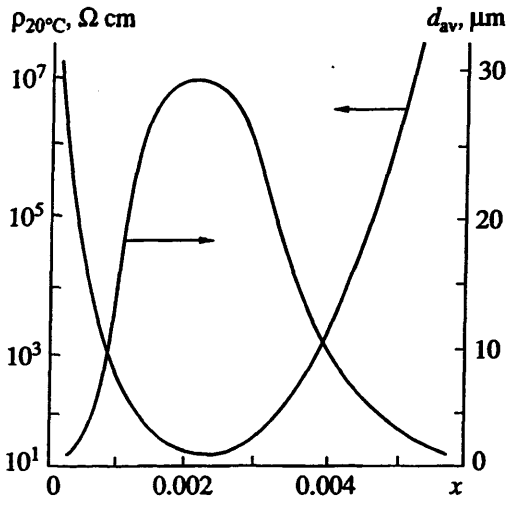

Fig. 4. Resistivity and average grain size vs. Nb content for $Ba(Ti_{1-x}Nb_x)O_3$ ceramics.

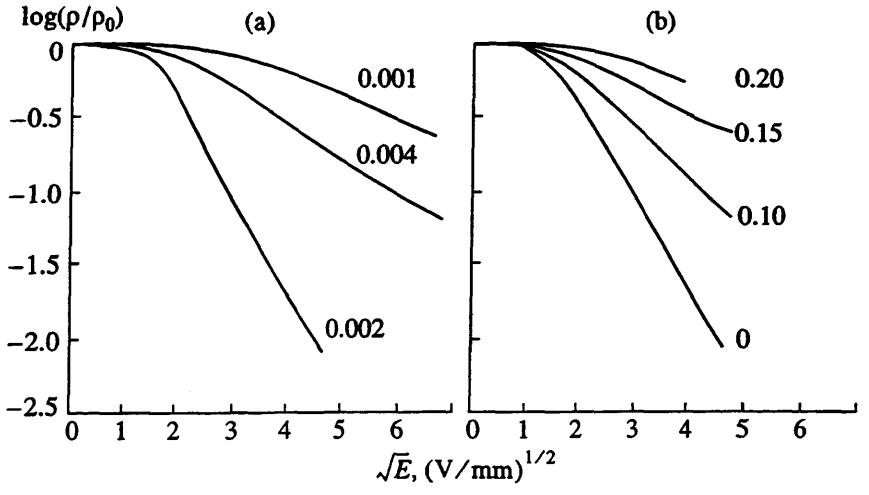

Fig. 5. Log normalized resistivity vs. field strength for (a) $Ba(Ti_{1-x}Nb_x)O_3$ and (b) $(Ba_{1-y}Ca_y)(Ti_{0.998}Nb_{0.002})O_3$ at different x and y; 300°C.

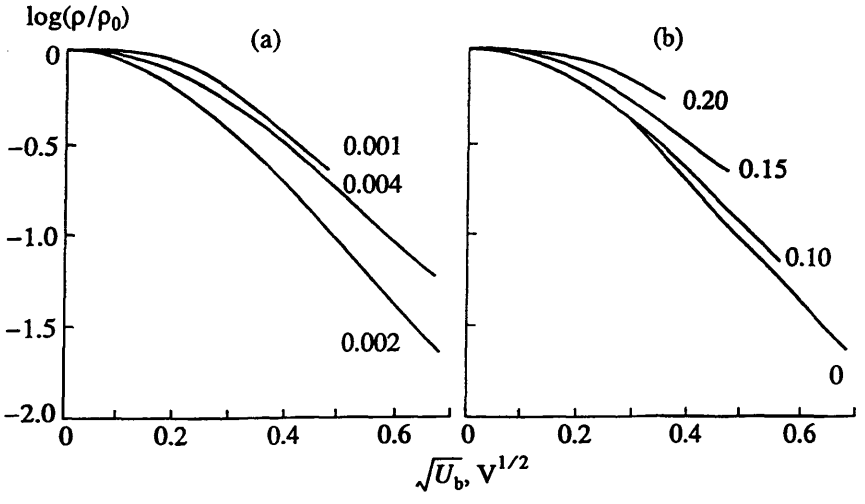

Fig. 6. Log normalized resistivity vs. voltage across an individual barrier for (a) $Ba(Ti_{1-x}Nb_x)O_3$ and (b) $(Ba_{1-y}Ca_y)(Ti_{0.998}Nb_{0.002})O_3$ at different x and y; 300°C.

CONCLUSION

Doping with Nb_2O_5 does not affect the sequence of chemical reactions involved in the synthesis of $BaTiO_3$ ceramics. In the range 0–0.6 mol % Nb, the lattice parameters of $Ba(Ti_{1-x}Nb_x)O_3$ are $a = 3.992$ Å and $c = 4.036$ Å.

The $Ba(Ti_{1-x}Nb_x)O_3$ ceramic exhibits semiconducting properties at x ranging between 0.001 and 0.004. Maximum conductivity is observed at $x = 0.002$.

The dependence of lattice parameters on Ca content for $(Ba_{1-y}Ca_y)(Ti_{1-x}Nb_x)O_3$ exhibits a positive deviation from Vegard's law, which can be explained by the existence of regions differing in phase composition.

Field stability of the ceramics increases upon the addition of Ca because of the diminishing average grain size.

ACKNOWLEDGMENTS

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