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Effect of Fluorine Doping on the Microstructure and Electrical Properties of Barium-Titanate-Based Ceramics

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Abstract—The effect of partial fluorine substitution for oxygen on the properties of $BaTiO_3$ has been studied using thermogravimetry, x-ray diffraction, electron microscopy, complex impedance measurements, and diffuse reflectance spectroscopy. The results indicate that partial fluorine substitution for oxygen influences the composition range of positive temperature coefficient of resistance behavior in ceramics with heterovalent substitution of lanthanum on the barium site.

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INTRODUCTION

Barium-titanate-based semiconductor ferroelectrics, widely used to fabricate materials with a positive temperature coefficient of resistance (PTCR), are commonly prepared via partial heterovalent substitutions on the Ba or Ti site. Titanium can be substituted by Group V ions (e.g., Nb^{5+} and Ta^{5+}) [1, 2], and barium can be substituted by Y^{3+}, La^{3+}, and some lanthanide ions [3, 4]. Relatively small rare-earth ions (Y, Dy–Ho) can substitute on both the barium and titanium sites, whereas larger sized ions have a marked preference for the barium site, in accordance with steric requirements [5, 6]. The high-temperature, conductive form of barium titanate doped with rare-earth metals, e.g., lanthanum, can be represented by the chemical formula $Ba_{1-x}La^{\bullet}_{x}Ti^{4+}_{1-x}Ti^{3+}_{x}O_3$ [7].

The properties of PTCR $BaTiO_3$ doped with lanthanum ions on the barium site have been studied by several groups [8–10]. The PTCR behavior of ceramics is influenced significantly by the characteristics of the grain-boundary barrier. According to the Heywang model, there is a grain-boundary potential barrier, whose height decreases below the ferroelectric transition temperature because of the internal fields associated with the spontaneous polarization of the material [11]. The potential barrier is due to the acceptor levels produced by grain-boundary impurities (e.g., 3*d* transition metals [12]), sorbed oxygen [13, 14], and cation vacancies [15, 16]. The characteristics of the barrier depend significantly on the sintering atmosphere [17]. Studies of fluorine-containing barium titanate without donor doping indicate that sintering in a halogen-containing atmosphere is accompanied by grain-boundary sorption processes, in which the fluorine acts as an acceptor [13, 18]. In addition, some of the sorbed fluorine substitutes on the oxygen site, acting as a donor [19]. The influence of fluorine doping shows up only after subsequent heat treatment in air (reoxidation), which gives rise to a PTCR effect [20]. At the same time, the introduction of fluorine from a fluorine-containing reagent would be expected to insure the incorporation of all the fluorine into the crystal structure of barium titanate. There has been little work on donor doping of barium titanate on both the cation and anion sites.

The objective of this work was to synthesize barium-titanate-based semiconductor ferroelectrics with partial heterovalent substitution of lanthanum ions on the barium site and to investigate the effect of fluorine doping on their properties.

EXPERIMENTAL

The starting chemicals used were reagent-grade LaF_3 and extrapure-grade $BaCO_3$, TiO_2, and La_2O_3. Phase transformations were followed using thermogravimetry (TG) with a Q-1000 OD-102 instrument. The heating rate was 10°C/min. The synthesized materials were characterized by x-ray diffraction (XRD) on a DRON-4-07 powder diffractometer (CuK_α radiation). Lattice parameters were refined by the Rietveld profile analysis method. Diffuse reflectance spectra of polycrystalline samples (powders) were taken on a Perkin-Elmer Lambda-9 spectrophotometer in the UV (200–400 nm) through visible (400–800 nm) spectral region, Crystal data for $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics at different lanthanum fluoride contents (x)

x	0.0005	0.001	0.0025	0.003	0.004	0.005
a, Å	3.9925(2)	3.9932(2)	3.9942(3)	3.9937(2)	3.9938(2)	3.9947(3)
c, Å	4.0341(2)	4.0342(2)	4.0318(3)	4.0324(2)	4.0308(2)	4.0282(3)
V, Å^3	64.302(6)	64.329(6)	64.321(7)	64.315(6)	64.293(6)	64.280(8)
c/a	1.0104	1.0103	1.0094	1.0097	1.0093	1.0084
Ba/La z	0.536(4)	0.533(4)	0.528(6)	0.49(1)	0.50(3)	0.478(7)
O1 z	0.496(9)	0.471(9)	0.534(9)	0.54(1)	0.52(3)	0.52(2)
O2 z	0.05(2)	0.04(3)	0.06(1)	0.02(2)	0.02(3)	–0.02(2)
R_B, %	5.72	6.87	4.18	4.42	4.64	4.66
R_f, %	4.56	6.05	3.40	3.61	3.35	3.56

using fine-particle MgO as a reference material. We measured the spectral dependence of the Kubelka–Munk function $F(R) = (1 - R)^2/2R = k/s$, where R is reflectance, k is the absorption coefficient, and s is the scattering coefficient.

In electrical measurements, we used cylindrical samples synthesized at 1340–1360°C in air. Ohmic contacts were made by firing aluminum paste. The grain size of the ceramics was determined on a JEOL JCXA-733 SuperProbe x-ray microanalyzer. In impedance measurements, we used a Solartron 1260 impedance/gain-phase analyzer in the range 100 Hz to 1 MHz and a VM-560 Q-meter in the range 50 kHz to 35 MHz. The components of the equivalent circuit were identified using the Frequency Response Analyser 4.7 program.

RESULTS AND DISCUSSION

XRD examination showed that both the $(Ba_{1-x}La_x)TiO_3$ and $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramic samples were single-phase and had a tetragonal structure. With increasing lanthanum fluoride content, the tetragonal distortion (c/a) decreases (table). The input data for refining the structural parameters of the samples in space group $P4mm$ by the Rietveld profile analysis method were taken from Evans [21]. The refined unit-cell volumes (V) are presented in Fig. 1. As seen, both $V(x)$ curves have a maximum, whose magnitude far exceeds the present experimental uncertainty. The maximum is attributable to a transition from one charge

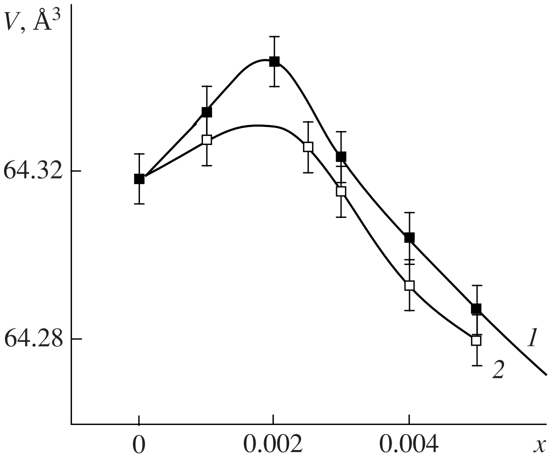

Fig. 1. Composition dependences of the unit-cell volume for (*1*) $(Ba_{1-x}La_x)TiO_3$ and (*2*) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics.

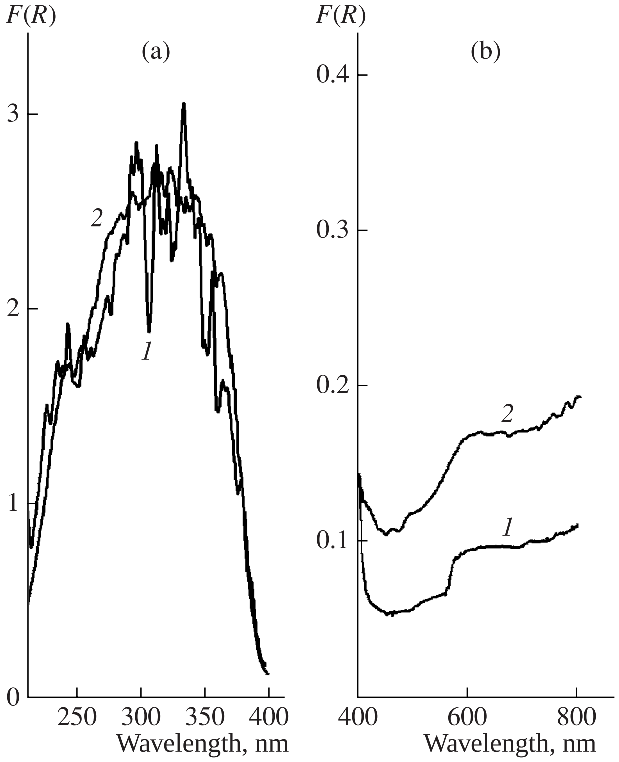

Fig. 2. (a) UV and (b) visible diffuse reflectance spectra of polycrystalline samples of (*1*) $(Ba_{1-x}La_x)TiO_3$ with x = 0.002 and (*2*) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ with x = 0.0025.

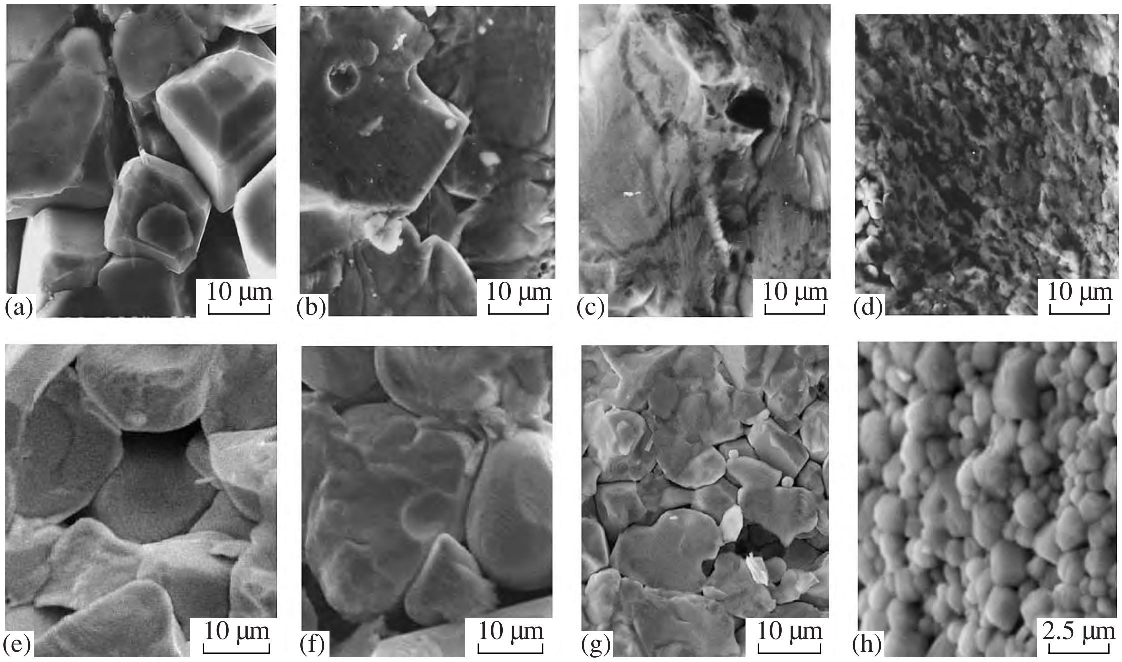

Fig. 3. Microstructures of (a) $BaTiO_3$, (b–d) $(Ba_{1-x}La_x)TiO_3$, and (e–h) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics: x = (b) 0.001, (c) 0.002, (d) 0.003, (e) 0.0005, (f) 0.001, (g) 0.003, (h) 0.004.

compensation mechanism to another [22]. In particular, the rise in unit-cell volume may be due to the formation of Ti^{3+} ions, whose content decreases as x deviates from the maximum in $V(x)$.

The diffuse reflectance spectra in Fig. 2 provide additional evidence that our samples contain titanium ions in reduced form. The UV diffuse reflectance spectra of the doped barium titanate samples show a strong structureless band centered around 300 nm (Fig. 2a), due to the $O^{2-} \longrightarrow Ti^{4+}$ charge transfer [23, 24]. At the same time, the visible-range spectra of the La_2O_3- and LaF_3-doped $BaTiO_3$ samples show a well-defined absorption band (Fig. 2b) with a broad maximum at 500–600 nm. This band is due to the 3*d*–3*d* intrashell transitions of the Ti^{3+} ions resulting from the heterovalent substitution [23, 24]. The relative intensities of the spectral curves indicate that the introduction of LaF_3 produces a higher Ti^{3+} concentration in comparison with La_2O_3.

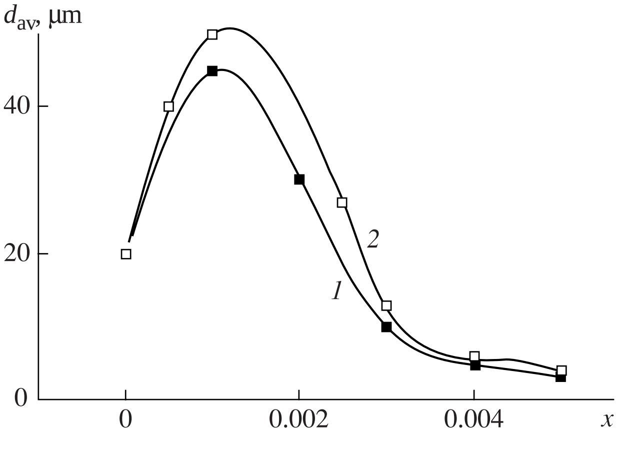

Fig. 4. Composition dependences of the average grain size for (*1*) $(Ba_{1-x}La_x)TiO_3$ and (*2*) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics.

Microstructural examination showed that both the $(Ba_{1-x}La_x)TiO_3$ and $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics with $x \leq 0.002$ consisted of coarse grains (Fig. 3), due to abnormal grain growth [25]. The composition dependences of the average grain size (Fig. 4) demonstrate that, over the entire range of doping levels studied, the fluorine-containing ceramics consisted of coarser grains compared to the fluorine-free ceramics with the same lanthanum content.

The temperature dependences of resistivity for the $(Ba_{1-x}La_x)TiO_3$ and $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics (Fig. 5) demonstrate that the $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ system exhibits PTCR behavior in a broader composition range compared to $(Ba_{1-x}La_x)TiO_3$.

The $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics have low room-temperature resistivities in a wider concentration range compared to $(Ba_{1-x}La_x)TiO_3$. In particular, the 20°C resistivity of the doped ceramics is below 10^3 Ω cm in the range $0.001 < x < 0.002$ in the $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ system and in a substantially broader range, $0.0006 < x <$

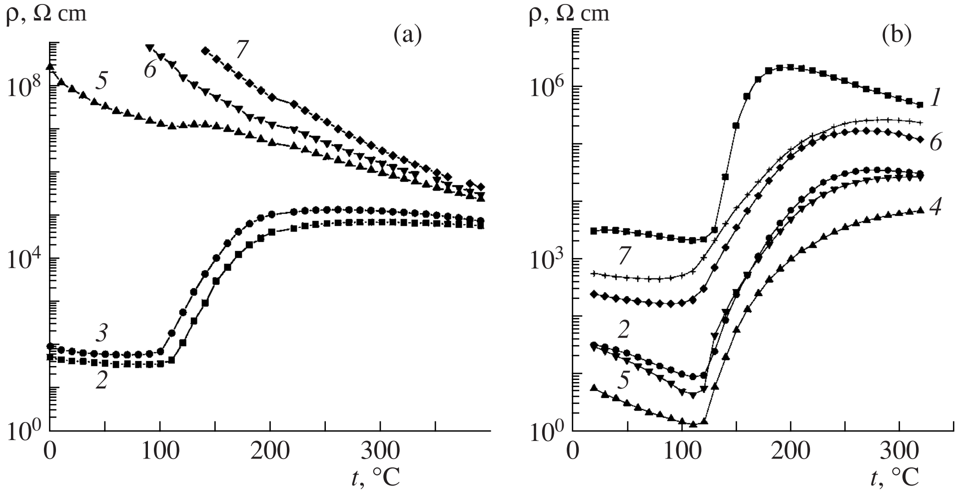

Fig. 5. Temperature dependences of resistivity for (a) $(Ba_{1-x}La_x)TiO_3$ and (b) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics: x = (*1*) 0.0005, (*2*) 0.001, (*3*) 0.002, (*4*) 0.0025, (*5*) 0.003, (*6*) 0.004, (*7*) 0.005.

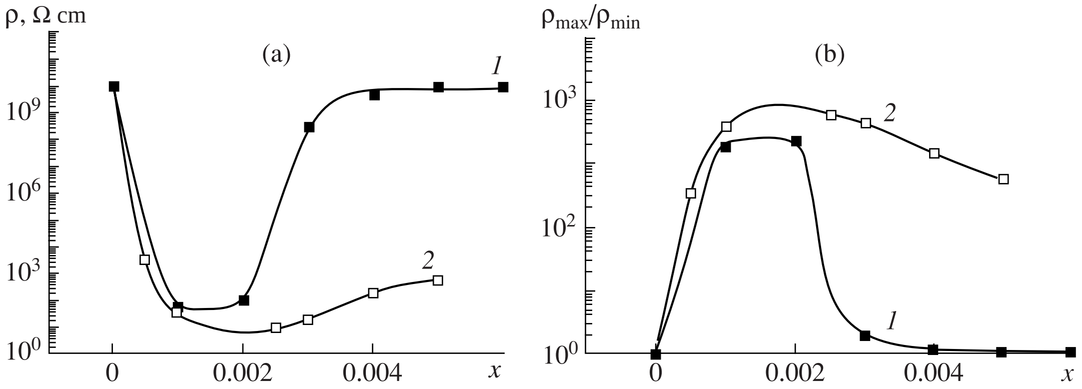

Fig. 6. Composition dependences of (a) 20°C resistivity and (b) $ρ_{max}/ρ_{min}$ for (*1*) $(Ba_{1-x}La_x)TiO_3$ and (*2*) $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramics.

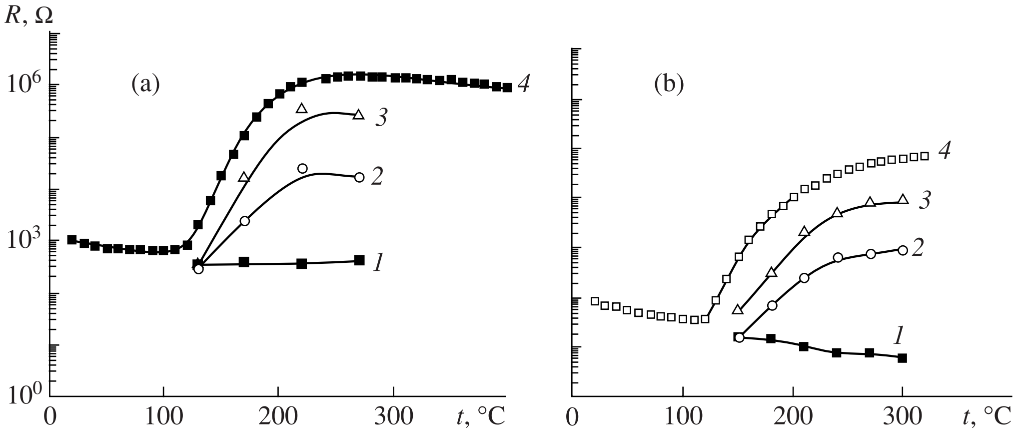

Fig. 7. Resistances of the grain bulk (*1*), outer layer (*2*), and grain boundaries (*3*) and the total resistance (*4*) as functions of temperature for (a) the $(Ba_{1-x}La_x)TiO_3$ ceramic with $x = 0.002$ and (b) the $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramic with $x = 0.0025$.

0.005, in the $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ system (Fig. 6a). In addition, partial fluorine substitution on the oxygen site broadens the maximum in ρ_{max}/ρ_{min} as a function of lanthanum content (Fig. 6b).

The grains in barium-titanate-based semiconductor ferroelectric ceramics are known to comprise several regions differing in electrical properties: the grain bulk, grain boundaries, and a layer between the grain bulk and boundaries [26]. To assess the effect of fluorine doping on the conductivities of these regions, we used complex impedance analysis.

The samples for impedance measurements were close in average grain size, $d \simeq 25$ μm (see Fig. 4). The electrical characteristics of the grains in the $(Ba_{1-x}La_x)TiO_3$ ceramic with $x = 0.002$ and the $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ ceramic with $x = 0.0025$ are presented in Fig. 7. It can be seen that, below the transition temperature (about 120°C), the resistance of the ceramics is dominated by the contribution from the grain bulk in both types of solid solutions. Partial fluorine substitution for oxygen in doped barium titanate reduces the resistance of the grain bulk.

CONCLUSIONS

At room temperature, doped barium-titanate-based ceramics in the $(Ba_{1-x}La_x)TiO_3$ and $(Ba_{1-x}La_x)Ti(O_{1-x}F_x)_3$ systems ($x < 0.005$) have a tetragonal unit cell. The unit-cell volume of the ceramics as a function of x has a maximum. The rise in unit-cell volume is attributable to the formation of Ti^{3+} ions, as supported by the diffuse reflectance spectra of the semiconductor ferroelectrics studied. The introduction of lanthanum fluoride into barium titanate extends the composition range of PTCR behavior and reduces the resistance of the grain bulk in the ceramics.

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