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ESR Study of $BaTiO_3$ Ceramics Doped by Y and Ca

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Electron spin resonance (ESR) investigation of $BaTiO_3$ ceramics doped by Y and Ca has been presented. It is shown that the most intensive resonance line belongs to the Ti^{3+}-Y^{3+} paramagnetic complex. The essential decrease of Ti^{3+}-Y^{3+} ESR spectra intensity in comparison with that in samples without Ca is revealed. This gives evidence that Ca ions decrease the number of Y^{3+} ions substituted for Ba ions and so the number of the Ti^{3+}-Y^{3+} centers decreases. It was shown that grain size of $BaTiO_3$ ceramics became smaller under Ca doping though the temperature region of the effect of positive temperature coefficient of resistivity remain practically unchanged.

Keywords: ceramics; ESR; paramagnetic center; PTCR effect

INTRODUCTION

One of the most important properties for the practical applications of $BaTiO_3$ ceramics is positive temperature coefficient of resistivity (PTCR). This effect is usually ascribed to the occurrence of the grain boundary layers, which are strongly affected by the bulk cubic to tetragonal phase transition [1]. Impurities influences on the PTCR and grain size has been widely studied by many authors [2-9]. M. Kchikech et al. [10] investigated $BaTiO_3$ ceramics doped by La. It was shown that ionization of $Ti^{4+} \rightarrow Ti^{3+}$ is related to heterovalent La^{3+}/Ba^{2+} substitution. Because of presence of Mn^{2+} as unavoidable impurities La doping made it possible to investigate Mn^{2+} spectrum. The latter can be useful to detect the presence of cubic or rhombohedral phases at room temperature. Both ESR and X-ray data has shown that $BaTiO_3$: La system containing more than 5 at % La is in a cubic phase at T = 300K. T.R.N. Kutty et. al. [11] studied La, Ce and Nd doped $BaTiO_3$ ceramics in a wide temperature range 78 - 525 K. The PTCR effect was supposed to be related to the activation of trap centers (like V_{Ba}) on grain boundaries [7]. In our previous paper [12] we reported the results of the ESR investigation and the influence of rare-earth ions doping on the conductivity and on the PTCR effect. The correlation between intensity of the paramagnetic centers and electrical resistivity was revealed. The observed correlation showed an essential role of the Ti^{3+} - Ln^{3+} (Ln^{3+} is rare-earth ion) complexes in the appearance of $BaTiO_3$ ceramics semi-conducting properties and the PTCR effect.

In the present work we investigated $BaTiO_3$ ceramics doped by Y and Ca. Such doping made it possible to obtain ceramic samples with small grain sizes although the temperature region of the PTCR effect remained practically unchanged. To find out the mechanism of this phenomenon as well as to understand the nature of centers responsible for aforementioned effect we performed ESR spectra measurements of these ceramics. The resistivity measurements as well as microstructure study are presented.

SAMPLES AND EXPERIMENTAL DETAILS

$BaTiO_3$ ceramic samples doped by Y and Ca were fabricated by a conventional solid-phase reaction technique. Extra pure $BaCO_3$ (purity >99.999 %), TiO_2, Y_2O_3, CaO (purity > 99.99 %) were used. The temperature of synthesis was chosen such a way that the concentration of free barium oxide after first treatment was not higher than 1 %. The yttrium content in the samples was 0.002; 0.004; 0.006; 0.008 and 0.01. These values correspond to the concentrations of 0.2; 0.4; 0.6; 0.8 and 1.0 at %. The Ca content was 5, 10, 15, 20, 25, 30 and 35 at % for each yttrium concentration. The ratio of components was taken in accordance with the formula $Ba_{1-x-y}Y_xCa_yTiO_3$. In order to ensure liquid-phase sintering, a sufficient amount of TiO_2 was added to produce 1 at % excess of Ti over the stoichiometric quantity [13]. A small amount of SiO_2 was also added as a sintering aid [14]. The pellet specimens about 3 mm in thickness and 10 mm in diameter were prepared by the semidry molding method with an organic binder and sintered at 1340 - 1360^{0}C in air atmosphere. The cooling rate for all samples was 300^{0}C h^{-1}. The ohmic contacts for resistivity measurements were fabricated by firing Al paste. The grain sizes were measured using the JCXA Superprobe 733 microanalyzer. ESR spectra were recorded at 9.4 GHz spectrometer operating at room temperature (T = 300 K).

ESR SPECTRA MEASUREMENT

The ESR spectra of $BaTiO_3$ ceramic samples doped by yttrium (Y) and calcium (Ca) are presented in Fig. 1. To point out the influence of the

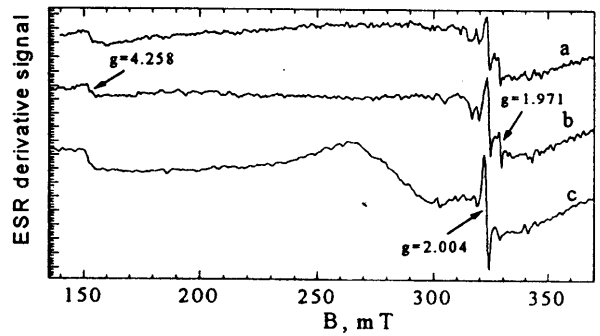

FIGURE 1. ESR spectra of $BaY_{0.002}Ca_yTiO_3$ ceramics doped by Ca: a) y=0.1, b) y=0.15, c) y=0.25.

Ca and Y doping in Fig. 2 the ESR spectra of nominally "pure" (undoped) $BaTiO_3$ ceramics and doped only by Y are also depicted. In

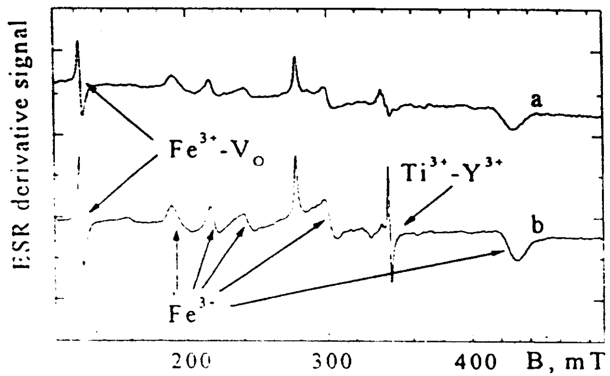

FIGURE 2. The ESR spectra of "pure" $BaTiO_3$ (a) and $BaY_{0.002}TiO_3$ (b)

our previous paper [15] we presented ESR studies of "pure" and doped by rare-earth ions $BaTiO_3$ ceramics in a wide temperature region 77 - 400 K. It was shown that the most intensive ESR lines in undoped sample belong to the Fe^{3+} and axial Fe^{3+} -V_o centers. After Y doping intensive resonance line with g-factor 1.971, which belongs to Ti^{3+}-Y^{3+} paramagnetic center was observed. The reason of the appearance of Ti^{3+}-Y^{3+} centers can be the necessity of rare-earth ion excess charge compensation. The influence of Y doping on the intensity of Ti^{3+}-Y^{3+} ESR spectra in a wide interval of concentration x = 0.002 - 0.01 is depicted in Fig. 3. The measurement of temperature dependence of ESR spectrum has shown that ESR with line g = 1.971 exists only in the tetragonal phase and disappears in the cubic phase. The reason of this disappearance can be sharp temperature dependence of the spin-lattice relaxation time, which is known to be characteristic of Ti^{3+} ions.

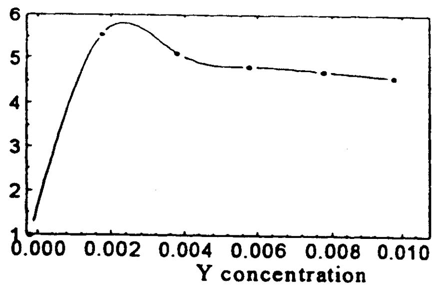

FIGURE 3. The influence of Y doping on the ESR line intensity of Ti^{3+}- Ln^{3+} center in BaY_xTiO_3 ceramics. The intensity of Ti^{3+}-Y^{3+} ESR line is normalized on that of the line in undoped $BaTiO_3$ ceramics.

In $BaTiO_3$ ceramics doped by Y and Ca the Ti^{3+} - Y^{3+} (g = 1.971) ESR spectrum as well as a new ESR lines with g-factors 2.004 and g = 4.258 are observed. As it is seen from Fig. 1, the intensity of the ESR line g=2.004 increases under Ca concentration increasing. In $BaTiO_3$ ceramics ESR line with close value of g-factor (g = 2.005) belonging to cubic Fe^{3+} center has been described by T. Sakudo [16]. In our view Ca doping leads to creation of small amount of cubic phase on grain boundaries and so cubic Fe^{3} center can be observed. Note that the ESR line g=4.258 could arise from Fe^{3+} center when the symmetry becomes lower than axial.

We have to emphasize that for fixed Ca content, yttrium doping leads to the Ti^{3+} - Y^{3+} ESR line intensity decrease and for the fixed Y concentration Ca doping leads to decreasing of aforementioned line intensity (see Fig. 4). The reason of such dependence can be the decreasing of number of Y ions substituted for Ba ions in crystalline lattice (see e.g. [15]).

THE PROPERTIES OF $BaY_xCa_yTiO_3$ CERAMICS

The properties of $BaTiO_3$ ceramics are strongly dependent on the concentration of dopants, phase content and grain size of these

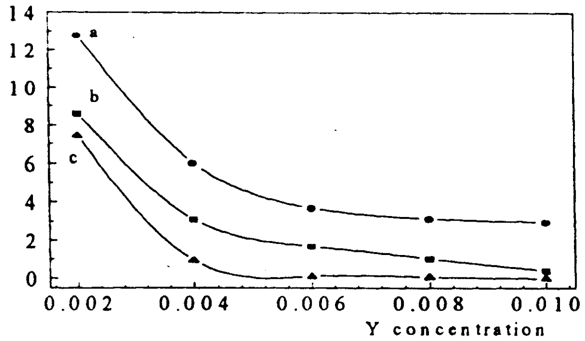

FIGURE 4. The influence of Y and Ca doping on the Ti^{3+}-Y^{3+} ESR line intensity in $BaY_xCa_yTiO_3$ ceramics. a) y=0.05, b)y=0.15, c) y=0.25. The intensity of Ti^{3+}-Y^{3+} ESR line is normalized on that of the line in undoped $BaTiO_3$ ceramics.

materials [17]. The influence of Ca and Y doping on resistivity and microstructure was studied at room temperature. We also investigated the temperature dependency of resistivity of these materials.

In Fig. 5 the influence of Y and Ca doping on $BaY_xCa_yTiO_3$ ceramics resistivity is presented. As it is seen from Fig. 5 in samples doped only by Y a minimum in resistivity is observed at Y concentration x = 0.004. Ca doping leads to increase of resistivity. Simultaneously, we observed decreasing of Ti^{3+} - Y^{3+} donor impurity concentration (see Fig.1), which is necessary for the PTCR effect appearance. This gives us evidence that Ca doping decreases the number of Y ions substituted for Ba ions and so the region of rare-earth's ions concentration, where PTCR effect arises, becomes more narrow. Note that for the samples with Y concentration x = 0.002 Ca doping leads to resistivity decreasing in comparison with $BaYTiO_3$ (curve a in Fig.5). Ca doping of the samples with x ≥ 0.004 results in resistivity rise.

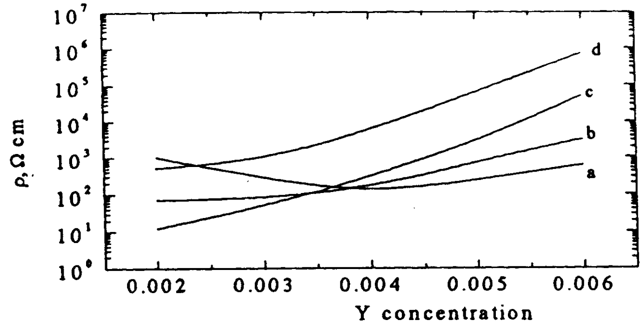

FIGURE 5 The influence of Y and Ca doping on $BaY_xCa_yTiO_3$ ceramics resistivity: a) y = 0; b) y = 0.05; c) y = 0.15; d) y = 0.25. T = 300 K

The influence of Ca doping on PTCR effect of $BaY_{0.004}Ca_xTiO_3$ ceramics is depicted in Fig. 6.

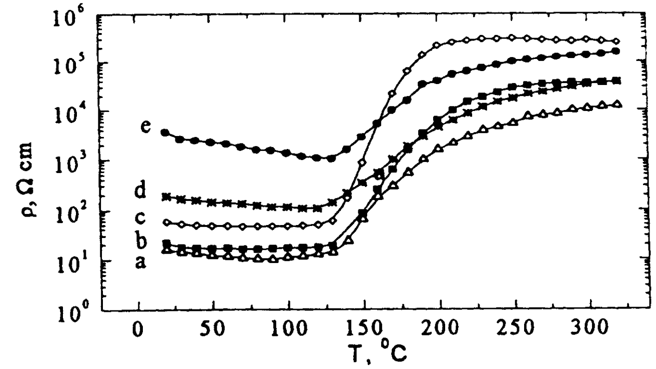

FIGURE 6. **The temperature dependency of resistivity of $BaY_{0.004}Ca_yTiO_3$ ceramics doped by Ca: a) y = 0; b) y = 0.05; c) y = 0.1; d) y = 0.15; e) y = 0.25.**

As it is seen, Ca doping leads to resistivity increasing at room temperature. The PTCR effect is maximal for y = 0.1 (see curve c in Fig.6) its value being more than two times large than in sample with y = 0. The temperature region of this effect remains unchanged under Ca and Y doping. The increasing of resistivity under Ca doping we explained by decreasing of the Ti^{3+} - Y^{3+} centers number (see Fig. 1). Grain size decrease and, therefore, the increasing of the numbers of the grains boundaries layers can influence on the resistivity also. To check this assumption the analysis of microstructure was carried out. From the microstructure data the average grain size of $BaY_xCa_yTiO_3$ samples were estimated and the results obtained for $BaY_{0.002}Ca_xTiO_3$ ceramic samples are presented in Fig. 7.

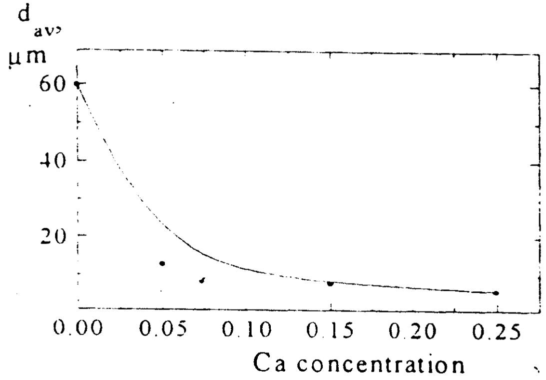

FIGURE 7 The influence of Ca doping on average grain size of the $BaY_{0.002}Ca_xTiO_3$ ceramics.

As it was shown in [17] donor-doped fine-grained $BaTiO_3$ ceramics are more insulating ($\rho \geq 2.4*10^6$ Ω*cm), whereas the same ceramics with grain size above 25 µm show lower resistivity ($\rho \leq 1*10^4$ Ω*cm). In our studies the Ca concentration increasing leads to resistivity rise (see Fig. 6) and grain size decreasing (Fig. 7) that is in qualitative agreement with [17].

CONCLUSIONS

In present paper the study of $BaTiO_3$ ceramics doped by Y and Ca in a wide range of both impurities concentrations have been performed. It was revealed the correlation between ESR intensity of Ti^{3+} - Y^{3+} centers and the resistivity of these samples. We observed essential decrease of Ti^{3+} - Y^{3+} ESR spectra intensity in comparison with those in samples without Ca. These data confirm evidence that Ca ions decrease the number of Y^{3+} ions substituted for Ba ions and so the region of rare-earth ions concentration, where PTCR effect arises, becomes more narrow. Ca doping leads to resistivity rise, grain size decreasing and change of the PTCR effect. Therefore we can conclude that Ti^{3+} - Y^{3+} centers as well as grain size of these materials can be responsible for appearance and value of PTCR effect observed in $BaY_xCa_yTiO_3$ ceramics.

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