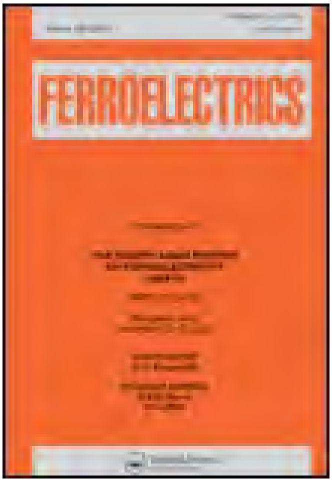

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Impurity and Intrinsic Defects in Barium Titanate Ceramics and Their Influence on PTCR Effect

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An electron spin resonance (ESR) study of $BaTiO_3$ ceramics doped by niobium or tantalum is presented. In both series of the samples six intensive lines corresponded to Mn^{2+} spectrum was observed. The intensity of the spectra increases with tantalum or niobium concentration increases. Besides Mn^{2+} spectrum we observed a single line with $g = 1.971$. The intensity of this line depends on the impurity concentration. The mechanism of excess positive charge compensation of Nb^{5+} or Ta^{5+} ions substituted for Ti^{4+} in perovskite type lattice is analyzed. The influence of tantalum and niobium impurities, their charge states and position in the lattice on PTCR effect is discussed as well.

Keywords: Barium titanate ceramics; ESR; impurity; posistor effect

1. INTRODUCTION

Ferroelectric barium titanate is a well known dielectric material, which reveals semiconductor properties when doped with transition metals. Suitably doped $BaTiO_3$ exhibits an interesting electrical property, the so-called PTCR effect—positive temperature coefficient of resistivity above the Curie temperature, i.e. above T_C resistivity increases stepwise by several orders of magnitudes. This increasing resistivity is useful for various technical applications, for instance, as PTC thermistors. The transition metal or rare-earth-doped $BaTiO_3$ has been studied extensively and much effort has been devoted to understand the PTCR mechanism as well as the type and concentration of suitable dopants (see, for instance Refs. [1, 2]).

Several articles were devoted to explain the PTCR effect in terms of change of the potential barrier height at grain boundaries, taking into account the fact that the barrier height varies inversely to the dielectric constant

[3–5]. Because the dielectric constant above T_C obeys the Curie-Weiss law, the model gives an exponential resistivity increase above T_C. This simple model, called “Heywang model”, has been modified by several authors [6, 7] to explain the low resistivity below Curie temperature and the anomalous current-voltage characteristics. However, several recent articles have pointed out that the thermal activation of the traps above T_C may play an important role in the PTCR effect. For a detailed and precise understanding of PTCR effects, it is necessary to evaluate the electric properties of the grain boundary and the bulk grain separately. Since semiconductor properties of barium titanate strongly depends on impurities and since electron spin resonance is the most sensitive method to their detection, we began a systematic study of $BaTiO_3$ ceramics by ESR [1, 8, 9]. In these works we studied $BaTiO_3$ ceramics doped by rare-earth elements to produce semiconducting properties. These properties can be created by Ta or Nb impurities as well. Both impurities provide low resistivity at room temperature with high resistivity jump above T_C. Recently it was shown [10] that the conductivity of Nb-doped barium titanate has a polaronic character. Polaronic conduction has also been pointed out for other n-type $BaTiO_3$ doped with La and Gd, although the polaronic conductivity has been controversial for long time [11]. For better understanding of the transport properties, including the PTCR effect, and for the development of ceramic materials of higher performance it is important to clarify the mechanism of low-temperature conduction in $BaTiO_3$ ceramics as well as the charge states of various impurities and intrinsic defects.

In the present work, we studied ceramic samples of barium titanate doped by Nb or Ta ions. Several paramagnetic centers were revealed; one of which was ascribed to the perturbed Ti^{3+} ion. The dependence of ESR spectra intensity and electrical resistivity on niobium or tantalum concentrations is presented. The observed correlation in their behavior showed an essential role of the revealed paramagnetic complex in the appearance of $BaTiO_3$ ceramic semi-conducting properties as well as on the effect of positive temperature coefficient of resistivity. A mechanism of charge compensation and the origin of the PTCR effect is discussed.

2. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Ceramic samples of $BaTiO_3$ doped by Nb or Ta were fabricated by a conventional solid-phase reaction technique. The temperature of synthesis was chosen such that the concentration of free barium oxide after the first treatment was not higher than 1%. The Nb or Ta ions content in the samples was X = 0.1; 0.2; 0.4; 0.6; 0.8 and 1 at.%. 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°C in air atmosphere. The cooling rate for all samples was 300°C h^{-1}. The ohmic contacts for resistivity measurements were fabricated by firing Al paste. Phase content of the obtained materials was examined by XRD of powders. ESR spectra were recorded at room temperature on a spectrometer operating at $\nu = 9.4$ GHz. Resistivity measurements were carried out in the temperature interval 20–400°C.

3. EXPERIMENTAL RESULTS AND DISCUSSION

ESR spectra measured at T = 300 K in $BaTiO_3$ ceramics doped by niobium are presented in Fig. 1. One can see, that at low Nb concentration (X < 0.6 at.%) only one intense ESR line with a g-factor value 1.971 is observed. The intensity of this line changes nonlinearly as the Nb concentration increases. After a marked maximum at 0.2 at.% it starts to decrease until it's complete disappearance above 1 at.% Nb. The dependence of the ESR intensity on the niobium concentration is depicted in Fig. 2.

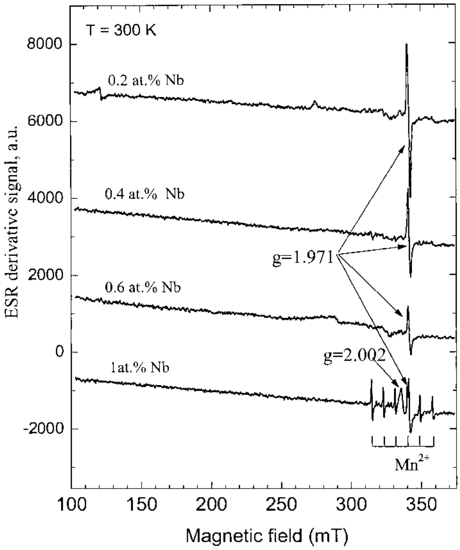

Figure 1. EPR spectra in $BaTiO_3$ ceramic samples doped by Nb.

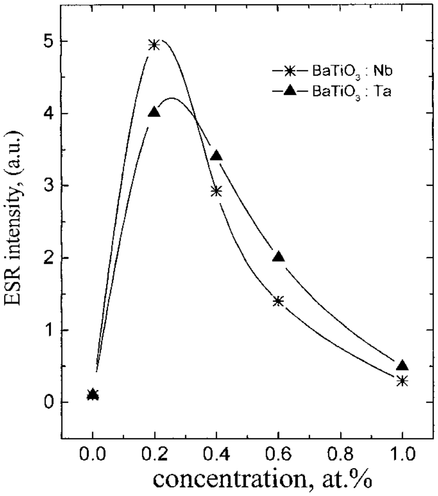

Figure 2. Dependence of the ESR line (g = 1.971) intensity in $BaTiO_3$ ceramics doped by Nb or Ta on dopants concentration.

When the concentration of the Nb ions in $BaTiO_3$ ceramics increases (X > 0.6 at.%), additional intensive ESR spectra appear. A well resolved hyperfine structure containing six lines is observed in the magnetic field 310–380 mT (g ∼ 2). This hyperfine sextet is characteristic of the ^{55}Mn isotope with nuclear spin I = 5/2. The spectra parameters of the sextet (g = 2.003 and |A| = 8.8 mT; A is coupling constant) reveals unambiguously traces of Mn^{2+}. Among these spectra lines in the samples with Nb content X > 0.6 at.% we observed a wide ESR line with g-factor value 2.002. The intensity of this line increases with increasing Nb concentration.

ESR spectra of Ta–doped barium titanate ceramics are depicted in Fig. 3. One can see that the spectra are the same at those we observed in $BaTiO_3$ samples doped by niobium: Mn^{2+} spectra and ESR line with g-factor values of 1.971 and 2.002 are detected. However in the Ta-doped barium titanate the Mn^{2+} spectrum as well as the ESR line with g = 2.002 appear when the tantalum concentration is more than 0.2 at.%. The dependence of Mn^{2+} ESR intensity on Ta concentration is depicted in Fig. 4. We also observed the same behavior for the ESR line with g-factor 2.002.

The character of the dependence of the ESR line with g = 1.971 intensity on tantalum concentration is qualitatively similar to that which we observed for niobium doped samples (Fig. 2). Because the ESR line (g = 1.971)

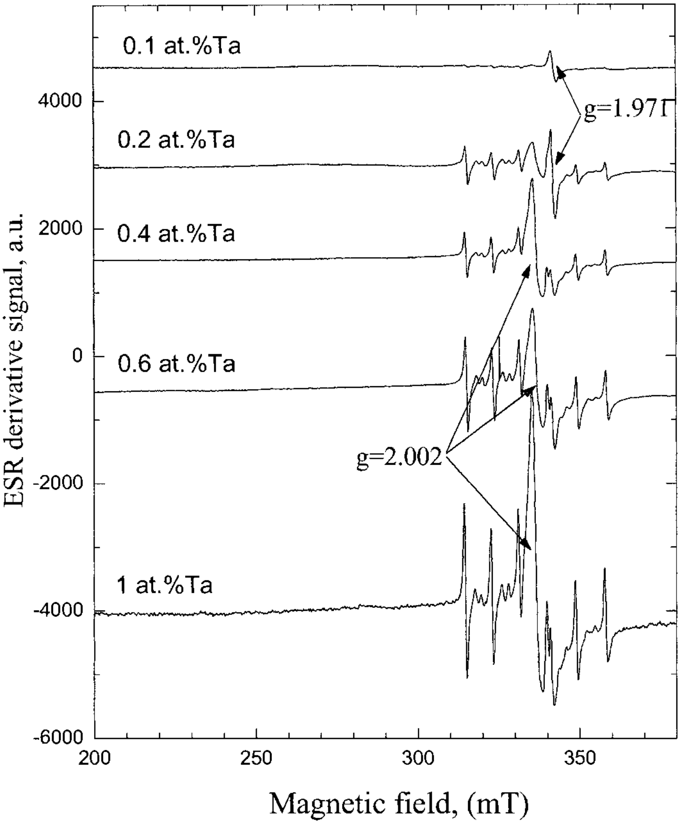

Figure 3. ESR spectra observed in Ta-doped $BaTiO_3$ ceramics.

overlaps with the intense Mn^{2+} spectra it appeared cumbersome to perform its quantitative analysis.

The dependence of the electrical resistivity on Nb or Ta content is depicted in Fig. 5. As one can see from Fig. 5, at room temperature resistivity decreases by several orders of magnitude in the samples with $X = 0.2$ at.%. The resistivity at minimum corresponds to the resistivity observed in semiconductor materials. When the tantalum or niobium concentration rises the resistivity increases rapidly and above 0.8 at.% of impurities concentration resistivity is near $10^{10}\,\Omega$ cm (as in insulator materials).

The temperature dependence of the resistivity of Nb-doped $BaTiO_3$ is depicted in Fig. 6. The similar temperature behavior of the resistivity was

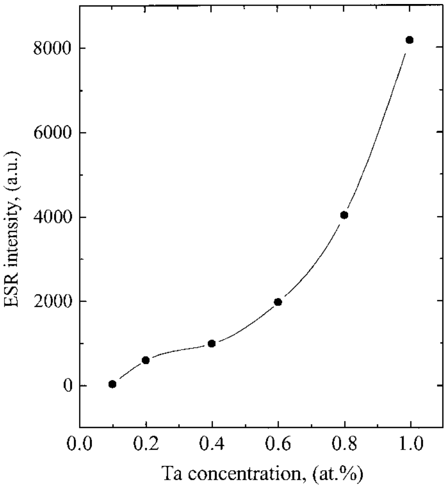

Figure 4. Dependence of Mn^{2+} ESR intensity in $BaTiO_3$:Ta on Ta concentration.

observed in Ta-doped $BaTiO_3$ samples also. The jump of the resistivity noticeably decreases for $X \geq 0.2$ at.% (see Fig. 6). Above T_C the value of resistivity is one order of magnitude for all samples, i.e. the multiplicity of PTCR effect is mainly defined by resistivity of barium titanate samples at room temperature.

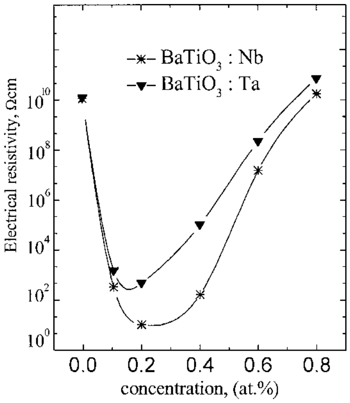

Figure 5. Concentration dependence of the resistivity of Nb- or Ta-doped barium titanate ceramics versus impurities content at T = 300 K.

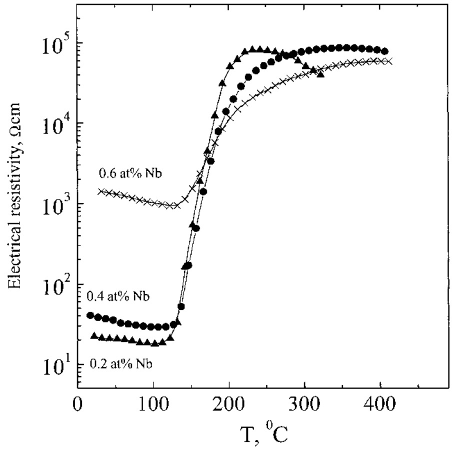

Figure 6. Temperature dependence of the resistivity of Nb-doped $BaTiO_3$ ceramics.

Let us briefly discuss the obtained results. We observed an ESR line with g-factor ($g = 1.965$) close to that observed in the work on $BaTiO_3$ ceramics doped by rare-earth ions [1]. It is known, that Y or La substitute for Ba ions in a perovskite type lattice and for excess positive charge compensation we suggested the appearance of a $Ti^{3+} - Ln^{3+}$ (where Ln is Y or La ion) paramagnetic complex. In that study we observed the dependence of $Ti^{3+} - Ln^{3+}$ ESR intensity on impurity concentration. Moreover, the strong correlation between ESR intensity and resistivity dependence on rare-earths concentration was observed. So, we concluded what Y or La are the sources of charge carriers, which are trapped on Ti ions with $Ti^{3+} - Ln^{3+}$ centers arising. Note that the existence of some additional defects in the vicinity of this center can not be excluded.

Niobium and tantalum ions substitute for Ti ions in the perovskite lattice and are the sources of carriers. The excess positive charge of Nb^{5+} or Ta^{5+} in $BaTiO_3$ can be compensated by several ways: by forming Ti^{3+} centers, barium vacancies or by unavoidable impurities, which are always present in ceramic materials. Therefore it could be either something like an F-center with the carrier smeared between two nearest to oxygen vacancy Ti^{4+} ions, or a $Ti^{3+} - V_O$ center if an electron is trapped by one of two Ti^{4+} nearest to the vacancy. A recent embedded-cluster calculation on singly charged oxygen vacancies performed for $BaTiO_3$ [12] had shown that $g = 1.98 - 1.97$ may correspond to an electron trapped on the e_g orbital of Ti^{3+}. However these centers were shown to be stable only at $T \leq 250$ K. Therefore validity of this model for our case is not so obvious.

On the other hand, the number of oxygen vacancies dependents on Nb^{5+} or Ta^{5+} concentration. From charge–balance condition we can expect that creation of oxygen vacancies will be suppressed by the excess positive charge of Nb^{5+} or Ta^{5+} ions. In this case, the intensity of the V_O associated center must decrease. As can be seen from Fig. 2, we observed the decreasing of the intensity of the ESR line with $g = 1.971$ at $X \geq 0.2$ at.%. To give an answer to the question, whether the ESR spectra decrease is related to oxygen vacancies, it is necessary to study the influence of thermal annealing in different atmospheres on the ESR intensity. These experiments are in progress now.

Another possibility to explain the origin of the ESR line with $g = 1.971$ is the anti-site position of Ti ion (Ti at a Ba lattice position). Such centers were observed in $SrTiO_3$ [13] and it was shown that this type of centers can be observed only at low temperatures ($T < 100$ K). In Nb- or Ta-doped $BaTiO_3$ ceramics these centers are the source of excess positive charge too so their appearance is undesirable.

Unavoidable impurity centers like Mn^{2+} produce acceptor electronic levels, which increase the sample resistivity. We suppose that firstly there were Mn^{3+} ions that are known to be ESR silent. With the increase of dopants content, for excess positive charge of Ta^{5+} or Nb compensation Mn^{2+} centers can arise. In fact, we observed the dependence of spectrum intensity on impurity content (see Fig. 4).

The origin of the ESR line with $g = 2.002$ can be barium vacancies or vacancy-pair center like $V_{Ba} - V_O$, as it was supposed in [14]. These pairs the main cause are in the response of the high resistivity of Nb- or Ta-doped $BaTiO_3$ ceramics above T_C.

In the conclusion we want to note, that samples with $X = 0.2$ at.%, which have the smallest resistivity at room temperature, are most suitable for application in current limiting devices and the samples with larger resistivity ($X \geq 0.6$ at.%) at room temperature can be useful for the production of heaters.

REFERENCES

[1] M. D. Glinchuk, I. P. Bykov, S. M. Kornienko, V. V. Laguta, A. M. Slipenyuk, A. G. Bilous, and O. I. V'yunov, "Influence of impurities on the properties of rare-earth-doped barium titanate ceramics," *Journal of Materials Chemistry* **10**, 941–947 (2000).

[2] T. R. N. Kutty, P. Muragaraj, and N. S. Gajbhiye, "Activation of trap centers in PTC $BaTiO_3$," *Mater. Lett.* **2**, 396–400 (1984).

[3] W. J. Heywang, *Solid-State Electron.* **3**, 51–60 (1961).

[4] T. R. N. Kutty and P. Murugaraj, “EPR study on the role of Mn in enhancing PTC of $BaTiO_3$,” *Materials Letters* **3**, 195–199 (1985).

[5] C. Gillot, J. P. Michenaud, M. Maglione, and B. Jannot, “DC electrical resistivity of Nb-doped $BaTiO_3$ and EPR measurements,” *Solid State Comm*. **84**, 1033–1038 (1992).

[6] M. Kchikech and M. Maglione, “Electron and lattice excitations in $BaTiO_3$:La,” *J. Phys. Cond. Matter.* **6**, 10159–10170 (1994).

[7] M. Drofenik, “Origin of the Grain Growth Anomaly in Donor-Doped Barium Titanate,” *J. Am. Ceram. Soc*. **76**, 123–128 (1993).

[8] A. M. Slipenyuk, M. D. Glinchuk, I. P. Bykov, V. V. Laguta, A. G. Bilous, and O. I. V’yunov, “ESR study of $BaTiO_3$ ceramics doped by Y and Ca,” *Ferroelectrics*. **254**, 349–357 (2001).

[9] A. M. Slipenyuk, M. D. Glinchuk, V. V. Laguta, I. P. Bykov, A. G. Bilous, and O. I. V’yunov, “ESR of Y and Pb-doped $BaTiO_3$ ceramics with positive temperature coefficient of resistivity,” *Ferroelectrics* **254**, 383–391 (2001).

[10] S. Kohne, O. F. Schiermer, H. Hesse, T. W. Kool, and V. Vikhnin, “Ti^{3+} Jahn-Teller polarons and bipolarons in $BaTiO_3$,” *J. of Supercond*. **12**, 193–195 (1999).

[11] E. V. Bursian, Y. G. Girshberg, and E. N. Starov, “Small polarons in conducting barium titanate crystals,” *Phys. Stat. Sol. (b)*, **46**, 529–533 (1971).

[12] H. Donnerberg and A. Birkholz, “Ab initio study of oxygen vacancies in $BaTiO_3$,” *J. Phys. Condens. Matter* **12**, 8239–8247 (2000).

[13] O. F. Schiermer and K. A. Muller, “Defects in neutron-irradiated strontium titanate: Ti^{3+} “Off center” on a Sr^{2+} site,” *Phys. Rev. B* **7**, 2986–2995 (1973).

[14] S. Jida and T. Miki, “Electron paramagnetic resonance of Nb-doped $BaTiO_3$ ceramics with positive temperature coefficient of resistivity,” *J. Appl. Phys.* **80**, 5234–5239 (1996).