which might be helpful in its experimental observation. One of such features may be nonexponential relaxation of polarization, different from that in glass and ferro-glass phases. Its investigation is interesting problem and can be done within above formalism.

Unfortunately, we don't know the direct experimental observation of the Griffiths phase in the aforementioned substances. For the description of possible (direct or indirect) experiments our approach can be easily extended to the case of nongaussian distribution function of random fields as well as for tunneling of the aforementioned off-center impurities between their permissible orientations (i.e. between minima of their multi-well potentials) in the host dielectric.

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ESR of Y and Pb-Doped $BaTiO_3$ Ceramics with Positive Temperature Coefficient of Resistivity

A.M. SLIPENYUK[a], M.D. GLINCHUK[a], V.V. LAGUTA[a], I.P. BYKOV[a], S.N. NOKHRIN[a], A.G. BELOUS[b], O.I. V'YUNOV[b], L.L. KOVALENKO[b] and L. JASTRABIK[c]

[a]*Institute for problems of Material Science, NASc of Ukraine, Krjijanovskogo 3, 252180 Kiev, Ukraine,* [b]*Institute of General and Inorganic Chemistry, Kiev, Ukraine and* [c]*Institute of Physics, Academy of science of Czech Republic, Na Slovance 2, 180 40 Prague 8, Czech Republic*

Electron spin resonance (ESR) and resistivity investigation of $BaTiO_3$ ceramics doped by Y and by both Y and Pb are presented. ESR spectra of the Ti^{3+}, Mn^{2+} and Fe^{3+} were observed. It is shown that the most intensive resonance line belongs to $Ti^{3+} - Y^{3+}$ paramagnetic complex. The essential decrease of the $Ti^{3+} - Y^{3+}$ ESR spectra intensity in comparison with those in samples without Pb was revealed. This gives evidence that Pb ions decrease the number of Y^{3+} ions substituted for Ba ions and so the number of $Ti^{3+} - Y^{3+}$ centers decreases. Essential shift of the temperature of the PTCR effect beginning and resistivity increasing under Pb – doping are observed.

Keywords: ceramics; ESR; paramagnetic center; PTCR effect

INTRODUCTION

Ferroelectric ceramics $BaTiO_3$ exhibits an interesting electrical property, so-called PTCR effect (positive temperature coefficient of resistivity at Curie temperature). This resistivity change is useful for various technical applications, for instance, as PTC thermistors. Creation of $BaTiO_3$ ceramic samples with prescribed properties and, in particular, with small grains remains actual up to now. There are few ways to resolve this problem: first – to optimize the technological process of ceramics preparation, second – doping of the ceramics. There are numerous numbers of articles devoted to the investigations of doping influence on microstructure as well as on the $BaTiO_3$ ceramics properties [1-9]. The transition-metal-ions doped $BaTiO_3$ has been studied extensively and many efforts have been devoted to understand the PTCR mechanism [see, for instance, 4-6] as well as to obtain technologically important parameters [2-6]. It was shown [10, 11] that the value of PTCR is strongly dependent on dopants type and its concentration. Kamioka et al. [12] studied rare-earth elements doping on properties of the semiconducting $BaTiO_3$ and it was revealed that the maximal PTCR effect occurs in the samples doped additionally by 0.127 mol % Mn.

In present work we study impurity centers in $BaTiO_3$ ceramics doped by Y and Pb ions by ESR method. The influence of the revealed paramagnetic centers on PTCR effect is discussed.

EXPERIMENTAL DETAILS

Two series of $BaTiO_3$ ceramic samples were fabricated by the conventional solid-phase reaction technique. The yttrium content in the first series was 0.2; 0.4; 0.6; 0.8 and 1.0 at % and in the second one for each of aforementioned yttrium concentration the Pb content was 5, 15, 25 and 35 at %. The temperature of synthesis was chosen such that the concentration of free barium oxide after the first treatment was not higher than 1 %. The ratio of components was taken in accordance with the formula $Ba_{1-x-y}Y_xPb_yTiO_3$. A small amount of SiO_2 was also added as a sintering aid [13]. The pellet specimens about 3mm in thickness and 10mm 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. ESR spectra were recorded at 9.4 GHz spectrometer at room temperature and at T = 77 K. The resistivity measurements were carry out in temperature interval 300 - 650 K.

THE RESULTS OF ESR STUDY

The ESR spectra at room temperature

The ESR spectra of the $BaTiO_3$ ceramic samples doped by yttrium (Y) are presented in Fig.1. As one can see two intensive ESR lines with g-factors 2.004 and 1.971 are observed.

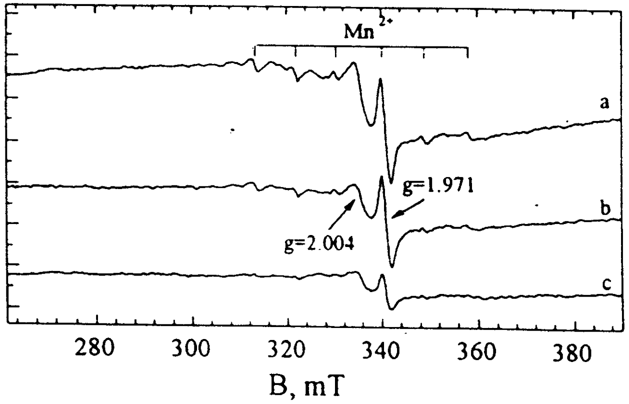

FIGURE 1 ESR spectra of BaY_xTiO_3 ceramic samples: a) x=0.002; b) x=0.004; c) x=0.01.

As it was shown in our previous paper [5] in $BaTiO_3$ ceramics doped by rare-earth elements the ESR line with g=1.971 belongs to Ti^{3+}-Ln^{3+} (Ln^{3+} is the rare-earth element) paramagnetic center. The nature of line with g=2.004 was widely discussed in literature [9,10]. Its g-factor value is close to that for free electron, thus it could be ionized barium vacancy or center Fe^{3+}. In our view it belongs to the center associated with iron ions Fe^{3+}, which are known to be unavoidable impurities in ceramic samples. Except this line we also observe Mn^{2+} spectrum (I=5/2). Its intensity decreases under Y concentration increasing.

The ESR spectra of $BaTiO_3$ ceramics doped both by Y and Pb are depicted in Fig.2.

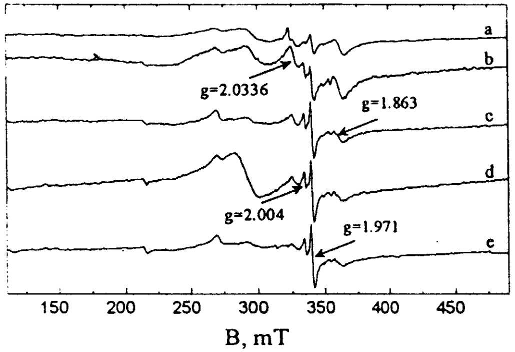

FIGURE 2 ESR spectra of $BaY_xPb_{0.05}TiO_3$ ceramics: a) x=0.002; b) x=0.004; c) x=0.006; d) x=0.008; e) x=0.01.

As one can see in these samples besides of the line of the Ti^{3+}-Y^{3+} (g = 1.971) and the line with g=2.004 a new ESR lines with g-factors 2.033 and 1.863 are observed. The intensity and width of the ESR line g=2.004 remain practically unchanged under Y concentration increase. So we can conclude that it belongs to Fe^{3+} center associated with unavoidable impurity.

The approximately equal intensity and width of the ESR lines with g factors 2.033 and 1.863 allows us to suppose that most probably they belong to one center. Moreover, the dependence of this ESR spectra intensity on Pb and Y concentration is also the same for both lines. The intensity of ESR lines with g-factors 2.033 and 1.863 decrease under Y or Pb concentration increasing.

The most intensive spectrum observed in $Ba_{1-x-y}Y_xPb_yTiO_3$ as well as in BaY_xTiO_3 is attributed to Ti^{3+}-Y^{3+} center (g-factor 1.971). The influence of rare-earth elements concentration on the ESR lines intensity and width were studied in detail in our previous paper [6]. In Fig.3 we depicted the dependence of Ti^{3+}-Y^{3+} ESR line intensity from Pb and Y concentration. As it is seen for Pb concentration 25 at % and 35 at % the intensity of aforementioned line decreases under yttrium concentration increasing. For samples with 5 at % and 15 at % of the Pb content the dependence of line's intensity is qualitative similar to that we observed for Ti^{3+}-Y^{3+} paramagnetic center in $BaTiO_3$ doped only by yttrium [see 3]. One can see from Fig.3, for the samples with 5 and 15 at %, the Ti^{3+}-Y^{3+} ESR lines intensity rise before some critical concentration of Y ions dependent on the Pb concentration the insignificant decreasing of its intensity was observed. We can note that for fixed Y concentration, the Pb content increasing leads to Ti^{3+}-Y^{3+} ESR line intensity decreasing.

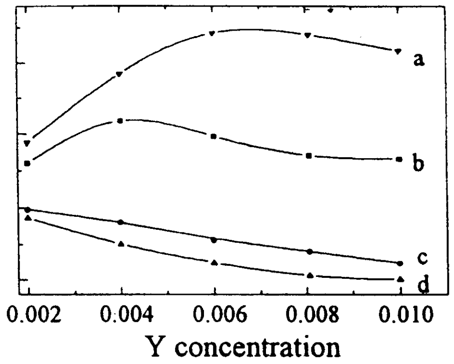

FIGURE 3 Ti^{3+}-Y^{3+} ESR line intensity dependence from Y and Pb concentration in $Ba_{1-x-y}Y_xPb_yTiO_3$: a)y=0.05, b)y=0.15, c)y=0.25, d) y=0.35. The intensity of Ti^{3+}-Y^{3+} line is normalized at that of the line in "pure" $BaTiO_3$ ceramics.

ESR spectra at T = 77 K

ESR spectra of the $Ba_{1-x-0.05}Y_xPb_{0.05}TiO_3$ in the rhombohedral phase of this ceramics are presented in Fig. 4. As one can see, for each Y concentrations we observed the intensive central line of complicated form with the value of g-factor close to 2 and six lines belonging to Mn^{2+} center. The intensity of Mn^{2+} ESR line decreases under Y concentration increasing. At Pb concentration more than 5 at. % we observed decreasing of its ESR spectra intensity and for Pb concentration 25 at % and 35 at % this spectra was not observed.

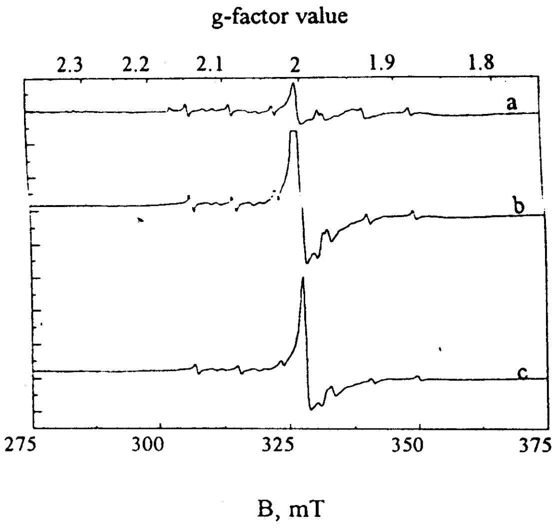

FIGURE 4 ESR spectra of $BaY_xPb_{0.05}TiO_3$ ceramics at T = 77 K.
a) x = 0.002; b) x = 0.006; c) x = 0.008.

The origin of the line with g = 2.004 will be discussed later.

DISCUSSION

ESR spectrum of the Ti^{3+}-Y^{3+} paramagnetic center

The ESR signal associated with Ti^{3+} ions observed in single crystals and ceramic samples is widely discussed in literature [14,15]. Three Ti^{3+} associated models: Ti^{3+}-V_O-Na (K), Ti^{3+}-V_O and isolated Ti^{3+} was proposed [14]. In $BaTiO_3$ ceramic samples the interest to Ti^{3+} ions is connected with PTCR effect explanation. In nominally "pure" ceramic $BaTiO_3$ the small intensity Ti^{3+} spectrum can be observed due to uncontrolled impurities that always are presented in ceramic samples. The excess positive charge arises in $BaTiO_3$ unit cell after rare-earth elements doping but the mechanism of charge compensation is unclear up to now. For instance, in our previous papers [5, 6] we proposed model Ti^{3+}-Y^{3+} where Y ion is substituted for Ba^{2+} ion.

In $BaTiO_3$ ceramics doped by Y and Pb both elements substituted for Ba^{2+} ion in lattice because of their ion radii are close to Ba ion. But Pb possesses the 100 % dissolubility so in this case the number of Y ions substituted for Ba must decrease and therefore the intensity of Ti^{3+}-Y^{3+} ESR line will decrease. Really, we observed the decreasing of this line intensity under Pb concentration increase. The decrease of the Ti^{3+}-Y^{3+} centers quantity related to Pb concentration increase will result in resistivity rise. To confirm this the measurements of the temperature dependence of the resistivity and the dielectric permittivity were carried out (see Figs. 5 and 6 respectively).

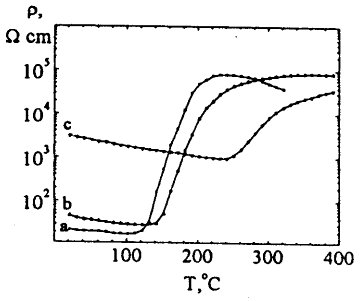

FIGURE 5 The temperature dependency of resistivity $BaY_{0.004}Pb_yTiO_3$ ceramics: a)y=0; b) y=0.05; c) y=0.35.

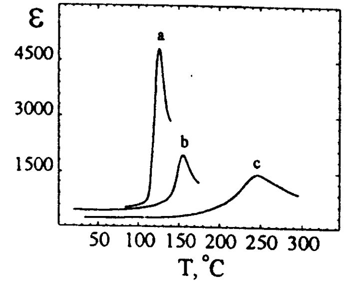

FIGURE 6 The temperature dependency of the dielectric permittivity at 1 GHz of $BaY_{0.004}Pb_yTiO_3$ ceramics: a) y=0; b) y=0.05; c) y=0.35.

As one can see Pb doping leads to resistivity rise at room temperature. Simultaneously the shift of the temperature of the PTCR effect beginning is observed. These data are confirmed with T_C displacement, which was determined from dielectric permittivity measurements. Under Pb content increase the solid solution of $BaTiO_3$ and $PbTiO_3$ occurs. As it is known $PbTiO_3$ is ferroelectric with T_C=760 K [16], so it must result in the shift of the temperature of the PTCR effect beginning toward high temperature.

ESR spectrum of the Mn^{2+} ion

The ESR spectra of Mn^{2+} ion at T=300 K in the $BaTiO_3$ single crystals was observed earlier [see for instance 17]. The value of hyperfine coupling constant $A=80.7 \cdot 10^{-4}$ cm^{-1} calculated for $BaTiO_3$ ceramics in tetragonal phase is close to the values in MgO and $SrTiO_3$ ($A=81.01 \cdot 10^{-4}$ cm^{-1} and $A=82.6 \cdot 10^{-4}$ cm^{-1} respectively) where it is known that Mn^{2+} ion is in Ti^{4+} site. In the samples doped by Y we observed six hyperfine ESR lines belonging to Mn^{2+} spectrum. The experimentally observed value of the hyperfine constant A is $78.28 \cdot 10^{-4}$ cm^{-1} that is in a good agreement with data on single crystals.

ESR spectra at T = 77 K

The most remarkable spectrum was an asymmetrical broad, intensive signal with g-factor value 2.005 (see Fig.2). Let us discuss the origin of this line. It is known that iron ions in $BaTiO_3$ give rise to an ESR signal at the $g \approx 2$ region [18, 19]. Schwartz et.al. [20] ascribed the singlet signal at g=2.005 belonging to Fe^{3+} ions. Sakudo [21] studied ESR of the Fe^{3+} in $BaTiO_3$ crystals at low temperatures. In this paper value of Fe^{3+} ion g-factor ($g = 2.0036 \pm 0.002$) is close to that obtained in our work and it was shown that the most intensive ESR line belongs to -1/2 +1/2 transition (Fe^{3+} in Ti^{4+} site). On the other hand, Gillot et.al.[7] observed a signal at g=2 in Nb-doped $BatiO_3$ single crystal, and assigned it to Nb^{4+} small polarons. Since we did not revealed any correlation between intensity of the ESR line at g = 2.005 and dopants concentration we supposed that this line origin is Fe^{3+} ions which are known to be unavoidable impurities in $BaTiO_3$ samples.

Thus we conclude that the Ti^{3+}-Y^{3+} paramagnetic centers observed in $BaYPbTiO_3$ ceramics could influence on these materials conductivity. Pb doping of $BaTiO_3$ ceramics gives possibility to fabricate samples with desired properties.

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