Journal of Applied Spectroscopy, Vol. 73, No. 3, 2006

EFFECT OF HEAT TREATMENT AND CONCENTRATION OF Mn AND Fe ON THE STRUCTURE OF BORATE GLASS

O. S. Ivanova,[1*] É. A. Petrakovskaya,[1] R. D. Ivantsov,[1]
I. S. Édel'man,[1] S. A. Stepanov,[2] and T. V. Zarubina[2]

UDC 537.632.4;537.635

We have studied the magneto-optic Faraday effect (FE) and electron paramagnetic resonance (EPR) in an aluminum potassium borate glass containing Fe oxides as an impurity in a concentration of 1.5 mass % and Mn impurity in variable concentration from 0 to 1.2 mass %. When manganese oxide is added to the glass composition, the paramagnetic contribution to the Faraday effect increases more slowly than the change in the total concentration of paramagnetic ions, which allows us to hypothesize the appearance of clusters in which the paramagnetic ions are coupled by antiferromagnetic interactions. Formation of clusters upon addition of manganese oxide is confirmed by the change in the nature of the EPR spectra, where we observe a manganese concentration dependence of the distribution of iron atoms with respect to the different positions in the glass matrix. Heat treatment leads to a strong increase in the Faraday effect and a change in the spectral dependences of the Faraday effect and the EPR, which is explained by enlargement of the clusters and appearance of nanoparticles.

Key words: *Faraday effect, electron paramagnetic resonance, transition ions in glass, transition ion clusters.*

Introduction. The steady demand for technology in efficient media for controlling a light beam has stimulated the search for and investigation of new material having high magneto-optical quality, in particular in the IR region of the spectrum at wavelengths of 1.0–1.5 μm. Glass containing magnetic nanoparticles can be considered as such a material (see, for example, [1, 2]). Creation of glasses with the required microstructure and specified physical properties requires detailed study of the processes of particle formation in all stages of glass manufacture. Usually nanoparticles having a crystalline structure are formed during additional heat treatments of the glass. However, inhomogeneities in the distribution of magnetic ions and the appearance of clusters which are nuclei for the magnetic phase occur even in the initial stages of glass manufacture, and to a significant extent determine the nature of the particles appearing as a result of additional heat treatments. In this work, we have studied a glass with the base composition $22.5K_2O+22.5Al_2O_3+55B_2O_3$, containing Fe_2O_3 and MnO as impurities. In glasses of this group, magnetic nanoparticles are formed as a result of heat treatments even for low concentrations of paramagnetic additives (≈2.0 mass %) [1, 2]. Therefore, while remaining transparent in the spectral region 800–2500 nm, the glasses are characterized by a significant Faraday effect and a nonlinear field dependence for the Faraday effect. The need to optimize the indicated parameters explains why steady attention has been focused on the processes of nucleation and formation of magnetic inhomogeneities in glasses of this system.

EPR is the method most often used for investigation of clusters of S transition metal ions in glasses, for example $Fe^{3+}(3d^5, {}^6S_{5/2})$ [3–6]. The EPR spectra of Fe^{3+} ions in glass matrices provide information about the immediate environment of the paramagnetic ion because different lines are observed for ions included in structural units with a certain symmetry and ions joined into clusters. These spectra are characterized by resonant absorption at some g factor values; in particular, the $g \approx 9.7$ line is assigned to ions located in rhombohedral positions [7]. The resonance at g

---

[*] To whom correspondence should be addressed.

[1] L. V. Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk 660036, Russia. E-mail: osi@iph.krasn.ru. [2] S. I. Vavilov State Optics Institute, St. Petersburg, Russia. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 73, No. 3, pp. 354–358, May–June, 2006. Original article submitted December 10, 2005.

≈ 6.0 is connected with uniaxial distortion of the environment of the paramagnetic ion significantly exceeding the Zeeman interaction [8–10]. The resonance at $g \approx 4.3$ is due to a transition within the lower Kramers doublet in ions occupying positions that are strongly distorted by a crystal field of axial symmetry with addition of a significant orthorhombic component (~1/3 of the axial component) [7, 11–14]. Absorption at $g \approx 2.0$ is usually assigned to Fe^{3+} ions bound in dimer magnetic clusters and/or located in slightly distorted octahedra [15, 16].

The Faraday effect is the sum of effects from the diamagnetic matrix and paramagnetic ions included in the matrix. These two contributions have opposite signs: respectively positive and negative. So as the concentration of paramagnetic ions increase, the total Faraday effect should decrease to a value proportional to the concentration, and for a certain concentration it should change sign. The paramagnetic ions joining into exchange-coupled clusters leads to deviations from this pattern due to the change in the magnetic properties. Thus a combination of the two methods may provide more detailed information about the state of the paramagnetic ions in the glasses under study.

Samples and experimental procedure. The procedure for synthesis of the glasses of the base composition $22.5K_2O+22.5Al_2O_3+55B_2O_3$ is given in [1]. The Fe_2O_3 concentration in the mix was 1.5 mass % above the 100 mass % of the base composition; the MnO concentration was 0.2, 0.4, 0.6, and 1.2 mass % (samples Nos. 2–5 respectively; only iron oxide was added to sample No. 1). The glasses were melted at a temperature of 1100^oC–1300^oC under oxidizing conditions. The melt was poured onto steel sheets, the glass sheets were cooled in air to a temperature of 380^oC and then held at that temperature for several hours. Additional heat treatment was carried out at a temperature of 560^oC for 2 h. The samples that did not undergo heat treatment will be called the original samples. For comparison, under the same conditions we prepared a sample containing no paramagnetic impurities. The EPR measurements were made on rectangular samples of dimensions 2 × 3 × 4 mm, and the Faraday effect measurements were made on optically polished samples of thickness 1.00 ± 0.05 mm.

The EPR spectra were recorded at 78 K and 300 K at *X* band (9.5 GHz) and *Q* band (35 GHz). The Faraday effect was measured using modulation of the plane of polarization of the light wave in the wavelength region 400–1000 nm in an external magnetic field of 0.2 T, directed normal to the plane of the samples, at 300 K; the accuracy of the Faraday effect measurements was ±0.2 min; for the magnetic field, ±0.002 T.

Results and discussion. *Faraday effect.* The spectral dependences of the Verdet constant $V = \alpha H^{-1} d^{-1}$ (where α is the Faraday effect, H is the magnetic field, d is the sample thickness) are shown in Fig. 1. Curve 1 corresponds to a sample with no paramagnetic additives. The spectrum is described by a dependence typical of a diamagnetic medium:

$$V_1 = \frac{A\lambda}{(\lambda^2 - \lambda_{01}^2)^2}, \tag{1}$$

where A is a constant; λ is the instantaneous wavelength; λ_{01} is the effective wavelength, corresponding to electronic transitions in ions of the matrix responsible for the Faraday effect, evidence for which is the linear dependence of $(\lambda/V_1)^{-1/2}$ on λ^2. The value of λ_{01} determined using this dependence is ≈350 nm. All the original samples containing paramagnetic additives are also characterized by a positive sign for the Verdet constant, which in this case we denote as V_2 (curve 2 in Fig. 1). The value of V_2 is less than V_1, which is easily explained by the negative contribution to the Faraday effect from the paramagnetic ions. This contribution is determined by the difference $V_{para} = V_2 - V_1$. Spectrum 3 in Fig. 1 corresponds to sample 3. The dependence of V_{para} on the total concentration of paramagnetic ions in the glass is shown in the insert in Fig. 1. We see that the change in V_{para} as we go from sample to sample does not correspond to an increase in the concentration of paramagnetic ions in the samples, as should happen in the case of isolated, noninteracting ions.

The spectral dependence of the Faraday effect for paramagnetic ions distributed uniformly in the glass matrix should be described by the expression

$$V_{para} = \frac{B}{(\lambda^2 - \lambda_{02}^2)}, \tag{2}$$

where B is a constant; λ_{02} is the effective wavelength of the electronic transition (or sum of transitions) associated with the paramagnetic ions. In fact, the V_{para} spectral curves (Fig. 1, curve 4) do not correspond to the indicated pat-

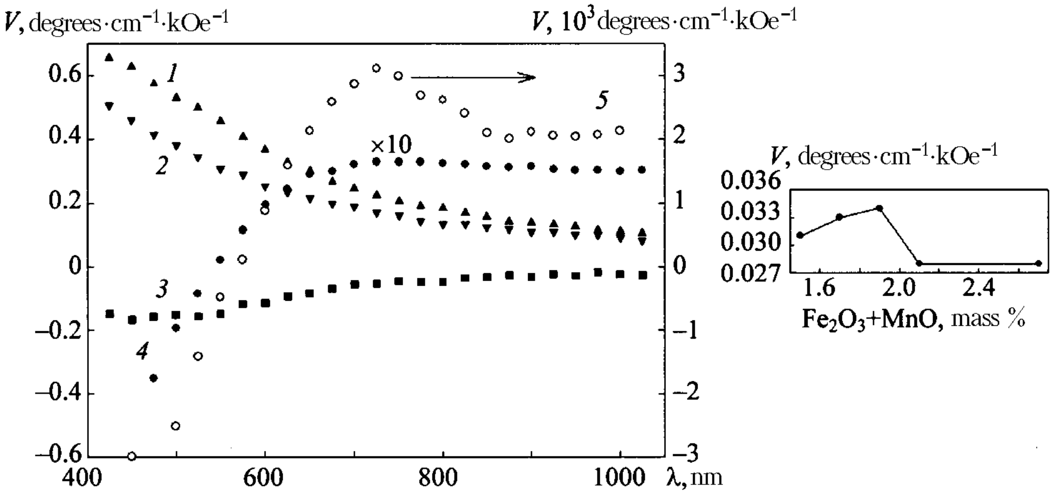

Fig. 1 Spectral dependences of the Verdet constant V in glasses: 1) base glass with no paramagnetic additives; 2) original glass No. 3 with 0.4% MnO; 3) paramagnetic contribution (differences between curves 2 and 1) in glass No. 3; 4) glass No. 3 with 0.4% MnO, heat-treated; 5) V in magnetite film. Insert: concentration dependence of paramagnetic contribution for all the studied samples, λ = 775 nm.

tern. This fact, together with the lack of a proportional dependence of V_{para} on Mn concentration, allows us to hypothesize that even in the original samples, an inhomogeneous distribution of paramagnetic ions over the volume occurs with formation of iron or manganese and iron clusters, coupled by antiferromagnetic exchange through the oxygen. In the magnetic fields used, the paramagnetic ions included in clusters do not make a contribution to the Faraday effect.

Heat treatment leads to a change in the magnitude and spectral dependence of the Faraday effect. The nature of the Faraday effect spectrum varies identically for all the compositions: it becomes positive in the long-wavelength portion (Fig. 1, curve 4). The point at which it passes through zero for all the samples is close to 550 nm. The smallest changes in the magnitude of the Faraday effect after heat treatment occur for samples that either do not contain Mn or else contain the maximum amount of Mn. Note the close match between the Faraday effect spectrum observed for samples subjected to heat treatment and the Faraday effect spectrum of a polycrystalline film of magnetite Fe_3O_4 (Fig. 1, curve 5), obtained by self-propagating high- temperature synthesis [17]. In contrast to the Faraday effect spectra of ferrites containing only $3d^5$ ion and characterized by a monotonic decrease in the effect as the wavelength of the light increases, in the case of magnetite we observe a broad, intense maximum in the 700–800 nm region. This maximum is associated with spin-allowed electronic transitions $^5T_{2g}(^5D) \rightarrow {}^5E_g(^5D)$ in the Fe^{2+} ions with a $3d^6$ electronic configuration. Thus we may hypothesize that as a result of heat treatment, nanoparticles are formed in the glass that are close to magnetite in composition and structure, i.e., some of the Fe ions change valency to +2. The sharp increase in the Faraday effect for samples 2–4 (containing both iron oxide and manganese oxide) after their heat treatment is also accompanied by the appearance of a nonlinear field dependence for the Faraday effect, which is typical of magnetically ordered materials. The situation in this case is analogous to what we described previously in [1, 2], and is connected with formation of magnetically ordered nanoparticles in the glass. However, for the maximum manganese concentration, the magnitude of the Faraday effect decreases again and becomes close to the Faraday effect for the sample not containing manganese.

Thus studying the Faraday effect in a series of glasses with iron and manganese oxide impurities in concentrations from 1.5 to 2.7 mass % revealed the complicated role of manganese ions in formation of the glass structure. An inhomogeneous distribution of paramagnetic ions with possible formation of clusters is observed even in glasses not subjected to heat treatment. In this case, the change in the Faraday effect characteristics depends nonmonotonically on the manganese concentration both in the original samples and in samples subjected to heat treatment.

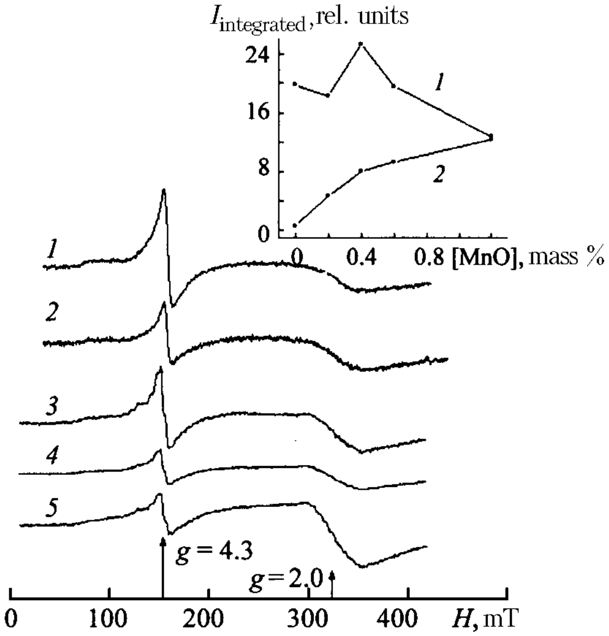

Fig. 2 X-band EPR spectra of original samples at $T = 300$ K; MnO concentrations in the mix: 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), and 1.2 (5) mass %. Insert: dependence of the integrated intensity of the $g = 4.3$ (1) and $g = 2.0$ (2) lines on the Mn concentration for the original samples at $T = 77$ K.

EPR. Fig. 2 shows the EPR spectra of the original glasses, recorded at 300 K. The most significant lines in these spectra have g factors of ≈4.3 and ≈2.0 (indicated by the arrows) with intensities I_1 and I_2. Weak lines with $g \approx 9.7$ and 6.0 are also present. Borate glasses with different modifiers have similar spectra: K and Ca in glasses with Fe^{3+} [4, 18], Al in glasses with Fe^{3+} and Mn^{2+} [19], Pb [20] and Sr [21] in glasses with Mn^{2+} etc. As noted above, these lines are associated with different positions of the Fe^{3+} and Mn^{2+} in the glass.

In the original sample containing 1.5 mass % Fe_2O_3, the observed lines belong to the Fe^{3+} ions and correspond to the spectra given in [4, 18]. The ratio of the intensities obtained by double integration of the derivatives of the absorption lines is $I_1/I_2 \approx 5$. This is evidence for preferential location of isolated iron ions in isolated, strongly distorted positions in the glass. At 77 K, this ratio increases up to 19, mainly as a result of the increase in the intensity of the $g = 4.3$ line; the intensity of the $g = 2.0$ line increases slightly. Addition of MnO leads to a redistribution of the ions over the positions in the glass matrix. The general pattern is clearly seen in the dependence of the intensities I_1 and I_2 (determining the quantitative rearrangement of the ions) on the MnO concentration (Fig. 2, insert). According to the data in [18], the Mn^{2+} ions prefer slightly distorted octahedral positions ($g \approx 2$), while the Fe^{3+} ions in contrast tend to occupy strongly distorted tetrahedral positions (g ≈ 4.3). The spectra obtained demonstrate that this tendency is also preserved in the glasses we studied: an increase in I_2 with an increase in manganese concentration. The Q-band spectra for the sample containing 0.4 mass % MnO (Fig. 3, curve 1) confirm the presence of both isolated Mn^{2+} centers (six lines of the hyperfine structure) and clusters (g ≈ 2). The width of the line associated with clusters is $\Delta H = 50$ mT. For 1.2 mass % MnO, no hyperfine structure is observed due to dipolar broadening.

The decrease in the intensity I_1 when the Mn concentration increases may be associated with rearrangement of the positions occupied by Fe^{3+} ions. Modification of the symmetry of the Fe^{3+} environment occurs, and the iron joins into cluster structures. Partial reduction of the iron down to Fe^{2+}, noted in the discussion of the Faraday effect, also leads to a decrease in the intensity of the $g = 4.3$ band. Analogous phenomena were observed in glasses with one type of ion, Mn or Fe, for concentrations of these ions equal to tens of mole percent [20, 21]. The manganese ions, which are at the same time modifiers of the glass matrix, can actually change the local structure. Consequently, Fe^{3+} and Mn^{2+} occupy undistorted octahedral positions and form Fe^{3+}–Fe^{3+} and Fe^{3+}–Mn^{2+} pairs associated with an antif-

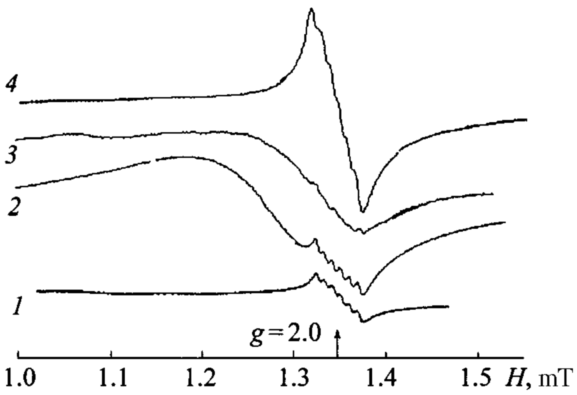

Fig. 3 Q-band EPR spectra at T = 300 K: (1) original sample (0.4% MnO); 2–4) heat-treated samples, [MnO] = 0.4% (2), 0.2% (3), and 1.2% (4) MnO.

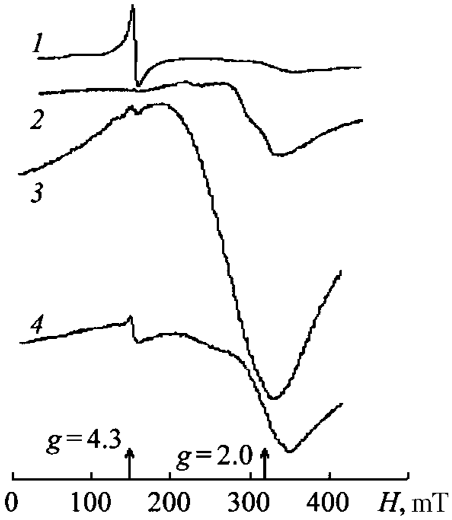

Fig. 4 X-band EPR spectra for heat-treated samples. MnO concentrations: 0 (1), 0.2 (2), 0.4 (3), and 1.2 (4) mass %, T = 300 K.

erromagnetic superexchange interaction [4], and the number of low-symmetry Fe^{3+} positions decreases. In the initial state of this process, for an Mn concentration below 0.6 mass %, we observe broadening of the g = 2.0 line, associated with some spread in the parameters of the structure, then the line narrows. Note that the general pattern somewhat breaks down for an MnO concentration of 0.4 mass % in the original glass (see Fig. 2), which is apparent in the behavior of the intensity I_1 (g = 4.3). Such a concentration characteristic reflects the internal interactions in this matrix.

Heat treatment of the glass not containing manganese does not lead to appreciable changes in the EPR spectrum (Fig. 4). The Faraday effect behaves similarly. In all the remaining cases, the spectra of the annealed samples change. Especially for all the original MnO concentrations, the intensity of the g = 4.3 line drops sharply. In the region of the spectrum corresponding to $g \approx 2$, the nature of the changes is different. As in the original glasses, the concentration of 0.4 mass % MnO stands out (Fig. 4). For this composition, we observe an intense symmetric line with ΔH = 142 mT, g = 2.4; g = 2.1 corresponds to it in the Q band spectra (Fig. 3). This is evidence for the formation of qualitatively new magnetic centers in the glass. The increase in the g factor and the line width when this sample is cooled down to 77 K allow us to say that we are dealing with superparamagnetic particles in the glass matrix, as in [6]. The position and width of the line, taking into account the data in [22], allow us to assign them to magnetite nanoparticles. The latter are formed as a result of active annihilation of local centers 1 and "liberated" Fe^{3+} ions joining together with Fe^{2+} ions with the help of oxygen. Such an explanation is consistent with the above-mentioned closeness between the Faraday effect spectrum and the spectrum of magnetite films. The Mn^{2+} ions obviously (see curves 1 and 2 in Fig. 3) retain their individual and cluster positions. The manganese oxide concentration of 0.4 mass % is the critical concentration at which Mn^{2+} catalyzes reduction of the amount of Fe^{2+} required for magnetite formation. The increase in the original MnO concentration up to 1.2 mass %, close to the concentration of Fe_2O_3 in the studied glass, "deprives" the Mn^{2+} of catalytic activity, and ferrite is not formed with heat treatment. The *Q* band spectra of the glass with 1.2 mass % MnO before and after heat treatment are practically identical (Fig. 3, curve 4).

Conclusion. All the Faraday effect and EPR results allow us to conclude that adding manganese oxide to the glass composition in concentrations of a few mass percent leads to redistribution of the paramagnetic ions and formation of magnetic clusters even in the original glasses. Heat treatment of the glass causes even greater decrease in the number of paramagnetic iron centers in strongly distorted positions ($g = 4.3$); the $g = 2$ positions are preserved. The processes occurring in the glass melt during its first quench depend on the manganese oxide concentration.

We would like to acknowledge V. V. Polyakov and K. P. Polyakova for providing the magnetic film for the measurements.

This work was done with the support of the Special Program on Development of Scientific Potential in Higher Education (2006–2008), project code RNP.2.1.1.7376.

REFERENCES

1. S. A. Stepanov, G. T. Petrovskii, T. V. Zarubina, E. E. Kornilova, and I. S. Edel’man, *Opt. Zh.*, **70**, No. 12, 46–53 (2003).
2. I. S. Edel’man, S. A. Stepanov, G. T. Petrovskii, V. I. Zaikovskii, R. D. Ivantsov, O. S. Ivanova, D. E. Prokof’ev, T. V. Zarubina, and E. E. Kornilova, *Fiz. i Khim. Stekla*, **31**, No. 2, 177–186 (2005).
3. R. Berger, J.-C. Bissey, and J. Kliava, *J. Phys.: Condens. Matter.*, **12**, 9347–9360 (2000).
4. I. Ardelean, P. Pascuta, and V. Ioncu, *Int. J. Modern Phys. B*, **17**, 2633–2641 (2003).
5. J. Kliava and R. Berger, *Recent Res. Devel. Non-Cryst. Solids*, **3**, 41–84 (2003).
6. J. Kliava and R. Berger, *J. Magn. & Magn. Mater.*, **205**, 328–342 (1999).
7. I. Ardelean, M. Peteanu, S. Filip, V. Simon, and G. Gyorgy, *Solid State Commun.*, **102**, 341–346 (1997).
8. D. Loveridge and S. Parke, *Phys. Chem. Glasses*, **12**, 19–27 (1971).
9. A. Paul, *Phys. Chem. Glasses*, **14**, 96–100 (1973).
10. T. Castner, G. S. Newell, W. C. Holton, and C. P. Slichter, *J. Chem. Phys.*, **32**, 668–673 (1960).
11. D. Loveridge and S. Parke, *Phys. Chem. Glasses*, **9**, 73–81 (1968).
12. D. L. Griscom, *J. Non-Cryst. Solids*, **40**, 211–272 (1980).
13. V. Cerny, B. Petrova, and M. Frumar, *J. Non-Cryst. Solids*, **125**, 17–24 (1990).
14. I. Ardelean, M. Peteanu, V. Simon, S. Filip, F. Ciorcas, and I. Todor, *J. Magn. & Magn. Mater.*, **258**, 196–197 (1999).
15. D. W. Moon, M. J. M. Aitken, R. K. MacCrone, and G. S. Cieloszky, *Phys. Chem. Glasses*, **16**, 91–102 (1975).
16. E. Burzo and I. Ardelean, *Phys. Status Solidi (b)*, **87**, K137–K140 (1978).
17. V. G. Miagkov, K. P. Polyakova, G. N. Bondarenko, and V. V. Polyakov, *J. Magn. & Magn. Mater.*, **258–259**, 358–360 (2003).
18. S. Simon, I. Ardelean, and M. Peteanu, *Mod. Phys. Lett.*, **14**, 1–6 (2000).
19. I. Ardelean and M. Flora, *J. Mat. Sci.: Mat. Electr.*, **13**, 357–362 (2002).
20. I. Ardelean, M. Peteanu, and S. Filip, *Solid State Commun.*, **105**, 339–344 (1998).
21. I. Ardelean, M. Peteanu, and V. Simon, *J. Mat. Sci.*, **34**, 6063–6068 (1999).
22. E. A. Petrakovskaya, V. G. Isakova, O. A. Bayukov, and D. A. Velikanov, *Zh. Tekh. Fiz.*, **75**, No. 5, 117–120 (2005).