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EPR method for investigation and diagnosis materials promising for quantum electronics ($PbGa_2S_4$, ZnSe)

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Abstract. Electron paramagnetic resonance (EPR) spectra of rare-earth Dy^{3+} and Ce^{3+} ions in lead thiogallate $PbGa_2S_4$ single crystals were discovered and investigated. EPR spectra were studied in X-band in the temperature range 4-30 K. Parameters of spin Hamiltonian of EPR spectra of Dy^{3+} and Ce^{3+} ions in $PbGa_2S_4$ single crystals were calculated. It was set that dysprosium and cerium ions replace lead ions in crystal lattice. Also we carried out a diagnosis of ZnSe crystals doped with different rare-earth and transition metal ions. It was shown that due to diffusion of transition elements of Cr^{3+}, Co^{2+} or Fe^{3+} along with the working admixture in the diffusion layer the EPR spectra of related admixtures are detected. The EPR diagnosis of these admixtures can be used in the development of modes, allowing minimizing the concentration of related admixtures, worsening the performance of laser materials. It was found that diffusion of Cr, Co and Fe transition metal ions leads to admixture of Mn ions. The EPR signals of Mn and Co are proposed as the ideal markers to control the crystal structure of the diffusion active layer.

1. Introduction

Dysprosium- and cerium-doped lead thiogallate single crystals are known to be promising active media for the lasers of mid-infrared range (3-5 μm). This range corresponds to so-called transparency window of the Earth's atmosphere, that leads to small losses of radiation under its propagation in the atmosphere and is very important for scientific and modern technological applications. Investigation of the optical and laser properties of $PbGa_2S_4$ single crystals activated by rare-earth ions is a subject of a number of papers [1, 2]. Nevertheless, there are no papers on the electron paramagnetic resonance (EPR) studies of $PbGa_2S_4$ crystals.

Materials based on ZnSe: Cr^{2+} are known to be the very efficient for producing compact wide continuously tunable lasers in the wavelength range of 2 - 3.4 μm at room temperature. ZnSe: Cr are used as passive shutter of holmium laser (wavelength of about 2 μm) also. ZnSe:Fe crystals are 3-5 μm tunable solid-state sources of coherent light. Using direct optical pumping at 2.698 μm ($Y_3Al_5O_{12}$:Er^{3+}) these crystals can be used as passive shutters. ZnSe:Co crystals are attractive candidates for a good saturable absorber for 1.5-μm eyesafe lasers. Thus, zinc selenide crystals doped with different ions are attractive for such applications as remote sensing, environment monitoring, mid-IR free space communications, as well as optical coherence tomography, ophthalmology and dermatology in medicine, etc.

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One of the most direct techniques of the investigation of the spectroscopic properties of materials for quantum electronics is the EPR method. The EPR allows one to determine the spin and charge state of an impurity, to find the local symmetry of the impurity center and the composition of its nearest environment, the structure of the energy levels, the specificity of interaction with the crystal lattice, the presence of structural defects in the vicinity of the impurity, etc.

2. Experiment and discussion

2.1. $PbGa_2S_4$:Dy

EPR spectra of Dy^{3+} and Ce^{3+} ions in lead thiogallate ($PbGa_2S_4$) single crystals were studied in the X-band in the temperature range 4 -30K on JEOL standard radio spectrometer. The crystals were synthesized by Bridgeman-Stokbarger technique.

The observation of the EPR spectra of $PbGa_2S_4$:Dy^{3+} in an arbitrary orientation of the external magnetic field is troublesome due to a number of specific features (anisotropy, low intensity). The EPR spectrum of $PbGa_2S_4$:Dy^{3+} observed in the low magnetic field H || [100] at T = 4K is shown in Fig.1.

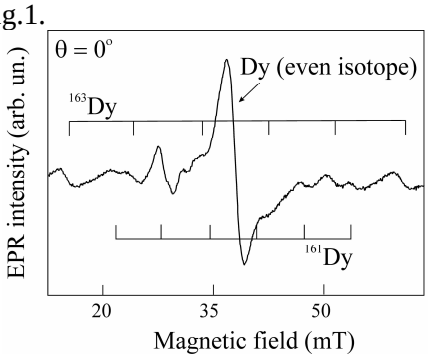


Figure 1. EPR spectrum of Dy^{3+} ions in $PbGa_2S_4$ single crystals in H || [100] orientation and T = 4K.

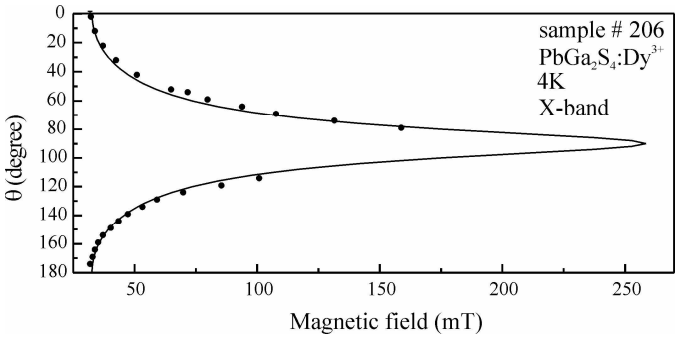


Figure 2. Calculated (curve) and experimental (circles) angular dependences of the resonance magnetic field of Dy^{3+} ions in lead thiogallate in the (010) plane.

On the basis of a detailed study of the hyperfine structure of observed EPR lines in the lead thiogallate crystals activated by dysprosium we can unambiguously state that the spectra belong to Dy^{3+} ions. Spectra consist of the intense line and two groups of low-intensity lines, each having six equidistant lines. It is worth noting, natural dysprosium has even isotope with zero nuclear spin and two odd isotopes, each having nuclear spin of five halves. The natural abundance of these isotopes (^{161}Dy and ^{163}Dy) is equal to 19.0 and 24.9 %, respectively, and the ratio of the nuclear magnetic moments ^{161}Dy/^{163}Dy is equal to 1.41. Experimental spectrum looks exactly as one would expect for dysprosium. The two groups of six lines each are the components of the hyperfine structure for the odd isotopes and the intense central line belongs to the even isotope. The ratio of the distances between the lines of the hyperfine structure in each group corresponds to the ratio of the nuclear magnetic moments of the odd isotopes, and the ratios of intensities of the lines in the spectrum correspond to the natural abundances of the isotopes.

As it could be seen from Fig. 1, a low-intensity signal is observed at the low-field side of the EPR spectrum also. This signal is split into two components at certain orientation of the magnetic field. According to the analysis, this line does not belong to dysprosium ion.

Paramagnetic Dy^{3+} centers have axial symmetry in the (001) crystal plane, i.e. the positions of the EPR lines remain unchanged under a change in the angle θ between the external magnetic field and the directions [100] and [010] within this plane. Fig. 2 shows the experimental (circles) and calculated (curve) values of the resonance magnetic field corresponding to the intense line position of the even dysprosium isotope in the (010) plane at a temperature of 4K. These angular dependences are described by an axially symmetric spin Hamiltonian

$$H = \beta \mathbf{HgS} + \mathbf{SAI}, \quad (1)$$

where the effective spin is S =1/2, **g** and **A** are the g-tensor and hyperfine interaction tensor, respectively.

The following values of the g-tensor were found from the experimental angular dependences: $g_{\parallel}$ = 15.06 and $g_{\perp}$ = 2.47. The local magnetic axis direction of the Dy^{3+} ion in lead thiogallate with respect to the crystallographic axes of the lattice coincides with the [001] direction. It should be mentioned that the above values of the g-factors are typical for dysprosium ions in various crystals previously studied by EPR [3].

The hyperfine structure of Dy^{3+} ions is also anisotropic. The hyperfine components are shifted toward higher magnetic fields and the distances between them are changed with a change in the orientation of the magnetic field with respect to the crystal.

The calculations yield the following values of the hyperfine constants $A_{\parallel}$ and $A_{\perp}$ for two odd dysprosium isotopes in lead thiogallate: $A_{\parallel} = 675 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 111 \times 10^{-4}$ cm^{-1} for ^{163}Dy and $A_{\parallel} = 472 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 77 \times 10^{-4}$ cm^{-1} for ^{161}Dy, respectively.

We come to the conclusion that the EPR spectra of dysprosium-doped lead thiogallate single crystals belong to Dy^{3+} ions localized in the Pb^{2+} sites. Only one type of the paramagnetic Dy^{3+} center was observed in the experiments, despite that there are three structurally non-equivalent positions (Pb1, Pb2, Pb3) of the lead ions in the $PbGa_2S_4$ lattice. These positions differ in anionic polyhedra of the nearest environment (in symmetry and distances to the nearest S^{2-} ions) [1, 4]. Apparently, only the Pb3 type of the lead ions corresponding to the nearest environment with the C_2 local symmetry is substituted at a low dysprosium concentration (0.05 at. %). The Pb1 and Pb2 centers have the local D_2 symmetry. Thus, the axial symmetry of the EPR spectra should not be observed in the case of substitution of these sites by paramagnetic ions. Heterovalent substitution of the ions Pb^{2+} by Dy^{3+} ion in the lead thiogallate crystal lattice requires a charge compensation, that is non-local at dysprosium concentration of 0.05 at. % in our sample.

2.2. $PbGa_2S_4$:Ce

At low temperatures, Ce^{3+}-doped $PbGa_2S_4$ single crystals exhibit an intense multi-component (more than 40 lines) EPR spectrum. The spectrum is assigned to cerium ions (g-factors are typical for cerium ions in various crystals). Angular dependences of the group of lines under the rotation in the (100) plane have been obtained. At the small angle θ between the external magnetic field and the crystallographic direction [010], four intense lines and a number of low-intensity EPR lines grouped nearby are observed. The spectrum becomes considerably more complicated with an increase in the angle ($\theta > 20^0$). The number of spectral components is increased, their intensity ratio is changed, that complicates unambiguous analysis of each separate line.

The intense and weak lines exhibit similar temperature dependences but nevertheless have different spin-lattice relaxation times. The weak lines broaden faster and their intensity decreases more abruptly with an increase of the temperature; three main centers can be distinguished. The experimental (symbols) and the theoretical (curves) resonant magnetic field angular dependences of these lines in the (100) plane at T = 26K are shown in Fig. 3. The same angular dependences of the most intense Ce^{3+} centers in lead thiogallate in the (001) plane at a temperature of 4K are shown in Fig. 4. It should be mentioned that one curve is split into two curves at the angle θ closed to 90^0 in the (001) plane. The angular dependences of all lines can be described by spin Hamiltonian

$$H = \beta \mathbf{HgS}, \quad (2)$$

where the effective spin is S =1/2.

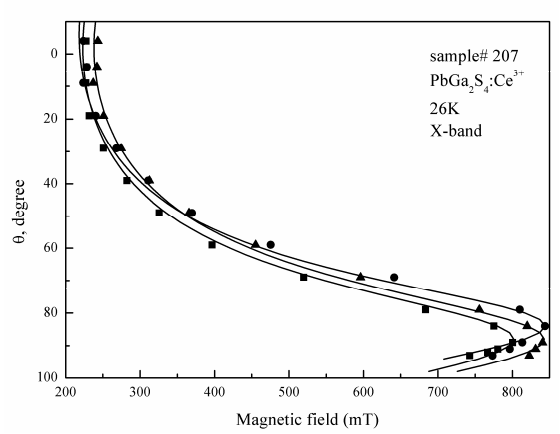


Figure 3. Experimental (symbols) and theoretical (curves) angular dependences of the intense Ce^{3+} centers in lead thiogallate at T = 26K in the (100) plane.

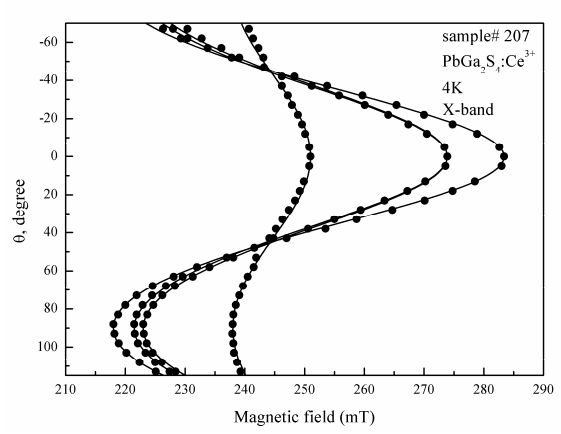


Figure 4. Experimental (dots) and theoretical (curves) angular dependences of the most intense Ce^{3+} centers in lead thiogallate at T = 4K in the (001) plane.

From the experimental angular dependences we obtained principal values of the g-tensor for the above four intense lines of cerium also (table 1). The local principal magnetic axes directions of two centers of Ce^{3+} ions in lead thiogallate with respect to the lattice crystallographic axes in the (100) plane coincide with the [001] axis. The same axis of third Ce^{3+} center deviates from the [001] axis by 4^0.

Table 1. The g-factors experimental values of four intense EPR lines of Ce^{3+} ions in $PbGa_2S_4$.

Ce center	g_x	g_y	g_z
Ce1	2.43	2.98	0.83
Ce2	2.65	2.79	0.79
Ce3	2.34	3.05	0.79
Ce4	2.43	3.00	0.83

Thus, the investigation of the angular and temperature dependences of the cerium-doped lead thiogallate single crystals EPR spectra lead to the conclusion that we observe the spectra of Ce^{3+} ions localized in the sites of Pb^{2+} in the crystal lattice.

In the case of Dy^{3+} we observed one type of paramagnetic centers despite the presence of three structurally non-equivalent positions Pb1, Pb2, Pb3 of lead ions in $PbGa_2S_4$ lattice. However, in the case of cerium, we observe much more various paramagnetic centers. Natural cerium does not have odd isotopes; therefore, the EPR spectra of these ions do not exhibit a magnetic hyperfine structure. Consequently, all observed lines are due to magnetically non-equivalent positions of Ce^{3+} in the lead thiogallate lattice.

In our opinion, a lot of lines are due to the distortion of the nearest environment of the paramagnetic center by a defect localized in the vicinity of Ce^{3+}. Heterovalent substitution of Ce^{3+} ions for Pb^{2+} ions requires compensation of the excessive positive charge. Local compensation defects can be formed by lead or gallium vacancies in the cationic environment of Ce^{3+}. The nearest environment of Pb^{2+} ions in lead thiogallate consist of 8 sulfur ions located at different distances from the center so that they form three structurally non-equivalent tetragonal antiprisms. The local symmetry of these polyhedra in the Pb3 position is C_2, and for Pb1 and Pb2 are D_2. In addition, the Pb3 site has two magnetically non-equivalent positions, whereas Pb1 and Pb2 have one per each site. The four detected intense EPR lines agree qualitatively with this picture. The next-nearest cationic shell of a Pb^{2+} ion consist of 8 lead ions and the next (gallium) shell of the lead ion is composed of 12 ions. In the case of the formation of vacancies in a lead or gallium site with all possible configurations of their positions in

the polyhedra, the multiplicity of non-equivalent paramagnetic centers greatly increases. More than 40 non-equivalent positions can occur under formation of a vacancy at the sites of Pb^{2+} or Ga^{3+}. Thus, the local compensation by lead or gallium vacancies is seemingly the reason of the observed a lot of the EPR lines of Ce^{3+}. Cerium doping of lead thiogallate results in the substitution of Ce^{3+} for lead sites. In this case, some Ce^{3+} ions exhibit non-local charge compensation (intense lines), whereas the others exhibit local compensation by a lead or gallium vacancy in the nearest environment of the paramagnetic center. The observation of a lot of paramagnetic Ce^{3+} centers in $PbGa_2S_4$ also indicates the substitution for exactly the lead sites. If Ce^{3+} ions were to be localized at gallium sites, no defects were required to compensate the excessive positive charge and we observed only four EPR lines due to magnetically non-equivalent positions. In addition, the probability of the substitution of Ce^{3+} ions for Ga^{3+} ions is very small owing to a considerable difference in their ionic radii.

2.3. ZnSe

We have carried out a diagnosis of ZnSe crystals doped with different rare-earth and transition metal ions, namely ZnSe: Cr, Co, Fe, Er. The crystals are doped with transition metal ions using diffusion method or during growth process. In the case of diffusion, the impurity centers are concentrated in the near-surface region that is involved in the diffusion process. The impurity concentration in this case can be an order of magnitude greater than that obtained using the doping in the course of the ZnSe crystal growth.

At first, we consider chromium doped zinc selenide single crystals. Fig. 5 shows angular dependence of ZnSe:Cr EPR spectra detected at 9.3 GHz and T = 4K under the magnetic field rotation in the plane (110). Thick green lines are EPR spectra belonging to Cr^{2+} centers of practical interest. Fig. 6 shows the experimental (green circles) and calculated (green curves) values of the resonance magnetic field corresponding to the chromium ion. Other symbols designate the most intense EPR lines other than Cr^{2+} ions.

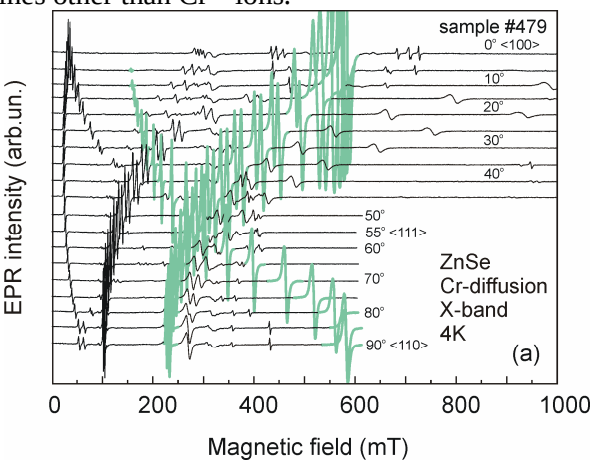


Figure 5. Angular dependence of ZnSe:Cr EPR spectra in the (110) plane at T = 4K.

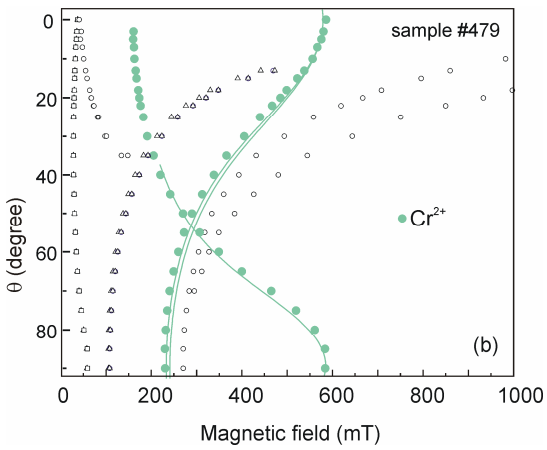


Figure 6. Experimental (green circles) and theoretical (green curves) angular dependences of the Cr^{2+} centers.

Along with chromium in the ZnSe:Cr crystal, anisotropic EPR spectra of iron, which, apparently, partly associated with other impurities, are detected. The signals except for chromium are undesirable, and the aim of further research is to minimize the related admixture content in laser materials. EPR diagnosis can be useful for solving this problem.

The study of cobalt doped zinc selenide crystals revealed the Co^{2+} and Fe^{3+} ions in a cubic environment. Co^{2+} fine structure is observed at a rotation in the (110) plane. It is worth noting, the presence of these lines in the EPR spectrum reflects the high quality of the crystal. The hyperfine interaction with the four nearest Se nuclei in the first coordination sphere has also been observed.

In contrast to the crystals in which cobalt has been introduced during the growth process, the EPR spectra of Co^{2+} centers in the diffusion layer are by an order of magnitude more intense that indicates a high concentration of cobalt introduced by diffusion method. However, with the introduction of cobalt by diffusion along with cobalt ions of practical interest, defects worsening the performance of laser materials are generated.

In the case of ZnSe:Fe, EPR spectra of Co^{2+} and Mn^{2+} ions in a cubic environment are detected. The spectra of Fe^{2+} ions are not observed. Nevertheless, since Fe^{2+} ions are optically detected, it is important to obtain an information about the quality of the diffusion layer on the surface of the crystal. Since Co^{2+} and Mn^{2+} ions are embedded into the lattice during diffusion process as uncontrolled impurities simultaneously with iron, the EPR spectra of these ions are proposed as ideal markers to control the diffusion layer. The presence of relatively narrow lines of the manganese fine structure indicates the high quality of the crystal in the diffusion layer.

Erbium doping of the ZnSe crystals is of particular interest because Er^{3+} ions have infrared laser luminescence band. Based on detailed study of the observed EPR hyperfine structure lines we can unambiguously state that spectra belong to Er^{3+} ions. Erbium spectrum has a characteristic hyperfine structure consisting of 8 lines caused the hyperfine interaction with the nuclear magnetic moment of ^{167}Er isotope, having nuclear spin of seven halves. The natural abundance of ^{167}Er is equal to 22.9 %.
Mn^{2+} ions are embedded into the lattice during diffusion also. As the manganese ions are in approximately the same diffusion layer that erbium ions, the EPR spectra can be used as markers for the diagnosis of the crystal quality. The presence of narrow and intense fine structure components in the EPR spectra of Mn^{2+} indicates good crystalline properties of the diffusion layer.

3. Conclusion

EPR spectra of Dy^{3+} and Ce^{3+} ions in $PbGa_2S_4$ single crystals were discovered and investigated. It was state that dysprosium and cerium ions replace lead ions in crystal lattice.

There is only one type of Dy^{3+} paramagnetic center (0.05 at. %.) localized at the Pb^{2+} position with the local symmetry C_2. In the case of $PbGa_2S_4$:Ce^{3+} a lot of paramagnetic centers were observed. Some Ce^{3+} ions exhibit non-local charge compensation, whereas the others exhibit local compensation by a lead or gallium vacancy in the nearest environment of the paramagnetic center. Parameters of spin Hamiltonian of EPR spectra of Dy^{3+} and Ce^{3+} ions in $PbGa_2S_4$ single crystals were calculated.

In ZnSe crystals investigated along with the working admixture in the diffusion layer EPR spectra of related admixtures worsening the performance of laser materials were detected. Introducing into the lattice during diffusion of transition metal ions of associated admixture of Mn was found. These spectra are proposed as the ideal markers for the control crystal structure of the diffusion active layer.

Acknowledgments

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