Dispersion of optical activity and absorption in $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals

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Abstract

The results for spectral dependences of the optical activity and optical absorption in $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals are presented and discussed.

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Introduction

It is well known that spatial dispersion phenomena may be described in terms of optical-frequency impermeability tensor dependent on the wave vector of light [1, 2]:

$$B_{ij}(\omega,\vec{k}) = B_{ij}^0 + ie_{ijl}g_{ln}m_n, \tag{1}$$

where B_{ij}^0 is the impermeability without taking spatial dispersion into account, e_{ijl} a unit antisymmetric Levi-Civita tensor, g_{ln} a second-rank axial tensor (a so-called gyration tensor) describing the natural optical activity, and m_n the unit wave vector. Then the specific optical rotatory power ρ may be written as

$$\rho = \frac{\pi}{\lambda n}G = \frac{\pi}{\lambda n}g_{ln}l_l l_n, \tag{2}$$

where G denotes the scalar gyration parameter, l_k, l_l the components of the unit wave vector **m** in the spherical coordinate system, λ the light wavelength, and n the refractive index.

Up to date, the optical activity has been studied for a great number of solid crystals, liquids and other materials. In crystalline materials, the effect manifests itself in the most intricate manner, due to their anisotropy. Among the classical crystals for which the optical activity has been well studied are those of lead germanate family. These crystals belong to the trigonal point group of symmetry 3 under the normal conditions. They are optically uniaxial and manifest a proper ferroelectric phase transition well above the room temperature [3].

Until now studies of the optical activity in the doped crystals of lead germanate family have been concentrated only on the compounds in which Pb^{2+} ion is substituted by the ions possessing almost the same ionic radius. For example, the ionic radiuses R for the solid solutions of $(Pb_{1-x}Bi_x)_5Ge_3O_{11}$ and $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ are equal to $R(Bi^{3+}) = 0.120$ nm and $R(Ba^{2+}) = 0.138$ nm, whereas $R(Pb^{2+}) = 0.132$ nm. Than one can assume that the substitution ions replace properly the lead ions in the crystalline lattice [4–8]. Here we should mention that the optical activity has been studied mainly for the wavelength of He-Ne laser ($\lambda = 632.8$ nm) and the dispersion of the effect has been touched upon only for the pure lead germanate [3]. The recent study [9] of the optical activity in $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals has testified that the optical rotatory power at $\lambda = 632.8$ nm almost coincides with that for the pure lead germanate (one has $(5.65\pm0.45)\times10^3$ deg/m for $Pb_5Ge_3O_{11}:Cu^{2+}$ [9] and 5.9×10^3 deg/m for $Pb_5Ge_3O_{11}$ crystals at $T = 300$ K [3]).

In this work we report the optical studies of the lead germanate crystals doped with Cu^{2+} ($Pb_5Ge_3O_{11}:Cu^{2+}$). They are interesting from the points of view of optical activity dispersion, since the crystal samples are green, and their optical absorption behaviour. According to the results for electronic paramagnetic resonance (EPR), Cu^{2+} ions occupy three decentric positions shifted in the lattice from the proper sites of Pb^{2+} ions. In other words, they are shifted in the plane normal to the polar three-fold axis, due to essential difference between the radiuses of Cu^{2+} and Pb^{2+} ions ($R(Cu^{2+}) = 0.070$ nm) [10]. It would be important to elucidate the effect of the above ionic substitution on the optical activity dispersion. The second aim of the present work is to study the absorption dispersion in the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals.

Experimental results

We have studied $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals doped with 0.14 weight % of Cu, using specimens with the faces perpendicular to the optic axis (the thickness of 5.50×10^{-3} m). Dispersion of the optical rotation has been measured with the aid of polarimetric set-up described in our recent report [9], for the case of normal conditions and the light propagation direction along the optic axis. The absorption spectra have been obtained with a Specord M40 spectrophotometer.

Spectral dependence of the absorption coefficient κ for the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals ($T = 300$ K) is presented in Fig. 1. When compare with the pure lead germanate for which the light wavelength corresponding to the absorption edge is equal to 430 nm [11], the absorption edge for our crystals is somewhat shifted towards longer wavelengths. A similar effect has been observed in the lead germanate doped with the iron ions [12]. As seen from Fig. 1, the spectral curve of the absorption coefficient of $Pb_5Ge_3O_{11}:Cu^{2+}$ reveals a minimum in the vicinity of $\lambda = 550$ nm. With further increase in the wavelength it increases sharply, though the absorption coefficient in the same spectral region (550÷700 nm) is almost zero for the pure lead germanate [12]. It is obvious that

increasing absorption of the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals in this region is caused by influence of copper impurities which, due to comparatively small ionic radius, most probably create colouring centres and impurity levels inside the band gap.

Dispersion of the specific optical power ρ for the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals measured at $T = 300$ K is displayed in Fig. 2. It looks quite reasonable that the minimum of the specific rotation dispersion coincides with that of the absorption coefficient.

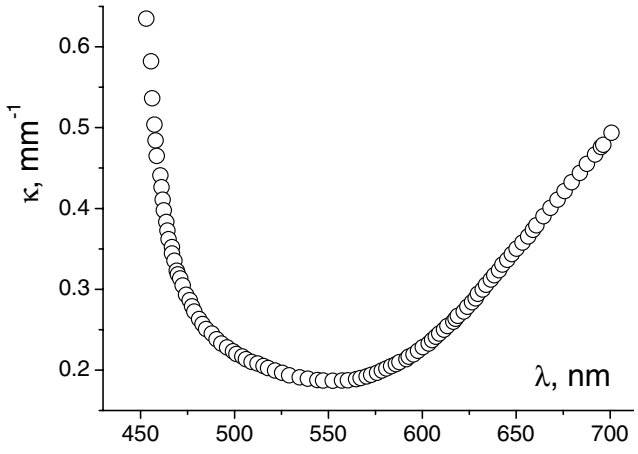

Fig.1. Dispersion of optical absorption coefficient κ for the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals at $T = 300$ K.

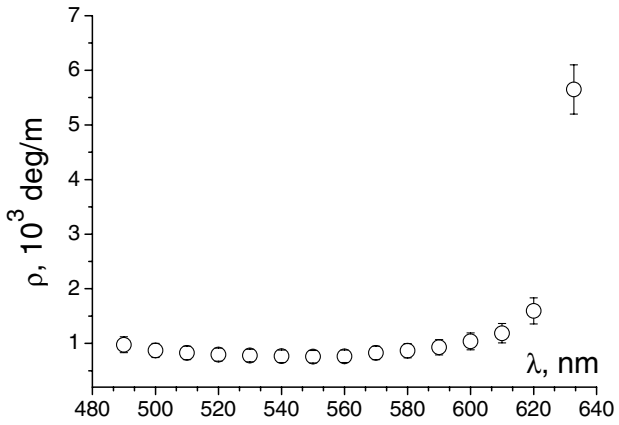

Fig.2. Dispersion of specific optical power for the $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals at $T = 300$ K.

We have to stress that, unlike the case of transparent crystals, the nontrivial optical activity dispersion in $Pb_5Ge_3O_{11}:Cu^{2+}$ is not easy to describe analytically. The relevant results involving the analysis of characteristic maximum absorption wavelengths and the corresponding effective oscillators' strengths will be the subject of our forthcoming work.

Conclusions

In the present work we have studied the dispersion dependences of the optical rotation and the absorption of $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals. It has been found that the absorption edge is somewhat shifted towards the long-wavelength range, when compare with that of the

pure lead germanate crystals. An increase in the both absorption and optical rotatory power has been detected in the region of 550÷700 nm. Most probably, it is caused by the impurities associated with the copper ions. As a result of comparatively small ionic radius, the latter form the colouring centres and impurity levels in the band gap.

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References

1. Agranovich V M and Ginzburg V L. Crystal optics with accounting of spatial dispersion, and excitons. Moscow: Nauka (1979).
2. Kizel V A and Burkov V I. Gyrotropy of crystals. Moscow: Nauka (1980).
3. Vlokh O G. Spatial dispersion phenomena in parametric crystal optics. Lviv: Vyshcha Shkola (1984).
4. Vlokh O G, Lazko L A and Shopa Y I, 1981. Electrooptic and electrogyration properties of the solid solutions on the basis of lead germanate. Phys. Stat. Sol. (a). **65**: 371–378.
5. Vlokh O G, Lazko L A and Shopa Y I, 1980. Electrogyration and electro-optic properties of the solid solutions on the basis of lead germanate. J. Phys. Soc. Jap., Suppl. B. **49**: 150–151.
6. Strukov B A, Sinyakov E V, Mayshchik E P, Minaeva K A, Monya V G and Vlokh O G, 1977. Ultrasonic relaxation, smearing of phase transition and some physical properties of lead germanate crystals and solid solutions on their basis. Izv. AN USSR, Ser. Fiz. **41**: 692–699.
7. Vlokh O G, Sinyakov E V, Lazko L A and Monya V G, 1978. Spontaneous and induced electrogyration in the $[Pb_{1-x}Bi_x]_5Ge_3O_{11}$ crystals. Fiz. Tverd. Tela. **20**: 2098–2100.
8. Iwasaki H, Miyazawa S, Koizumi H, Sugii K and Niizeki N, 1972. Ferroelectric and optical properties of $Pb_5Ge_3O_{11}$ and its isomorphous compound $Pb_5Ge_2SiO_{11}$. J. Appl. Phys. **43**: 4907–4915.
9. Adamenko D I, Klymiv I M, Vasylkiv Yu and Vlokh R O, 2009. Optical activity and critical exponent of the order parameter in lead germanate crystals. 1. The case of diffused phase transition in $Pb_5Ge_3O_{11}$ doped with Cu, Ba and Si ions. Ukr. J. Phys. Opt. **10**: 182–193.
10. Trubitsyn M P, Vaplak S and Ermakov A S, 2000. EPR and dielectrically properties $Pb_5Ge_3O_{11}$ crystals with decentric ions Cu^{2+}. Fiz. Tverd. Tela. **42**: 1303–1309.
11. Xianjun Wu, Jiayue Xu, Jingzhong Xiao, Anhua Wu and Weiqing J, 2004. Growth of ferroelectric lead germanate single crystal by the vertical Bridgman method. J. Cryst.

Growth. **263**: 208–213.

12. Yue Xuefeng, Mendricks S, Hu Yi, Hesse H and Kip D, 1998. Photorefractive effect in doped $Pb_5Ge_3O_{11}$ and in $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$. J. Appl. Phys. **83**: 3473–3479.

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