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SPECTROSCOPY OF CIRCULAR DICHROISM OF CRYSTALS STRUCTURE Ca - GALLOGERMANATE ACTIVATED BY IONS OF Fe-GROUP

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The spectra of absorption the spectra of circular dichroism are investigated, refractive indices are measured, the optical activity of crystals with the structure Ca - gallogermanate, not activated and activated by the ions of the group of iron is investigated.

The absorption spectra, circular dichroism, values of refractive indexes and optical activity of pure and doped by elements of Fe – group crystals with structure Ca – gallogermanate are investigated.

Introduction

The trigonal phase of $Ca_3Ga_2Ge_4O_{14}$, left investigated during the study of the crystallization of the pomegranate of $Ca_3Ga_2Ge_3O_{12}$ [1], had type of structure unknown earlier, in which the significant number of mixed germinates, gallates and silicates [2] were crystallized.

The ability to generate the stimulated radiation, discovered in the crystal of $La_3Ga_5SiO_{14}$ with the impurity of Nd^{3+} [3], stimulated the subsequent comprehensive studies of these disordered activated and nonactivated crystals, which showed that the connections with the structure Ca -gallogermanate possess the unique combination of physical properties-luminescent, laser, optical (including nonlinear), elastic, dielectric, piezoelectric, and others [4-6].

Present article is dedicated to a comprehensive study of the optical properties of crystals 1 – $La_3Ga_5SiO_{14}$, 2 – $La_3Ga_5GeO_{14}$, 3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$, 4 – $Ca_3Ga_2Ge_4O_{14}$, 5 – $Sr_3Ga_2Ge_4O_{14}$, 6 – $La_3Ga_{5.5}Ta_{0.5}O_{14}$. Furthermore the spectroscopic properties of the crystals of $Ca_3Ga_2Ge_4O_{14}$ and of $Sr_3Ga_2Ge_4O_{14}$, activated by chromium ions, and also the crystal of $La_3Ga_5SiO_{14}$, , activated by the ions of the group of iron: by chromium, by manganese and by nickel are investigated.

The crystals of high optical quality were obtained according to Chohralski's method with the use of VCh- heating on the technological installation with the platinum crucible [7]. The concentration of the activating admixtures/impurities of Cr^{3+}, Mn^{2+}, Ni^{2+} in the fusion/melt during the crystal growth composed 0.1%. [3].

Structure of crystals of the type Ca – gallogermanate

The crystals of $Ca_3Ga_2Ge_4O_{14}$, $Sr_3Ga_2Ge_4O_{14}$, $La_3Ga_5SiO_{14}$, $La_3Ga_5GeO_{14}$ relate to the trigonal-trapetsoedricheskomu class of 32 trigonal syngonies and have space group D_3^2 – P321 with one molecule in the unit cell [1,6].

Crystal structure of $Ca_3Ga_2Ge_4O_{14}$ (Fig.1) is formed by the tetrahedral layers, perpendicular to the axis C, between which are located the layers of the tompsonovskikh cubes, populated by the large ions of Ca^{2+} or Sr^{2+}, La^{3+} (position with symmetry 2).

In the work [6] it is shown that the octahedrons " a " are filled together with the ions of Ge^{4+} and Ga^{3+}. Tetrahedral layers consist of the tetrahedrons of two types: some are located on the triad axes (position " d " with symmetry 3), others in the position " f " with symmetry 2 are grouped around the octahedrons according to the law of triad axis.

Tetrahedrons of " d " type are filled with the ions of Ge^{4+}. Tetrahedrons of " f " type are populated together by the ions of Ga^{3+} and Ge^{4} or Si^{4+} in ratio 3:2. In the crystals, activated by chromium ions, the ions of Cr^{3+} enter into octahedrons " a ", replacing the ions of Ga^{3+} in the position with local symmetry 32. The statistical filling with the ions of Ga^{3+} and Ge^{4+} of positions " a " and " f " leads to the partial disordered state of the structure of crystal and causes the fluctuation of crystalline field on the ions of Cr^{3+}, which has an effect on its spectral-generation characteristics [3].

Spectra of absorption of the gallogermanates crystals.

The spectra of absorption of the nonactivated crystals were measured in the polarized light on the spectrophotometer ERS-3T Hitachi in region 200 - 2500 mmk are presented in Fig. 2 [8]. The spectra of the linear dichroism $\Delta\kappa(\lambda)$ were calculated by the formula:
$\Delta\kappa = \Delta D\lambda/4\pi dlge$, where $\Delta D = D_1 - D_2$; D_1, D_2 - optical density for usual and unusual waves (usual (ordinary) and extraordinary waves) (Fig. 3)

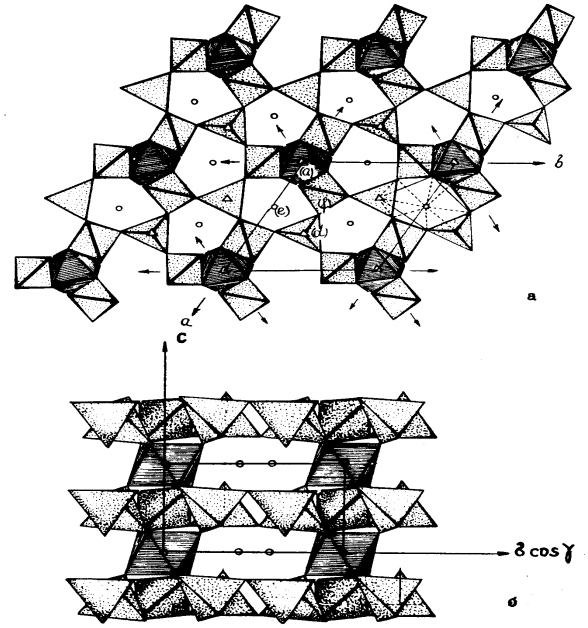

Fig. 1. Fragment of the structure of the crystal of $Ca_3Ga_2GeO_{14}$.

In neighbor ultraviolet and visible range of spectrum all investigated crystals have absorption bands and, as can be seen from Fig.3 they possess noticeable linear dichroism. In the neighbor infrared region of the spectrum all crystals are transparent.

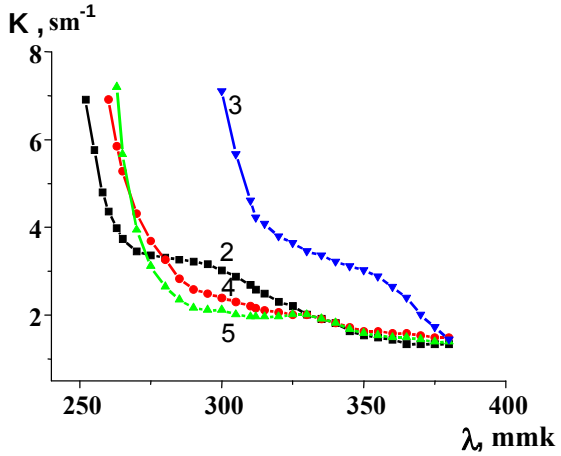

Fig. 2. Spectra of absorption of the crystals:
2 – $La_3Ga_5GeO_{14}$, 3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$,
4 -$Ca_3Ga_2Ge_4O_{14}$, 5 – $Sr_3Ga_2Ge_4O_{14}$

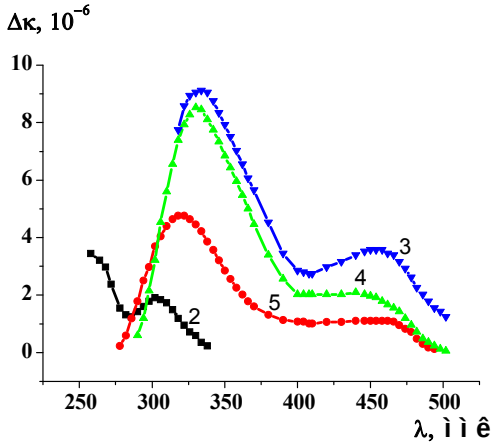

Fig. 3. Spectra of linear dichroism of the crystals:
2 – $La_3Ga_5GeO_{14}$, 3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$,
4 -$Ca_3Ga_2Ge_4O_{14}$, 5 – $Sr_3Ga_2Ge_4O_{14}$

Refractive indices and the double refraction of the gallogermanates crystals

The refractive indices of crystals are measured on the goniometer GS -5 by the method of minimum deviation on the prisms, prepared from the data of crystals [8]. The optical axis of crystal is directed along the edge of prism with the deviation not more than 10 '. For the measurement in the IK region of the spectrum the installation with the use as the receiver of emission of image converter was assembled (EOP). Mercury and sodium-vapor lamps were used as the light sources. For the liberation on the screen EOP of the line of mercury in the IK region of the spectrum was used the silicic filter, whose transmission begins from 1.05 mkm. It was defined a refractive index for the wavelength of mercury 1.13 mkm the accuracy of the definition of refractive indices in visible range of the spectrum of $2 \cdot 10^{-4}$, while in the IK region $8 \cdot 10^{-3}$. The dispersion formulas of the usual refractive indices of the investigated crystals are given in Fig.4.

It is obvious that the double refraction of crystals can be determined, after measuring the refractive indices of crystals in visible range of spectrum. The double refraction of crystals in the wide spectral interval was determined by the spectrophotometric method. For this sample it was placed to the position of the extinction between those crossed by polarizer and analyzer, then it was turned to 45° relative to this position. In this case the intensity of passed light **I** is described by formula: $I/I_0 = K_0 \sin^2\Delta/2$, where $\Delta = 2\pi d\delta n/\lambda$, K_0 - coefficient, connected with the absorption of sample, δn - double refraction. With a change in the wavelength, the oscillating curve recorded, moreover the positions of the minimums are determined by formula

$\delta n = \lambda m/d$, and maximums $\delta n = \lambda(m + 1)/d$, where m-order of interference. After determining the position of extremum and **m** number, double refraction δn for the given wavelength was calculated. In order to determine **m** number, were used the values δn , determined in visible range of spectrum. Values of double refraction for all investigated crystals calculated from such oscillating curves are given in Fig. 5.

It is evident from Fig.5 that almost all crystals have regions of the anomalous double refraction, which correspond to the strips of dichroism. If the anisotropic material, from which is manufactured the plate, possesses the anomalous motion of double refraction, then relation $\delta n/\lambda$ will change insignificantly, and plates can be used as the achromatic plates $\lambda/4$ or $\lambda/4$ in the region of wavelengths, where $\delta n/\lambda \approx$ const [9].

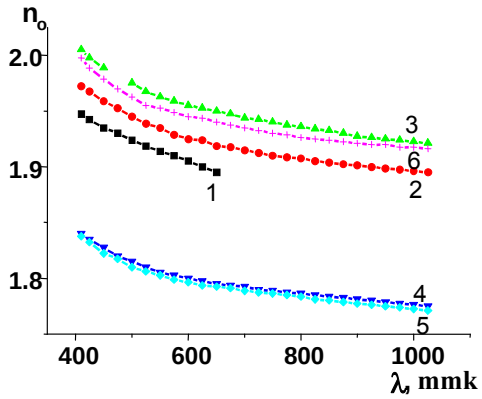

Fig.4 The dispersion formulas of the usual refractive index of the crystals:
1 – $La_3Ga_5SiO_{14}$, 2 – $La_3Ga_5GeO_{14}$,
3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$, 4 – $Ca_3Ga_2Ge_4O_{14}$,
5 – $Sr_3Ga_2Ge_4O_{14}$, 6 – $La_3Ga_{5.5}Ta_{0.5}O_{14}$

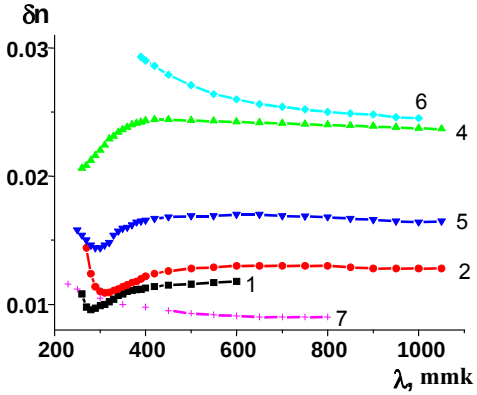

Fig.5 The dispersion formulas of the double refraction of the crystals:
1 – $La_3Ga_5SiO_{14}$, 2 – $La_3Ga_5GeO_{14}$,
4 – $Ca_3Ga_2Ge_4O_{14}$, 5 – $Sr_3Ga_2Ge_4O_{14}$,
6 – $La_3Ga_{5.5}Ta_{0.5}O_{14}$, 7 – SiO_2

For the refractive indices was carried out the approximation of the obtained results with the aid of the formula to Zelmeyera-Drude: $n_{o,e}^2 - 1 = K_{o,e}\lambda^2/(\lambda^2 - \lambda_{o,e}^2)$. (1)

The calculated values M_o, M_e, λ_o, λ_e are given in Table 1.

The table 1.Characteristic constants for the crystals in formula (1)

Crystal	λ_o, mmk	$K_o,10^6$	λ_e, mmk	$K_e,10^6$
$La_3Ga_5SiO_{14}$	128.0	2.50310	128.0	2.54370
$La_3Ga_5GeO_{14}$	135.2	2.56265	134.2	2.61191
$La_3Ga_{5,5}Nb_{0,5}O_{14}$	141.6	2.65666	144.2	2.76264
$Ca_3Ga_2Ge_4O_{14}$	127.8	2.13330	124.1	2.22340
$Sr_3Ga_2Ge_4O_{14}$	127.7	2.12918	125.6	2.19258
$La_3Ga_{5,5}Ta_{0,5}O_{14}$	135.1	2.63090	373.0	2.72430

We carried out the estimation of refractive indices with the aid of the methods of structural refractometry, which give the possibility to evaluate refractive indices, on the basis of structural data taking into account the method of the additivity of the molecular refractions of the separate fragments, on which it is possible to decompose crystal [10]. In structural refractometry the substance is characterized by the molecular refraction:

$$R = (n^2 - 1)/(n^2 + 2)\, M/d_0 = Mr , \qquad (2)$$

where M- molecular weight of substance, d_0 - the density of substance, r- the specific refraction. In tab. 2 the values of the molecular refractions for the investigated crystals, calculated by formula 2 for the average refractive indices **n** and for the wavelength 589 mmk are given. Re- the molecular refraction, calculated from the experimental data, $R_к$, $R_и$ - covalent and ionic refraction, calculated on the basis of tables [10], R_p,- the molecular refraction, calculated from the partition of crystals into the fragments [10].

The table 2.The molecular refraction of crystals1 – $La_3Ga_5SiO_{14}$, 2 – $La_3Ga_5GeO_{14}$, 3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$,4 – $Ca_3Ga_2Ge_4O_{14}$, 5 – $Sr_3Ga_2Ge_4O_{14}$

№	N	d_o	R	$R_э$	$R_к$	$R_и$	R_p
1	1.9088	5.754	0.081	82.8	191.5	77.7	82.89
2	1.9327	5.937	0.080	85.3	193.5	78.9	85.06
3	1.9711	5.934	0.082	88.4	198.7	79.6	88.10
4	1.8123	4.589	0.094	72.9	175.4	69.3	74.08
5	1.8076	5.087	0.085	77.5	208.4	73.8	78.40

It is evident that it is obtained a good agreement of experimental values $R_э$ and calculated R_p , which indicates the possibility of calculating the molecular refraction according to the diagram of additivity. Thus, for this class of crystals during the calculation of the molecular refraction it is possible to use the principle of additivity and on the calculated molecular refraction it is possible to evaluate the refractive indices of new crystals of such type. Knowing the molecular refraction at different wavelengths for the separate structural fragments, it is possible to judge the dispersion of the refractive indices of complex crystals in the region of transparency. In this case the calculated and experimental values of refractive indices must coincide with an accuracy to the second sign of afterward comma.

Optical activity of the gallogermanates crystals.

The rotation of the plane of polarization of light in the samples, oriented along the optical axis, for all crystals was measured on the spectropolarimeter with the accuracy $5 \cdot 10^{-2}$ grad/mm [8]. The values of the rotation of the plane of polarization are represented in Fig. 6. In the figure for the comparison the values of specific rotation for the quartz are given.

According to measured data it was carried out the approximation of the specific rotation of the investigated crystals of $\rho(\lambda)$ according to the formula [11]:

$$\rho = K_1\lambda^2/(\lambda^2 - \lambda_0^2)^2 + K_2/(\lambda^2 - \lambda_0^2) \qquad (3)$$

In this work as the characteristic wavelength the value of wavelength, obtained from the approximation of average refractive index, is used. Values for K_1, K_2, λ_0 are given in Table 3.

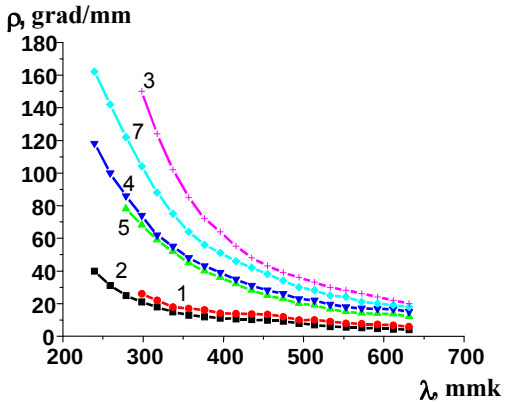

Fig. 6. The specific rotation of crystals:1 – $La_3Ga_5SiO_{14}$, 2 – $La_3Ga_5GeO_{14}$, 3 – $La_3Ga_{5,5}Nb_{0,5}O_{14}$, 4 – $Ca_3Ga_2Ge_4O_{14}$, 5 - $Sr_3Ga_2Ge_4O_{14}$, 7 – SiO_2

The table 3.Characteristic constants for the crystals in formula (3)

Crystal	λ_0, mmk	K_1, 10^6	K_2, 10^6
$La_3Ga_5GeO_{14}$	135.2	0.4682	0.7034
$La_3Ga_5\ Nb_{0.5}O_{14}$	141.6	–9.2831	15.4936
$Ca_3Ga_2Ge_4O_{14}$	127.8	3.4242	1.5491
$Sr_3Ga_2Ge_4O_{14}$	127.7	4.8827	0.0438

Analogously we carried out the measurements of rotatory ability in the direction of optical axis for the crystals, activated by the impurities: $Ca_3Ga_2Ge_4O_{14}:Cr^{3+}$, $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$, $La_3Ga_5SiO_{14}:Cr^{3+}$, Fe^{3+}, Ni^{2+} and $Mn2^+$. Experimental results practically coincide with the results, obtained for the transparent crystals. Thus, the impurity, introduced into the matrix in the limits of 0.1 wt.%, does not influence the rotatory ability of crystals with the structure of Ca-gallogermanata. The dispersion of rotatory ability is determined by strips, which are located in the vacuum region of the spectrum. From the measurement of the specific rotation of $\rho(\lambda)$ it is possible to define only the component of g_{33}.

As it was shown in [12], for determining the component of g_{11} it is necessary to conduct measurements on the plate, cut out in parallel to optical axis. Since all crystals in question have weak absorption bands in the neighbor UF region and possess dichroism, during a study of optical activity in the directions, different from the direction of optical axis, this must be considered. In this case $tg2\chi_{\parallel} = -2ke^{-\delta}\sin\Delta$ и $tg2\chi_{\perp} = -2ke^{\delta}\sin\Delta$, (4)

where for the plate, cut out in parallel to optical axis $k = g_{11}/2n_{cp}\delta n$ - the ellipticity of natural waves in the crystal, n_{cp} - average refractive $\Delta = 2\pi d(\delta n)/\lambda$, $\delta = 2\pi d(\Delta\kappa)/\lambda$.

The measurements of the angles of $\chi_{\parallel}$ and $\chi_{\perp}$ in the range of wavelengths from 270 to 660mmk were carried out on the plates from the crystals of $La_3Ga_5SiO_{14}$ [13] and $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$ [14], cut out parallel to optical axis. The dispersion formula of the azimuth of the polarization of the passed light for these crystals is shown in Fig. 7 and 8.

Knowing values δn and $\Delta\kappa$, from the dependences of $\chi_{\parallel}(\lambda)$ and $\chi_{\perp}(\lambda)$ it is possible to calculate the component of g_{11}. For determining the sign the components of g_{11} of measurement were conducted on the thin plate (d = of 0.01 mm). In this case it turned out that g_{11} - has positive sign, and g_{33} -negative for the right-handed crystal. The dispersion of the components of g_{11} and g_{33} for the crystals of $La_3Ga_5SiO_{14}$ and $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$ is shown in Fig. 9 and 10.

For the analytical description of the experimental dependence of the dispersion of the components of g_{11} and g_{33} in the crystal of $La_3Ga_5SiO_{14}$ were obtained the formulas:

$$g_{33} = -A(n_{cp}\lambda/\lambda^2 - \lambda_1^2)\ 10^{-5}, \quad (4)$$

$$g_{11} = \lambda n_{cp}[B/(\lambda^2 - \lambda_2^2) + C\lambda^2/(\lambda^2 - \lambda_2)^2]\ 10^{-5} \quad (5)$$

where $A = 0.6072 \cdot 10^3$, $B = 0.6106 \cdot 10^6$, $C = 0.6278 \cdot 10^6$, $\lambda_1 = 198$ mmk, $\lambda_2 = 156$ mmk

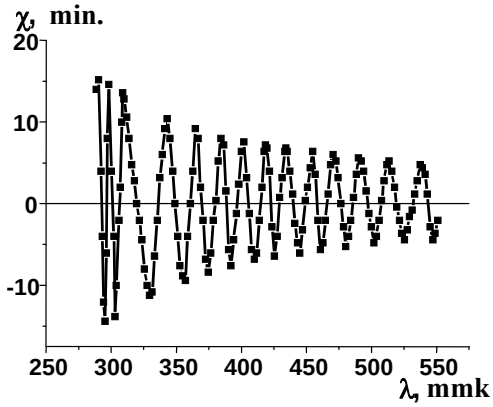

Fig. 7. The dependence of the azimuth of the polarization of the passed light for the plate, cut out parallel to optical axis from the crystal of $La_3Ga_5SiO_{14}$ (d = 1.1 mm).
light is polarized: it is perpendicular to optical axis and parallel to the optical axis

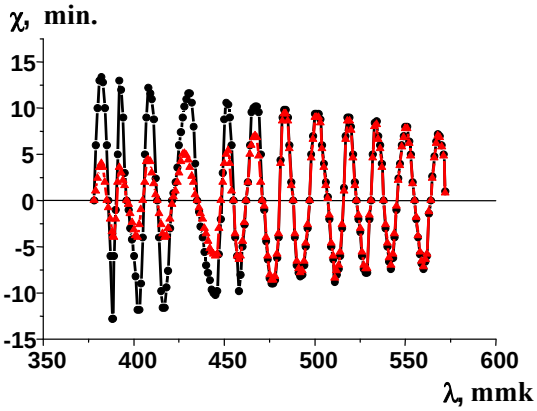

Fig. 8. The dependence of the azimuth of the polarization of the passed light for the plate, cut out parallel to optical axis from the crystal of $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$ (d = 0.96 mm).
light is polarized:• – it is perpendicular to optical axis, σ – in parallel to the optical axis

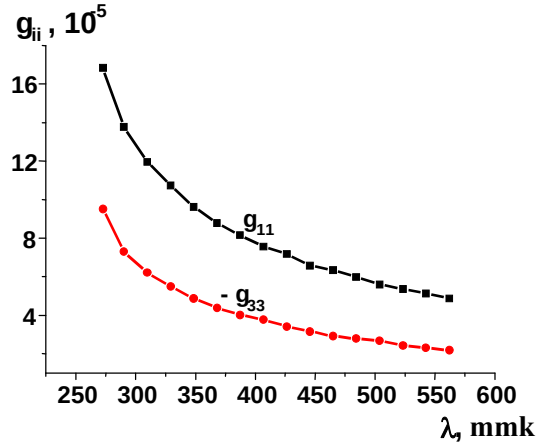

Fig. 9 . Dispersion of the components of g_{11} and g_{33} for the crystal $La_3Ga_5SiO_{14}$

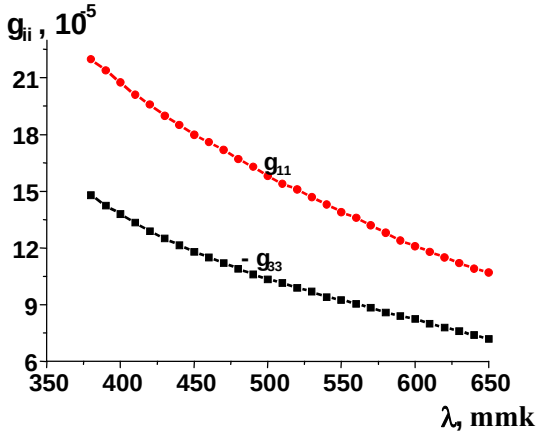

Fig. 10. Dispersion of the components of g_{11} and g_{33} e for the crystal $Sr_3Ga_2Ge_4O_{14}$: Cr^{3+}

Spektroskopical properties of the gallogermanate of calcium of $Ca_3Ga_2Ge_4O_{14}$, activated by chromium ions crystal

The spectra of absorption of the crystals of $Ca_3Ga_2Ge_4O_{14}$, activated by chromium ions are investigated on the spectrophotometer of Specord-40 in the range 250- 900 mmk (40000-11300 sm^{-1}) with 300K in the samples with a thickness of 1.9 and 0.45 mm, oriented perpendicularly to optical axis [15].

In the absorption spectra there are registered three intensive strips with frequencies in the maximums 35088 sm^{-1} (285 mmk), 22650 sm^{-1} (440 mmk) and 15750 sm^{-1} (635 mmk), and bend in interval of 14160 is also noted. 14347 sm^{-1} (695. 700 mmk) and weakly-intensive strips with 12000 sm^{-1} (830 mmk), ~ 17500 sm^{-1} (570 mmk) and ~2y000 sm^{-1} (475 mmk). With 300K it is registered pure- electron transition with a frequency of 11374 sm^{-1} (879 mmk), which relates to the strip with 12000 sm^{-1} (830), which is the beginning of electron-vibrational progression with the period of 130 sm^{-1} in the range 11500. 12500 sm^{-1} (870. 800 mmk). For the interpretation of experimental data the calculation of the parameters of crystalline field and frequencies in the maximums of strips is executed (tab. 4).

The values of the calculated wavelengths in the ion of Cr^{3+} correlate with their experimental values. However, weak strips with 830 mmk, 570 mmk and pure- electron transition are not plotted in this diagram, apparently, these maximums correspond to the ion Of Cr^{4+} in the tetrahedral coordination, which coincides with the conclusions of the works [16].

Spectral measurements of circular dichroism (CD) in the crystals of $Ca_3Ga_2Ge_4O_{14}$ were conducted on dikhrografe in the range 250- 800 mmk, in the samples, oriented perpendicularly to optical axis, with the use of procedures, which make it possible to eliminate the possible effect of circular and linear double refraction and linear dichroism (Fig. 11).

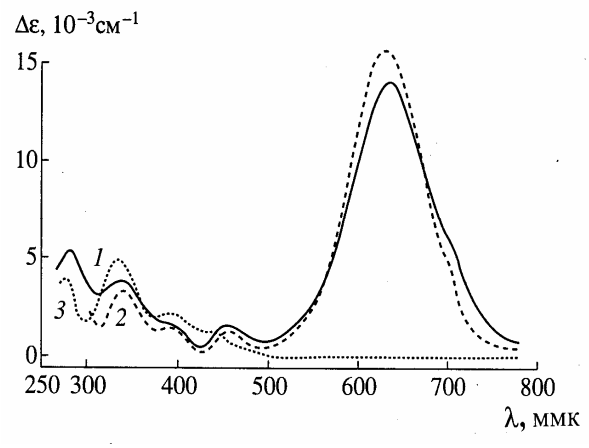

Fig. 11. Spectra of circular dichroism of the crystals:1 – $Ca_3Ga_2Ge_4O_{14}$:Cr^{3+} with T =300K, 2 – $Ca_3Ga_2Ge_4O_{14}$:Cr^{3+} with T =77K,3 – nonactivated $Ca_3Ga_2Ge_4O_{14}$

It is established that in the crystals $Ca_3Ga_2Ge_4O_{14}$ with the impurity of the ions of Cr^{3+} CD is manifested at frequencies of all four absorption bands. Since CD appears only on the passages, for which electrodipole and magnetodipole moments simultaneously are not equal to zero, the intensities of strips in the maximums are substantially outstanding in SA and spectra CD in SA of $I(b^4T_1) : I(a^4T_2) : I(^4T_2) = 6:2:1$, and in the spectra CD 3:1:6. Furthermore, in the spectra CD (Fig. 11, curve 1) they are observed maximum with 335 mmk and arm in region 380-400 mmk, which according to calculation are not connected with the ions of Cr^{3+}.

With a temperature decrease to 77K strips slightly are displaced into the short-wave region of the spectrum. The maximum with 390 mmk is determined at frequencies of bend, and strip with 450 mmk partially is resolved, the fixture of asymmetric (Fig. 11 curve 2). With 470 mmk the arm, which, probably, corresponds to passage $^4A_2 \rightarrow {}^2T_2$ (table 4). ($^4A_2$ was formed $\rightarrow {}^2T_2$).

The spectra of magnetic circular dichroism (MCD) were measured on dikhrografe with the use of a permanent magnet, which creates the field of the strength of ~14кЕ. During the application of magnetic field even with 300K on the long-wave side of spectrum with 635 mmk of the ion of Cr^{3+} it is permitted purely electron transition with the maximum with 13072 sm^{-1} (765 mmk) and electron-vibrational structure with a frequency of 190 sm^{-1}.

For the interpretation of spectra photos CD of the crystal of $Ca_3Ga_2Ge_4O_{14}$, activated by the ions of Cr^{3+}, were investigated the spectra CD of the crystals, grown without the impurity of the ions of Cr^{3+}. During a study of the spectra of absorption of unalloyed crystals with the large tension of spectra in the intensity were fixed only very weak strips with 330 and 430 mmk.

In the spectra CD were discovered the well permitted strips with 272, 330, 390 and 440 mmk (Fig. 11 curve 3). Strips with 330 and 390 mmk, as noted above were observed in the spectra CD of the crystals of $Ca_3Ga_2Ge_4O_{14}$, activated by the ions of Cr^{3+}.Other maximums with 272 and 440 mmk overlap with spectrum bands CD with 276 and 450 mmk, which correspond to the ions of Cr^{3+}. Thus from the spectra CD it is possible to conclude that the strip with 453 mmk is complex and consists of three components 440, 453 and 470 mmk.

Probably, all strips, observed in the spectra CD of unalloyed crystal can be explained by their own defects, which are formed in the process of an increase in the crystal

The table 4.Calculated and experimental values of wavelengths in the maximums of the spectra of absorption (SA) and circular dichroism (CD) of activated by ions Cr^{3+} and nonactivated crystals Of $Ca_3Ga_2Ge_4O_{14}$

Passage	SA	SA	CD	CD
			с Cr^{3+}	без Cr^{3+}
	λ_{calc}, mmk	λ_{exp}, mmk	λ_{exp}, mmk	λ_{exp}, mmk
$^4A_2 \rightarrow {}^2E$	694	700	700	
$^4A_2 \rightarrow {}^2T_1$	660			
$^4A_2 \rightarrow {}^4T_2$	635	635	635	
$^4A_2 \rightarrow {}^2T_2$	474		470*	
$^4A_2 \rightarrow a^4T_1$	441	440	453	
				440
			390*	390
			330	330
$^4A_2 \rightarrow b^4T_1$	283	285	275	275

The calculated wavelengths λ_{calc} were calculated in the parameters: Dq = 1575, B = 761, C = 2811, a = 70; * – measurements are carried out with T = 77K.

Spectroscopic properties of the crystal of $Sr_3Ga_2Ge_4O_{14}$, activated by chromium ions.

In this division there are represented the results of the studies, carried out on the activated by chromium of gallogermanate crystals of strontium of $Sr_3Ga_2Ge_4O_{14}$ (SGGO:Cr), which have different color [17]. As samples served oriented perpendicularly to the optical axis of the plate with a thickness of from 0.5 to 1.5 mm. the absorption spectra were measured in the range 250.700 mmk on the spectrophotometers of Hitachi and Spekord-40. Spectral measurement of circular dichroism was conducted in the range 250-800 mmk. The obtained results were compared with the results of the similar studies, carried out on the crystals of $Ca_3Ga_2Ge_4O_{14}$:Cr^{3+} [15].

The investigated crystals of $Ca_3Ga_2Ge_4O_{14}:Cr^{3+}$ had green color, while the crystals of $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$ had red and green color. The spectra of absorption of these crystals are represented in Fig. 12. In all spectra there are observed wide electron-vibrational absorption bands typical for the ion of Cr^{3+} in the octahedral crystalline field: one in the ultraviolet and two in visible ranges of spectrum. The positions of the maximums of strips for all investigated samples are represented in Table 5.

According to the experimental data carried out the estimation of the parameters of crystalline field Dq and B, which will agree with the data of work [16].

During the comparison SA of the green samples of CGGO:Cr and SGGO:Cr should be noted their similarity, which attests to the fact that the replacement Ca on Sr in the gallogermanates practically did not influence on the value of crystalline field at the center of the octahedron, where the ion of Cr^{3+} is located. As can be seen from Fig. 12, for the crystals of SGGO:Cr the intensity of wide absorption band in the red region of the spectrum for the red sample is lower than the intensity of the corresponding absorption band for the green sample, which indicates the smaller concentration of the ions of Cr^{3+} in the red sample.

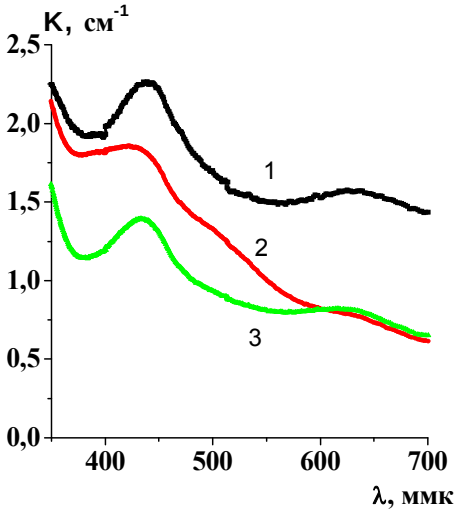

Fig.12. Spectra of absorption of crystals in visible range of the spectrum:1 - $Ca_3Ga_2Ge_4O_{14}:Cr^{3+}$, 2– $Sr_3Ga_2Ge_4O_{14}Cr^{3+}$(red), 3–$Sr_3Ga_2Ge_4O_{14}$ Cr^{3+} (green)

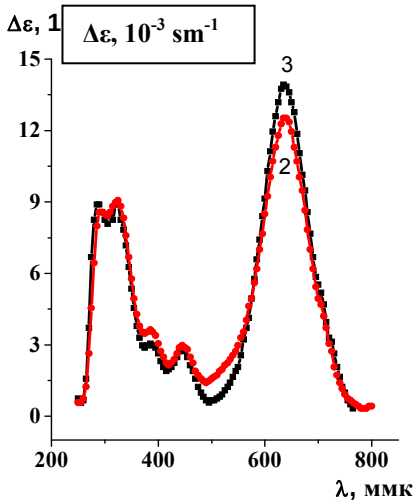

Fig.13. Spectra of circular dichroism of the crystals: 2 – $Sr_3Ga_2Ge_4O_{14}$ Cr^{3+} (red), 3 – $Sr_3Ga_2Ge_4O_{14}$ Cr^{3+} (green)

The table 5.The basic spectroscopic parameters of the crystals. $Sr_3Ga_2Ge_4O_{14}:Cr^{3+}$ (SGGO:Cr) and $Ca_3Ga_2Ge_4O_{14}:Cr^{3+}$ (CGGO)

Crystals	Optical passages from the level $^4A_2$ to the levels b^4T_1 a^4T_1 $^4T_2$ ^2E	The centres of colouring (color centers).
SGGO:Cr (red)	a) 290 430 640 b) 295 445 635 700 c) 2.8 12.4 d) 0.69 4	320 385
SGGO:Cr (green)	a) 295 435 630 b) 290 445 635 700 c) 2.9 14 d) 0.64 5.6	320 385

CGGO:Cr	a) 285 440 635	
(green)	b) 275 450 630 700	335 390
	c) 1.5 14	
	d) 1.2 6.3	
CGGO		275 330 390 440
not activated by		

Note. The parameters of crystalline field for the crystals are the following:
SGGO:Cr(red) Dq = 1560 sm^{-1}..B = 690 sm^{-1} Dq/B = 2.26.
SGGO:Cr(green) Dq = 1590 sm^{-1}..B = 690 sm^{-1} Dq/B = 2.3.
CGGO:Cr(green) Dq = 1570 см-1 B = 660 sm^{-1} Dq/D = 2.
a) the maximums of absorption bands (mmk).
b) the maximums of strips CD (mmk).
c) the intensity of strips CD in the maximum ($\Delta\varepsilon$, 10^{-2} sm^{-1}).
d) the rotatory forces of strips CD (R, 10^{-40} unit. CGSE).

It must be noted that besides the strips, connected with the ions of Cr^{3+}, in SA of the red sample of SGGO:Cr there is observed the additional wide absorption band in the green region of the spectrum (470 - 580 mmk). Apparently, this absorption can be taken as the wide absorption bands of the ions of Cr^{4+} by maximums with ~ 500 and ~ 550 mmk [16]. Since the intensities of wide absorption bands in the red region of the spectrum (with 625 and 630 mmk) for the red and green samples are small, the contribution of these strips to color of crystals is insignificant. The greatest contribution to color of crystals give the ions of Cr^{4+}, and also absorption, connected with the quality of crystal.

The spectra of circular dichroism are investigated in the same samples. (Fig. 13).

It is established that CD is manifested on all three wide absorption bands and in the narrow R- line (~ 700 mmk) of the ion of Cr^{3+} (table 5). Furthermore in the spectrum CD of the red sample of SGGO:Cr just as in SA, appears weakly-intensive wide absorption band in a green region of the spectrum (470- 580 mmk), which can be related to CD of the ions of Cr^{4+}. Spectra CD for the red and green samples differ little: the positions of the maximums of all strips practically coincide, the intensities of the corresponding strips are distinguished insignificantly.

From the comparison of the spectra CD of the green samples of CGGO:Cr^{3+} and SGGO:Cr^{3+} it follows that the ratios of the intensities of strips in the maximums, which correspond to one and the same electron transitions of the ions of Cr^{3+}, are different and compose 1 (with λ ~ of 630 mmk), ~ 0.5 (with λ ~ of 440 mmk) and 0.6 (in THE UF region of the spectrum).

The ratio of the intensities of strips in these spectra is different because of different selection rules for the passages in SA and CD. In the spectra CD of the crystals activated by chromium are discovered also the additional broad bands, not connected with chromium ions, which also are observed also in the spectra CD of unalloyed crystals CGGO. Apparently, these strips with the maximums in region 330 and 390 mmk can be taken to the color centers (table 5), connected with the structural imperfections, which are formed in the process of growing the crystals.

Rotatory forces of the strips CD of electron transitions $^4A_2 \rightarrow a^4T_1$ и $^4A_2 \rightarrow {}^2T_1$ of the ions of Cr^{3+} in the crystals CGGO and SGGO were calculated from the formula

$R = 0{,}407 \cdot 10^{-38}\ \Delta\varepsilon_{oi} \cdot \Delta_i / \nu_{oi}$, where $\Delta\varepsilon_o$, Δ_i and ν_{oi} were determined from corresponding to these passages absorption bands in the spectrum CD. ($\Delta\varepsilon_{oi}$ - intensity of strip in the maximum, Δ_i - the half-width of strip, ν_{oi} - transition frequency). The basic spectroscopic parameters of the investigated samples are given in table 5.

The study SA and SD activated by chromium ions and unalloyed crystals CHGGO, SGGO made it possible to conduct the separation of the absorption bands and CD, caused by ions Cr^{3+} in the octahedral coordination, and by the ions of Cr^{4+} in the tetrahedral coordination

and of strips CD, connected with the defective centers of matrix. It should be noted that in conclusion as a result of the investigations of the optical properties of gallogermanates of calcium and strontium conducted by us it is established that in the crystals CGGO and SGGO, activated by chromium ions, the contaminant ion enters into structure; moreover the ion of $Cr3^{+}$- in the octahedral coordination and the ion of Cr^{4+} - in the tetrahedral coordination.

In the spectra of magnetic circular dichroism of the octahedral coordination ion of Cr^{3+} and the spectra of absorption of the tetrahedrally coordinated ion of Cr^{4+} in the crystal CGGO are determined the characteristics of the oscillations/vibrations, which appear during the excitation of electron transitions in these ions of chromium.

During a study of circular dichroism with 300 and 77K it is obtained information about purely electron transition $4A_2 \rightarrow {}^2T_2$ of the ion Cr^{3+} of the investigated crystals. In the unalloyed and activated crystals the strips, caused by growth defects, are discovered by the method of circular dichroism.

Spectroscopic properties of the crystals of $La_3Ga_5SiO_{14}$,, activated by the ions of the group of iron

As it has already been spoken there have been grown crystals $La_3Ga_5SiO_{14}$ (LGS), activated by the ions of the group of iron, where impurity was introduced into the charge in the concentration to 0.1 wt. %.

The spectra of absorption (SA) of the crystals LGS, activated by chromium ions, manganese, and nickel, are investigated in the range 250- 900 mmk with 300K in the samples with a thickness of d = 2.4 – 3.5mm, oriented perpendicularly to optical axis. SA are measured on the spectrophotometer of Specord-40. It is established that the absorptions of the crystals of strip observed in the spectra correspond to the ions of Cr^{3+} and Cr^{4+} in the octahedral and tetrahedral coordination's respectively, to the ions of Mn^{2+} and Ni^{2+} in the octahedral coordination. In the spectra of circular dichroism of all investigated crystals the strips, which correspond to electron transitions in the activating ions and observed in the absorption spectra, are discovered.

An example in Fig.14 is represented the spectrum CD of the crystal of $La_3Ga_5SiO_{14}$: Ni^{2+}. It is evident that in visible range of spectrum CD is observed the strip with the maximum with 400 mmk, and also the broad band in the range 500-800 mmk, which corresponds to two electron transitions of the ions of Ni^{2+} in the octahedral coordination: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ [18].

Furthermore in the ultraviolet region of the spectrum CD is discovered the nonelementary strip with the maximum with ≈340 mmk, which is not caused by the ions of Ni^{2+}. Analogous strip CD is observed in the nonactivated crystal of $La_3Ga_5SiO_{14}$, as is evident in Fig. 15.

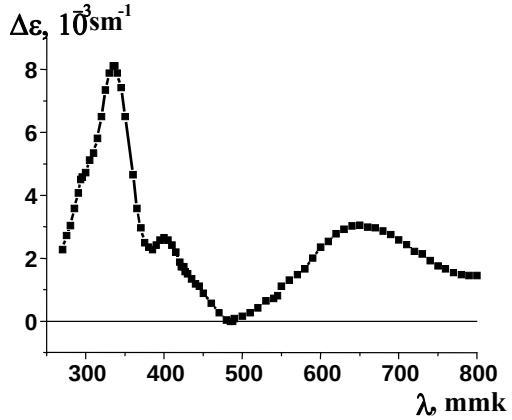

Fig. 14. Spectrum of circular dichroism of the crystal of $La_3Ga_5SiO_{14}$: Ni^{2+}

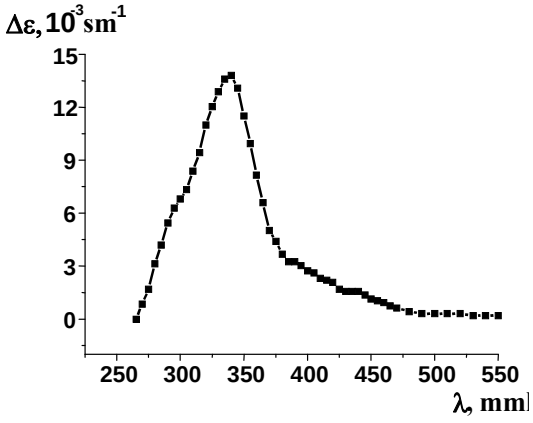

Fig. 15. Spectrum of circular dichroism of the nonactivated crystal of $La_3Ga_5SiO_{14}$

As it was shown (see Fig.11 and 13) an analogous strip CD was observed also in the crystals of Ca – and Sr – gallogermanates.

Since in all investigated by us crystals with the structure of Ca - gallogermanate, activated and not activated by the ions of the group of iron, there is observed the broad nonelementary band CD which is not connected with electron transitions of contaminant ions, nature of this strip, apparently, is connected with the structural imperfections of crystal, which appear in the process of growth. Our studies in the pure crystals of $La_3Ga_5SiO_{14}$ did not reveal defective paramagnetic centers in the spectra EPR. The defects, observed in the spectra CD, are not paramagnetic. However, till percent time these defects were observed in the absorption

spectra only after the X-ray irradiation of crystal. Because of the high sensitivity of dikhrografe they were discovered in the nonirradiated crystals.

The Conclusion

Thus it as been carried out an investigation of the optical properties of crystals with the structure Ca- the gallogermanates: $La_3Ga_5SiO_{14}$, $La_3Ga_5GeO_{14}$, $La_3Ga_{5,5}Nb_{0,5}O_{14}$, $Ca_3Ga_2Ge_4O_{14}$, $Sr_3Ga_2Ge_4O_{14}$, $La_3Ga_{5.5}Ta_{0.5}O_{14}$, and also the crystals of $Ca_3Ga_2Ge_4O_{14}$ and of $Sr_3Ga_2Ge_4O_{14}$, activated by the ions of chromium and crystal of $La_3Ga_5SiO_{14}$, activated by the ions of the group of iron: by chromium, by manganese and by nickel. The measurement of the refractive indices, absorption coefficients have been carried out, optical activity, including circular dichroism of these crystals has been studied. All investigated crystals are grown at the Moscow State University by B.V. Millem, for what the authors are very grateful to him.

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