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Spectroscopy of V^{4+} and V^{3+} ions in a forsterite crystal

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Abstract. The absorption spectra of impurity vanadium ions in forsterite crystals are studied in the wavelength range from 600 to 2000 nm. It is found that the V^{4+} ion in the tetrahedral coordination in crystals grown by the Czochralski technique exhibits strong absorption in the range from 600 to 1200 nm. The intense electron-vibrational progressions in the absorption spectra of impurity *d*-ions in crystals were observed for the first time at temperatures 300 and 77 K. In the authors' opinion, these progressions appear due to the formation of the oxovanadate complex and distortions of the structural tetrahedron. The forsterite crystal doped with V^{4+} ions has a very high absorption cross section (up to 2.1×10^{-18} cm^2) and a continuous broad absorption band, which makes this crystal promising as a passive laser switch in the range between 600 and 1200 nm. At the same time, the V^{4+} ions in the forsterite crystal do not emit luminescence because of a high probability of the nonradiative relaxation of their excited state. It is shown that luminescence of a V : Mg_2SiO_4 crystal is related to the tetrahedral V^{3+} ion.

1. Introduction

The vanadium ion is a promising activator of crystals used in quantum electronics. One such crystal is forsterite. Forsterite Mg_2SiO_4 contains Mg octahedrons of two types and Si tetrahedrons, all distorted to symmetry C_s. The distance between one of the oxygen ions, O_I^{2-}, and the Si^{4+} ion in the silicon – oxygen tetrahedron is smaller than that for the other ions O^{2-}. This is explained by the fact that the Coulomb repulsion between the Si^{4+} ion and three Mg^{2+} ions at the apex and the base of the tetrahedron is not compensated. The length of the shortest bond is 1.615 Å and the lengths of the other bonds are 1.635, 1.641, and 1.654 Å [1].

In this paper we describe in detail the absorption spectra of vanadium ions in forsterite crystals in the wavelength range from 600 to 2000 nm at 300 and 77 K. Crystals were grown from the melt by the Czochralski technique (see details, for example, in Ref. [2]) on a 'Kristall-2' setup. The concentration of ions in crystals was measured with a Camebax-SX-50 x-ray spectral microanalyser. The absorption spectra were recorded with a SF-50-spectrophotometer. The spectra were approximated by decomposition into Gaussian components by using the OPTIS optimisation package [3]. The maxima of the absorption and luminescence spectra were assigned to the impurity centres of certain types.

2. Spectroscopic properties of the V^{4+} ion

The correlation between the experimental and theoretical polarisation dependences of the absorption bands at 1000, 830, and 700 nm (Figs 2 and 3) and the very high intensity of the electron-vibrational progressions (Figs 4 and 5) allow us to assign an intense absorption band in the region from 600 to 1200 nm (Fig. 1) to the V^{4+} (d^1) ion in the oxygen tetrahedron. We are not aware of any cases of such dramatic manifestation of the electron-vibrational interaction at 300 and 77 K in crystals doped with transition metal ions. Thus the ratios of intensities of the vibrational peaks and the absorption band at 700 nm are 1:10 and 1:5 at 300 and 77 K, respectively (Figs 4b and 5b).

The intensities of vibrational peaks increase strongly upon passing from a neutral to weakly oxidising atmosphere of the crystal growth (Figs 1 and 4). This trend is manifested

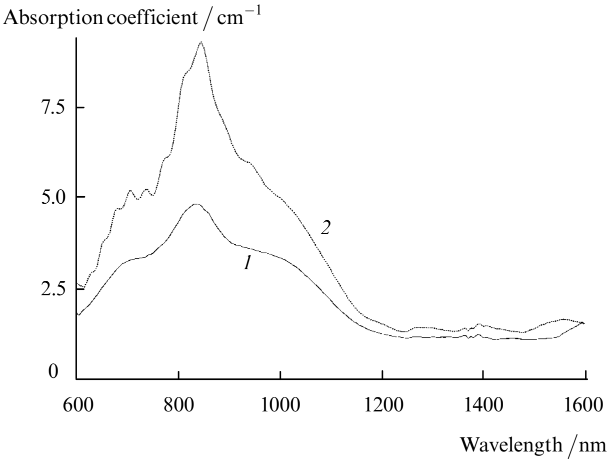

Figure 1. Absorption spectra of V : Mg_2SiO_4 crystals grown in neutral (1) and weakly oxidising (2) atmosphere.

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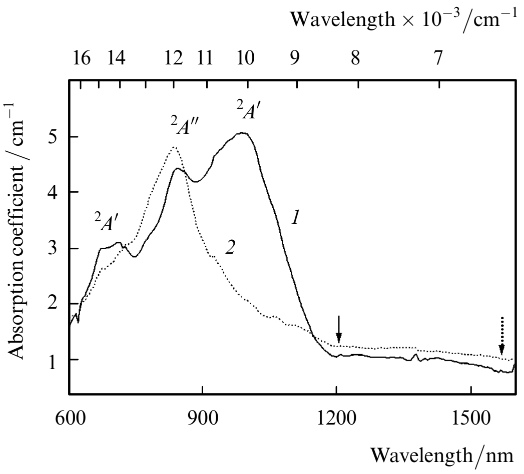

Figure 2. Absorption spectra of V : Mg_2SiO_4 polarised parallel to the crystallographic axes c (1) and b (2) (the solid arrow shows the zero-phonon transition to the $^2A'$ level of the V^{4+} ion; the dashed arrow shows the zero-phonon transition to the $^3T_2$ level of the V^{3+} ion)

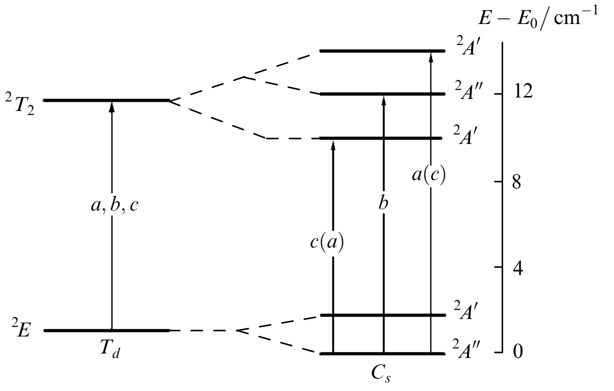

Figure 3. Energy level diagram and allowed transitions of the V^{4+} ion in the tetrahedral environment with local symmetries T_d and C_s.

most dramatically in the wavelength range from 600 to 850 nm (Figs 4a and 4b). The intensity of the absorption band in the region between 600 and 1200 nm is almost doubled, although the total concentration of vanadium ions of all valences in crystals remains approximately the same (4.2×10^{18} cm^{-3}). These facts also suggest that this absorption band and electron-vibrational progressions belong to the highly oxidised vanadium ion.

We separated the components of the electron-vibrational progression by using the following approach. The experimental spectrum was approximated by a sum of Gaussian functions. The difference between the approximating curve and the experimental spectrum yielded a complete set of components of the electron-vibrational progression (Fig. 5). Brunold et al. [4] also observed the electron-vibrational progression in the region from 900 to 1200 nm at cryogenic temperatures. According to our data obtained at 300 and 77 K, the frequency of the highest-frequency mode of this progression is 780 cm^{-1}, the vibrational modes with frequencies 615, 360, and 130 cm^{-1} also being observed. The zero-phonon transition of the $^2A'$ component of the $^2T_2$ term has a frequency of 8264 cm^{-1} (1210 nm) (shown by the arrow in Figs 2 and 5). The progression origin is shifted with respect to this frequency by the energy of the lattice phonon equal to ~ 130 cm^{-1}. The origin of the progression in the range from 600 to 1000 nm corresponds to the frequency 9901 cm^{-1} (1010 nm) (Fig. 5) and it was related to the fine structure of the spectrum at $T = 77$ K (Fig. 6). According to the decomposition of the spectrum, the origin of this progression corresponds to the unshifted zero-phonon transition of the $^2A''$ band (Fig. 5a). The frequency of the most intense vibrational mode in the progression is 615 cm^{-1}. The frequencies of other vibrational modes are 360 and 130 cm^{-1} and the number of components of the progression is no less than ten.

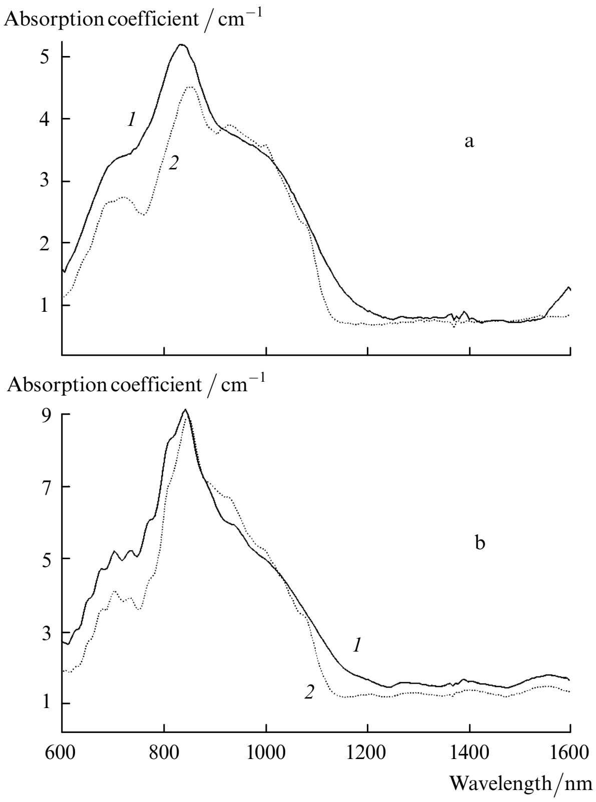

Figure 4. Absorption spectra of the V^{4+} ion at 300 (1) and 77 K (2) in Mg_2SiO_4 crystals grown in neutral (a) and weakly oxidising (b) atmosphere.

The intensity of the vibrational peaks in the absorption spectrum in the range from 600 to 1000 nm is explained by the properties of the V^{4+} ion and the structure of the silicon – oxygen tetrahedron. As noted above, the Si^{4+} ion is displaced towards the O_I^{2-} ion. On the other hand, it is known that the V^{4+} ion tends to form the oxovanadate complex $V^{4+} - O^{2-}$ [5]. The overlap of the bonding orbitals upon the complex formation should lead to the displacement of the vanadium ion in the symmetry plane to the O_I^{2-} ion, resulting in a further decrease in the bond length with the O_I^{2-} ion. Also, the influence of the Jahn – Teller pseudo-effect caused by small energy gaps between oxygen orbitals and degenerate components of the ^2E ground state of the V^{4+} ion must not be ruled out. This effect is known to increase the distortion in the direction of one of the bonds in distorted tetrahedrons [6]. As the charges become less compensated along the $V^{4+} - O^{2-}$ bond upon the replacement of Si^{4+} ions by V^{4+} ions, the dipole moment of nuclei in impurity tetrahedrons increases.

The high dichroism of the spectrum (Fig. 2) suggests that the absorbing centre is strongly axially distorted, and the frequencies 700 – 800 cm^{-1} are assigned to the valence vibrational modes of the excited state of the oxovanadate ion [5].

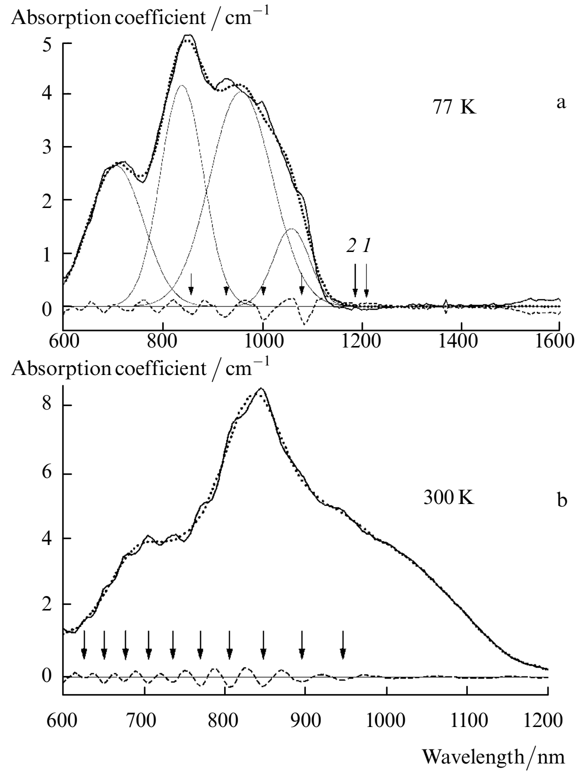

Figure 5. Absorption spectra of V : Mg_2SiO_4 crystals grown in neutral (a) and oxidising (b) atmosphere. The thick curves are experimental spectra; the dashed curves are the separated progressions; the thin curves are the Gaussian components of the decomposition; the dotted curves are approximating spectra (the arrows show the zero-phonon transition (1) and its replica at a frequency of 130 cm^{-1} (2), as well as the calculated wavelengths of the progression peaks).

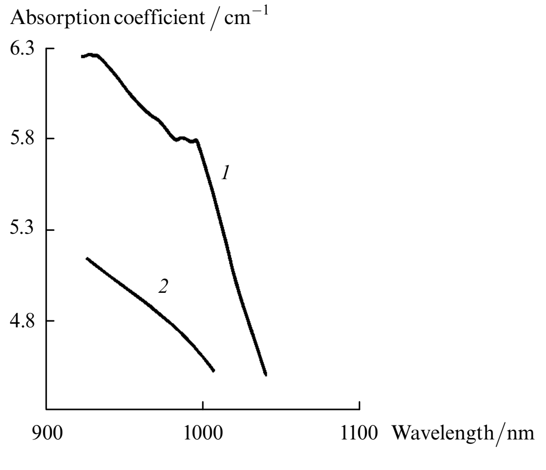

Figure 6. Fragments of the absorption spectra of a V : Mg_2SiO_4 crystal grown in a weakly oxidising atmosphere in the region of 1000 nm at 77 (1) and 300 K (2).

It is obvious that vibrations along the shortened bond most strongly affect the dipole moment, and they are the most probable. Only two t_2 vibrations with frequencies ν_3 and ν_4 in a regular tetrahedron correspond to such vibrations [7]. In the vibrational spectrum of forsterite in the region $\sim$ 600 nm, only components of the t_2 vibration with the frequency ν_4 are manifested [8].

Thus the high intensity of the peaks corresponding to the 615 cm^{-1} vibration is caused by an increase in the dipole moment of nuclei in the tetrahedron upon the formation of the stable $[VO]^{2+}$ complex in the $[[VO]O_3]^{4-}$ cluster, the high probability of vibrations along the $V^{4+}-O^{2-}$ bond, and maximum fluctuations of the dipole moment upon excitation of these vibrations. In addition, a strong electron-vibrational interaction (in this case, the $E-t_2$ interaction) typical for the V^{4+} ion, which causes the Jahn–Teller pseudo-effect, can play an important role.

Another specific feature of the spectrum studied, which indicates the presence of tetrahedral V^{4+} ions, is the enhancement of absorption in the range from 900 to 1100 nm with decreasing temperature to 77 K (Fig. 4). This anomalous behaviour can also be explained by the polarisation of nuclei in the impurity tetrahedron.

It is obvious that the dipole moment of nuclei in the impurity tetrahedron increases with decreasing temperature because of the ordering of the dipoles. The wavelengths of the peaks whose intensities exhibit the anomalous temperature dependence are 1090, 1005, 930, and 870 nm, and the frequencies are 9174, 9954, 10753, and 11494 cm^{-1} (Fig. 4). These frequencies correspond to the peaks of the progression over the frequency 780 cm^{-1}. As noted above, the frequency 780 cm^{-1} is most likely related to the valence vibration of the oxovanadate complex in the excited state, which, as the t_2 vibration mode, causes small fluctuations of the dipole moment. Thus the anomalous temperature dependence of the absorption is caused by an increase in the intensity of the first four components of the progression in the range from 900 to 1200 nm.

This effect is analogous in some degree to an increase in the absorption upon the ferroelectric order–disorder phase transition in crystals containing distorted tetrahedrons as structural units. The temperature ordering of the dipole moments in such tetrahedrons affects a local crystal field and enhances the intensity of the vibrational peaks [6].

Note that the anomalous temperature dependence of the absorption was observed in a number of compounds containing the oxovanadate ion [5], which suggests that this effect is caused by a strong polarising action of this ion.

3. Spectroscopic properties of the V^{3+} ion

The correlation of the wavelengths (see Table 1) and polarisation dependences of the intensities (Figs 2 and 7) of the narrow lines at 1570 nm (6369 cm^{-1}) and 1380 nm (7246 cm^{-1}) and also of the broad band at 1550 nm (6450 cm^{-1}) with the calculated values for the V^{3+} (d^2) ion in the tetrahedral coordination suggests that the absorption spectrum belongs to this centre. Parameters of the Coulomb interaction

Table 1. Calculated and experimental positions of maxima of the spectrum of absorption from the $^3A_2$ ground state of the V^{3+} ions in the tetrahedral coordination in a forsterite crystal (the crystal-field strength parameter $Dq = -645$ cm^{-1}, $B = 400$ cm^{-1}, $C = 2090$ cm^{-1}).

Level	ν_{exp}/cm^{-1}	λ_{exp}/nm	ν_{calc}/cm^{-1}	λ_{calc}/nm
$^3T_2(t_2e)$	6450	1550	6450	1550
$^1E(e^2)$	7246	1380	7237	1382
$^3T_1(t_2e)$	–	–	9884	1012
$^1A_1(e^2)$	–	–	12051	830
$^1T_2(t_2e)$	–	–	13560	737
$^3T_1(t_2^2)$	–	–	15466	647
$^1T_1(t_2e)$	–	–	15430	648

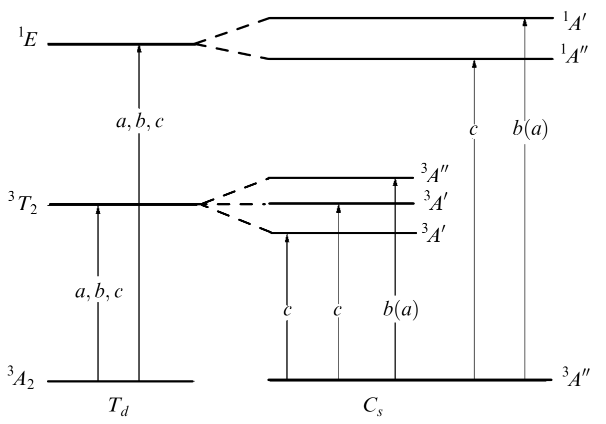

Figure 7. Energy level diagram and allowed transitions for the V^{3+} ion in the tetrahedral environment with local symmetries T_d and C_s.

$B = 400$ cm^{-1} and $C = 2090$ cm^{-1} (see Table 1) correspond to a partially covalent chemical bond in the tetrahedron.

The energy level diagram of this centre differs substantially from that presented in Ref. [2] and was calculated based on more extensive experimental studies (samples grown in various atmospheres were studied in a broader wavelength range, including the long-wavelength range).

4. Discussion

4.1 The V^{4+} ion in the tetrahedral coordination

Our study showed that electronic excitation of the V^{4+} ion substantially changes its polarising action on the neighbouring ions. We observed intense vibrations of the tetrahedron involving 10–12 phonons, valence vibrations of the excited oxovanadate complex with frequency 780 cm^{-1}, and crystal vibrations.

We failed to observe the luminescence of V^{4+} ions in a forsterite crystal at both 300 and 77 K (excitation was performed by the fundamental and second harmonics of a neodymium laser and also by a Ti : sapphire laser). The luminescence was absent, obviously because of the fast multiphonon nonradiative relaxation.

Luminescence depends on the parameters of vibrations interacting with the lower $^2A'$ component of the $^2T_2$ term. The ratios of intensities I_m $(m = 1, 2, 3, 4)$ of the first peaks of the 780 cm^{-1} progression to the intensity I_0 of the zero-phonon line yield the estimate of the temperature factor in the expression for the probability of nonradiative relaxation $W_{\rm nr}$ at the temperature T:

$$W_{\rm nr}(T) = W_{\rm nr}^{(0)} \exp\left(-\frac{E}{kT}\right) , \qquad (1)$$

where

$$E = \frac{\hbar\omega^2}{2\Delta\Omega} ; \qquad (2)$$

$W_{\rm nr}^{(0)}$ is the probability of nonradiative relaxation at the absolute zero; ω is the frequency of the active vibration; $\Delta\Omega = a\sum_{\varkappa}\omega_{\varkappa}$ is the Stokes shift; a is the thermal release parameter, and summation is performed over all active vibrations $\varkappa$. It is known that

$$\frac{I_m}{I_0} = \frac{(a^2/2)^m}{m!} . \qquad (3)$$

According to our estimates, $I_m/I_0 \approx 25, 20, 15, 15$ for $m = 1$, 2, 3, 4, respectively. A rough estimate, taking only the 780 cm^{-1} vibrational mode into account, gives a very large Stokes shift $\Delta\Omega$ (no less than 5000 cm^{-1}). Thus a consideration of the temperature factor in Eqn (1) shows that the probability of the radiative transition is close to zero at both 300 and 77 K.

The probabilities $W_{\rm nr}^{(0)}$ for a number of impurity ions in forsterite were estimated in Ref. [8]:

$$W_{\rm nr}^{(0)} = |P_{2\to 1}|^2 (S^m/m!) \exp(-S) . \qquad (4)$$

Here $|P_{2\to 1}|$ is the electronic matrix element; S is the Huang–Rhys factor; $m = (E_2 - E_1)/\hbar\omega$; E_2 and E_1 are the energies of the initial and final levels. According to the estimate in Ref. [8], the probability $W_{\rm nr}^{(0)}$ was 35×10^3 times greater than that for a $\rm Mn_6 : BaSO_4$ crystal. We obtained a somewhat larger value of $W_{\rm nr}^{(0)}$, because we used the values of $\hbar\omega$ and $E_2 - E_1$ equal to 780 and 8264 cm^{-1}, respectively, whereas in Ref. [8] the values 780 and 8264 cm^{-1} were used. Thus it is unlikely that the V^{4+} ion can emit luminescence at cryogenic temperatures, and its luminescence is excluded at higher temperatures.

The electron-vibrational interaction may also lead to large oscillator strengths of the transitions in the V^{4+} ion at 300 and 77 K (the absorption cross section at 830 nm reaches 2.1×10^{-18} cm^2), broadening, and overlap of the transitions. This results in a continuous and comparatively smooth absorption band in the range from 600 to 1200 nm. These properties of a forsterite crystal doped with V^{4+} ions make it a promising material for passive optical switches.

4.2 The V^{3+} ion in the tetrahedral coordination

The energy level diagram obtained for this centre explains absorption in the long-wavelength region and all maxima of the luminescence spectrum (Fig. 8) (the luminescence can be used to obtain tunable lasing).

The validity of this scheme is also confirmed by a high intensity of the 1570 nm zero-phonon transition for the $^3T_2(t_2e)$ band compared with that of the phonon sideband. A small displacement of the minimum of the configuration surface of the $^3T_2(t_2e)$ state relative to the minimum of the $^3A_2(e^2)$ ground state is naturally explained by small energy gaps between the $^3T_2(t_2e)$,$^1E(e^2)$, and $^3A_2(e^2)$ levels and by a substantial admixture of the wave function of the two latter states to the wave functions of the first state.

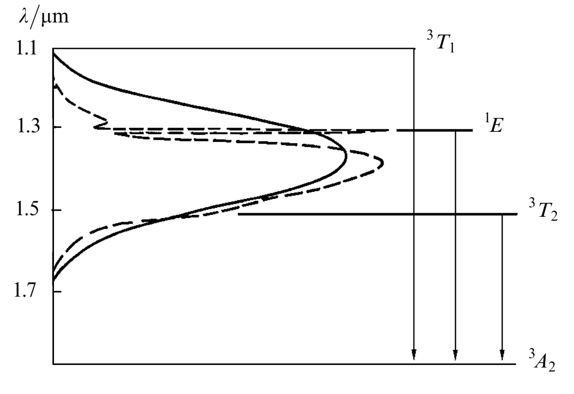

Figure 8. Comparison of maxima of the luminescence spectrum [2] with transitions in the V^{3+} ion in the tetrahedral environment in a $\rm Mg_2SiO_4$ crystal at 77 K (dashed curve) and 300 K (solid curve).

We can also explain the shoulder observed on the long-wavelength wing of the luminescence band at ~ 1550 nm at 77 K (Fig. 8), which was not described by the energy level diagram suggested in Ref. [2]. According to our data, this shoulder corresponds to the transition from the first excited $^3T_2$ state of the V^{3+} ion. Thus the luminescence spectrum exhibits broad bands corresponding to the transitions from the $^3T_1$ and $^3T_2$ levels and the narrow line corresponding to the transition from the ^1E level.

Analysis of the data obtained for the V^{3+} ion in the tetrahedral configuration in many compounds (or example, see Ref. [5]) showed that in forsterite this ion is located in an unusually weak crystal field in the oxygen tetrahedron ($Dq = -645$ cm^{-1}, $Dq/B = 1.6$). This fact is probably explained by a strong low-symmetry distortion of impurity tetrahedrons.

5. Conclusions

The study of the absorption spectra of forsterite crystals doped with vanadium ions in the range from 600 to 2000 nm at 300 and 77 K gave the following results.

(1) The strong absorption of the crystal in the spectral range between 600 and 1200 nm is related to the V^{4+} ion in the tetrahedral environment. The broad absorption band and high absorption cross section (up to 2.1×10^{18} cm^2) of the $V : Mg_2SiO_4$ crystal are caused by the extremely strong excitation of the phonon subsystem upon the electronic transition in the V^{4+} ion. These features make this crystal promising for use in passive laser switches. Strong excitation of the phonon subsystem also results in fast multiphonon nonradiative relaxation of the excited state, which prevents the luminescence of the ion.

(2) The luminescence of the crystal in the spectral range from 1.1 to 1.7 μm is related to the V^{3+} ion in the oxygen tetrahedron. The maxima of the luminescence spectrum correspond to the transitions from the $^3T_2$, ^1E, and $^3T_1$ levels to the $^3A_2$ ground level. This luminescence can be used to obtain tunable lasing in the 1.5 μm region. However, to do this, the concentration of the V^{3+} ions should be substantially increased compared with that of the V^{4+} ions, which requires the development of the proper method of crystal growth.

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