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Optical Spectroscopy and Density Functional Calculations of Chromium(V)-Doped YVO_4 and YPO_4: Influence of the Second Coordination Sphere

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Low temperature polarized single-crystal absorption and luminescence spectra of Cr(V)-doped YVO_4 and the powder luminescence spectrum of Cr(V)-doped YPO_4 are reported and discussed. A rich fine structure and strong polarization effects are observed in the near-infrared. Due to a strong interaction of the Cr(V) ion with two Y^{3+} ions in the second coordination sphere of the Cr(V) ion, the electronic ground state is different from the one expected on the basis of an angular overlap calculation in which only the four oxygen ligands are taken into account. This effect of the Y^{3+} ions on the ground state of Cr(V) is confirmed by a density functional calculation and by literature EPR data. CrO_4^{3-} bending modes are responsible for the fine structure in the d−d transition and the resulting distortion in the emitting excited state.

Introduction

Cr(V) ions ($3d^1$) can be doped into phosphate, arsenate, and vanadate host lattices, where they substitute for the tetrahedrally coordinated pentavalent ions. The EPR and optical absorption properties of Cr(V)-doped lattices have been studied rather extensively in the past, mainly in order to test molecular orbital and ligand field models of the electronic structure of tetra oxo transition metal complexes. For reviews see refs 1 and 2. The luminescence properties of Cr(V) doped crystals were not explored until recently when the luminescence of various Cr(V) doped materials was reported.[3,4] These materials show broad band luminescence in the near-infrared region. The quantum efficiencies are very low, even at cryogenic temperatures.

In this paper we report the optical absorption and luminescence properties of Cr(V)-doped YVO_4 and YPO_4. We will show that the second coordination sphere of the Cr(V) ion, formed by two Y^{3+} ions, has a strong influence on the nature of the ground state of the Cr(V) ion and on the optical spectroscopic properties.

Experimental Section

YVO_4 and YPO_4 both have the tetragonal zircon structure. The Cr(V)-doped YVO_4 single crystals were grown from a $Bi_2O_3-V_2O_5$ flux. This solvent was preferred over the more commonly used $Pb_2V_2O_4$[5,6] because the presence of the divalent Pb^{2+} ion may favor the incorporation of Cr(VI) in YVO_4 by charge compensation. The starting mixture, composed of 69.5 mol % Bi_2O_3, 23 mol % V_2O_5, 7 mol % Y_2O_3, and 0.5 mol % CrO_3, was slowly heated to 1320 °C in a Pt crucible. After a soaking period of 18 h, the mixture was cooled at a rate of 5 °C/h to 800 °C, after which the furnace was turned off. The crystals were separated from the flux by leaching with hot diluted hydrochloric acid. The average size of the crystals was about $1 \times 2 \times 3$ mm. The crystals grow like rods along the crystallographic *c*-axis. Some of the crystals were orange-yellow, probably due to the presence of Cr(VI). Others were green, the usual color of Cr(V)-doped materials.[7,8] The real concentration of Cr(V) in the green crystals is not known. The preparation of a YPO_4 powder doped with 0.1% Cr(V) was reported in ref 4.

The polarized absorption spectra were measured on a Cary 5e double beam spectrophotometer, equipped with a Displex closed cycle helium refrigerator. The luminescence spectra were measured by excitation with a Kr^+ ion laser at 647.1 nm. The luminescence was dispersed through a 0.75 m Spex 1702 single monochromator and detected by a ADC 403 L N_2(lq)-cooled germanium detector. The decay times were measured by excitation at 1064 nm with a Quanta-Ray pulsed Nd:YAG laser and detection with a fast InGaAs photodiode. Details of the equipment are found in ref 4 and references therein.

Calculations in the framework of the angular overlap model (AOM) were performed with the program Ligfield.[9] The ab initio calculations were performed using the HFS-LCAO method as implemented in the ADF program system (version 2.1) by Baerends et al.[10,11] The basis sets consisted of triple-ζ Slater type orbitals, expanded by a polarization function. For chromium the core orbitals up to 2p were kept frozen, whereas for oxygen only the 1s orbital was kept frozen. We applied the local density approximation with Vosko−Wilk−Nusair parametrization of the exchange correlation potential[12] to all calculations. An electric field, given by a point charge model, was included to simulate the electrostatic effects of the Y^{3+} ions in the second coordination sphere of the Cr(V) ion.

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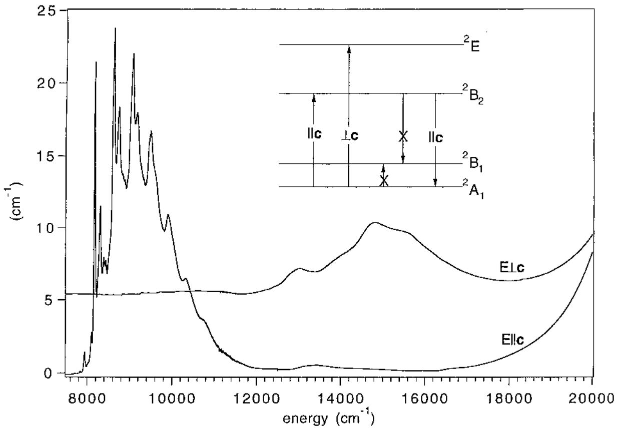

Figure 1. Crystal absorption spectra of Cr(V)-doped YVO_4 at 15 K, polarized parallel and perpendicular to the crystallographic *c*-axis. The $E\perp c$ spectrum is vertically shifted for more clarity. The inset shows the energy level diagram with the selection rules in D_{2d}.

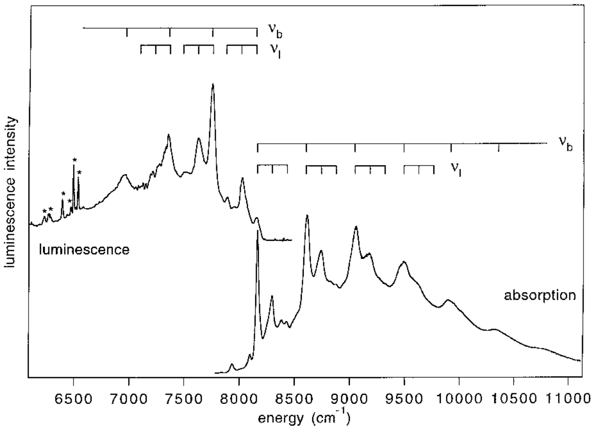

Figure 2. Unpolarized luminescence spectrum and $E||c$ polarized absorption spectrum (as in Figure 1 but on an expanded energy scale) of Cr(V)-doped YVO_4 at 15 K. Coupling with ν_b and ν_l is indicated. The luminescence lines marked with asterisks are discussed in the text.

Results

In Figure 1 the absorption spectra at 10 K of Cr(V)-doped YVO_4 polarized parallel and perpendicular to the crystallographic *c*-axis are shown. There is a very strong polarization dependence. For $E||c$, one absorption band around 9000 cm^{-1} is observed with a rich vibrational structure. For $E\perp c$ this band is completely absent, and a broad band around 15 000 cm^{-1} is found with a rather peculiar band shape, showing several broad overlapping maxima. For both polarizations the onset of a very strong band is observed above 18 000 cm^{-1}. The absorption band around 9000 cm^{-1} ($E||c$) is shown on an expanded energy scale on the right side of Figure 2. Progressions in a vibrational mode ν_b of 440 cm^{-1} and a mode ν_l of 130 cm^{-1} are observed, as indicated in the figure. The prominent electronic origin is at 8164 cm^{-1}.

On the left side in Figure 2, the unpolarized luminescence spectrum at 15 K of the same compound is presented. Despite the low temperature, the luminescence is very weak. The luminescence spectrum is more or less the mirror image of the lowest absorption band. Two vibrational progressions are observed in a mode ν_b of 400 cm^{-1} and a mode ν_l of 130 cm^{-1}, as indicated in the figure . The origin is at 8164 cm^{-1} and coincides with the origin of the lowest absorption band. The sharp lines on the low energy side marked with asterisks are most probably not due to the Cr(V) ion but to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+},[13] which is apparently present as a small impurity in the Y_2O_3 starting material. The "noise" between 7000 and 7400 cm^{-1} is due to absorption of atmospheric water vapor.

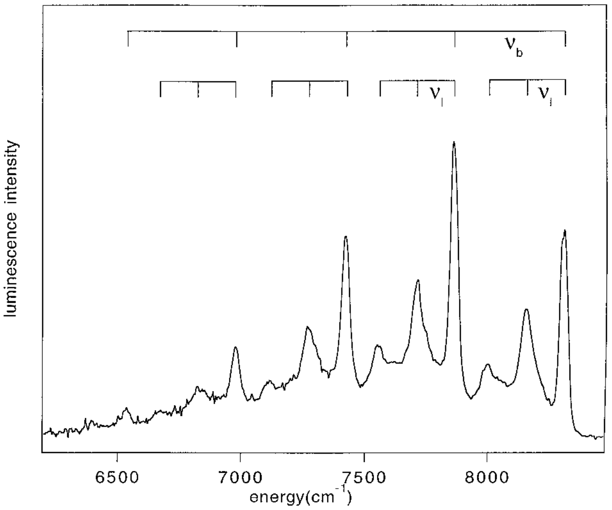

Figure 3. Unpolarized luminescence spectrum of Cr(V)-doped YPO_4 at 15 K.

In Figure 3 the luminescence spectrum at 15 K of Cr(V)-doped YPO_4 is shown. The spectrum is sharper and shifted some 150 cm^{-1} to higher energies with respect to that of Cr(V)-doped YVO_4, but the general appearance is similar. Vibrational progressions in a mode ν_b of 443 cm^{-1} and a mode ν_l of 149 cm^{-1} are observed, built upon the electronic origin at 8307 cm^{-1}. For this compound it was checked that in the spectral region between 3300 and 11 000 cm^{-1} there are no other luminescence bands other than the one shown in Figure 3 by using a PbS infrared detector. The luminescence decay times at 15 K of Cr(V)-doped YVO_4 and YPO_4 are very short, viz. <40 ns.

Discussion

Pure $YCrO_4$ is a stable Cr(V) compound which has the zircon structure, just as YVO_4 and YPO_4.[14] Hence, we assume that Cr^{5+} substitutes for the tetrahedrally coordinated V^{5+} and P^{5+} ions in YVO_4 and YPO_4, respectively. For a d^1 transition metal ion in an undistorted tetrahedral coordination, the ground state is ^2E and the ligand field excited state $^2T_2$. In the zircon structure the tetrahedron is tetragonally elongated along the *c*-axis so that the site symmetry is D_{2d}.[15] Due to this lower symmetry the ^2E state splits up into a $^2B_1$ ($d_{x^2-y^2}$) and a $^2A_1$ (d_{z^2}) component and the $^2T_2$ state into a $^2B_2$ (d_{xy}) and a ^2E (d_{xz}, d_{yz}) component. The two absorption bands at 10 K around 9000 and 15 000 cm^{-1} of Cr(V)-doped YVO_4 are thus assigned to the ligand field transitions from the lower energy component of ^2E (the ground state) to the two components of $^2T_2$. Ligand field transitions of Cr(V) in other host lattices are found in the same spectral region.[7,8,16] Large splittings of the $^2T_2$ state of about 6000 cm^{-1} are not unusual for strongly distorted CrO_4^{3-} tetrahedra, as is the case for YVO_4.[7,8] The broad absorption band with the onset at 18 000 cm^{-1} (see Figure 1) is assigned to a charge transfer

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band. It is probably due to Cr(V) as well as Cr(VI) centers in the YVO_4 crystal (see the Experimental Section).[16,17]

The coincidence of the electronic origins in absorption and luminescence and the mirror symmetry of the absorption and luminescence bands proves the identity of the chromophore and luminophore in Cr(V)-doped YVO_4. The two very weak sharp lines in the $E||c$ absorption spectrum at 7936 and 8096 cm^{-1} (i.e. at lower energies than the electronic origin) are probably due to Cr(V) in minority sites, which do not show luminescence. The very short luminescence decay times at 15 K for the two materials are ascribed to strong multiphonon relaxation. Weak and short-lived luminescence, even at low temperatures, due to efficient nonradiative processes, seems to be the rule for Cr(V)-doped materials.[4]

On the basis of an angular overlap model (AOM) calculation (taking into account only the four oxygen ligands and neglecting spin−orbit coupling) the energy order of the four states within the d^1 configuration is predicted to be $^2B_1(^2E) < {}^2A_1(^2E) \ll {}^2B_2(^2T_2) < {}^2E(^2T_2)$ for the tetragonally elongated tetrahedron of D_{2d} symmetry in the YVO_4 host lattice. Using the AOM parameters $e_\sigma = 13\,500$ cm^{-1} and $e_\pi = 3375$ cm^{-1} and assuming the same O−Cr−O angles as for the VO_4^{3-} unit in YVO_4,[18] the relative energies of the four above-mentioned d^1 states are calculated to be 0 cm^{-1}, 2380, 9530, and 14490 cm^{-1}, respectively. These AOM parameters are very similar to the ones used before for other Cr(V)-doped systems.[8]

Thus, on the basis of this AOM calculation, for Cr(V)-doped YVO_4 it may seem reasonable to assign the absorption band at 9000 cm^{-1} to $^2B_1(^2E) \rightarrow {}^2B_2(^2T_2)$, the absorption band at 15000 cm^{-1} to $^2B_1(^2E) \rightarrow {}^2E(^2T_2)$, and the luminescence band to $^2B_2(^2T_2) \rightarrow {}^2B_1(^2E)$. However, the intensities and polarization behavior observed in our spectra are inconsistent with this assignment. Group theory predicts that the $^2B_1 \rightarrow {}^2B_2$ absorption transition is electric dipole forbidden in all polarizations and the $^2B_1 \rightarrow {}^2E$ absorption transition is electric dipole allowed only in $E\perp c$ polarization. The absorption band of Cr(V)-doped YVO_4 at 15 000 cm^{-1} is $E\perp c$ polarized as predicted, but the $E||c$ polarized absorption band at 9000 cm^{-1} is even stronger than the band at 15 000 cm^{-1}, so that it cannot be due to the forbidden $^2B_1(^2E) \rightarrow {}^2B_2(^2T_2)$ transition. Further, group theory predicts that the $^2B_2 \rightarrow {}^2B_1$ luminescence transition is forbidden, but the $^2B_2 \rightarrow {}^2A_1$ luminescence transition electric dipole allowed in $E||c$ polarization. If we assign the luminescence of Cr(V)-doped YVO_4 and YPO_4 to the forbidden $^2B_2(^2T_2) \rightarrow {}^2B_1(^2E)$ transition, we would expect a second, much stronger luminescence due to the allowed $^2B_2(^2T_2) \rightarrow {}^2A_1(^2E)$ transition at lower energy than the observed luminescence band. Such a luminescence band was not found for Cr(V)-doped YVO_4 above 6000 cm^{-1} and not for Cr(V)-doped YPO_4 above 3300 cm^{-1}.

On the basis of our clear-cut polarized spectra we are thus forced to conclude that the energy order of the two ^2E components $^2B_1$ and $^2A_1$ is reversed. This situation, with the $^2A_1$ state being the ground state instead of $^2B_1$, is depicted in the inset of Figure 1. This level order can explain the observed intensities and polarization behavior in the absorption and luminescence spectra. This assignment is also in agreement with the results of an EPR study on Cr(V)-doped YVO_4 and YPO_4, in which it was found that the unpaired electron occupies a d_{z^2} orbital (i.e. $^2A_1$ in D_{2d}).[19] In this EPR study the energy reversal was attributed to covalency and an interaction of the d_{z^2} orbital with two Y^{3+} ions in the second coordination sphere of Cr(V). We have performed ab initio calculations in the framework of the density functional theory (DFT) to study this effect.

Table 1. Influence of Positive Point Charges at the Y^{3+} Positions on the DFT-Calculated Total Ground State Energies (TGSE) of CrO_4^{3-} for the Two Relevant Electron Configurations

point charge	TGSE (eV) d-electron in a_1	TGSE (eV) d-electron in b_1	energy difference (eV)
0	−27.772	−27.901	−0.129
+1	−55.469	−55.561	−0.093
+2	−86.161	−85.011	+1.150
+3	−118.073	−116.427	+1.646

First, we performed DFT calculations on the ground state of a tetragonally elongated CrO_4^{3-} molecule of D_{2d} symmetry and neglected the possible influence of the Y^{3+} ions. We assumed the same O−Cr−O angles as for the VO_4^{3-} unit in YVO_4[18] and took the Cr−O bond length to be 1.7 Å, a typical Cr−O distance in pure Cr(V) compounds.[8] In two separate calculations we forced the single unpaired d-electron either in the b_1 orbital (which implies a ground state $^2B_1$) or in the a_1 orbital (ground state $^2A_1$) and calculated the total energy of the molecule in its ground state for the two cases. The results of the calculations are given in Table 1, second row. The total energy of the CrO_4^{3-} molecule is 0.129 eV (1042 cm^{-1}) smaller when the unpaired electron is in the b_1 orbital than in the a_1 orbital. Thus, as expected on the basis of qualitative arguments, a $^2B_1$ ground state is found when only the four oxygen ligands are taken into account.

In the subsequent DFT calculations the effect of two Y^{3+} ions in the second coordination sphere of the Cr(V) ion was simulated by placing two point charges at the appropriate positions. In YVO_4 these two Y^{3+} ions lie on the crystallographic c-axis, i.e., on the S_4 symmetry axis of the VO_4^{3-} tetrahedron with a V−Y separation of 3.16 Å.[18] The results of these calculations with point charges of +1, +2, and +3 are shown in Table 1, rows 3, 4, and 5, respectively. It is found that for point charges of magnitude +2 and +3 it is clearly favorable to have the unpaired electron in the a_1 orbital (energy differences are −1.150 eV = 9263 cm^{-1} and −1.646 eV = 13 259 cm^{-1}, respectively). Hence, for the latter two cases the influence of the positive charges becomes so large that $^2A_1$ is strongly stabilized, leading to reversal of the energy order in the ground state. This is in agreement with our spectroscopic results and the conclusions reached from EPR spectroscopy.[19] We note (see inset of Figure 1) that the energy order of the $^2T_2$ (T_d notation) excited-state splitting is not reversed by the presence of the Y^{3+} ions. This is qualitatively explained by the fact that the d_{z^2} orbital, pointing directly toward the positive charges, is much more strongly affected than the orbitals of the t_2 set. The distance of 3.16 Å between Cr^{5+} and Y^{3+} is extremely short and thus leads to an extremely large electrostatic crystal field effect on the d_{z^2} orbital. In the EPR spectra of the two materials, structure due to superhyperfine interaction between the unpaired electron on Cr(V) and the two Y^{3+} ions is observed.[19] Thus, there is also an interaction between Cr(V) and Y^{3+} by wave function overlap, most probably via the commonly shared oxygens.

We assign the 400 cm^{-1} vibrational mode in the luminescence spectrum (440 cm^{-1} in absorption) of Cr(V)-doped YVO_4 to an internal bending mode of the CrO_4^{3-} tetrahedron.[20−22] For

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other CrO_4^{3-} doped systems and also for MnO_4^{2-} (d^1) doped systems, the dominant progression is always in a bending vibration.[4,23,24] For MnO_4^{2-} in various host lattices, progressions are observed in an e (ν_2) bending mode due to a Jahn–Teller (JT) effect in the $^2T_2$ excited state.[23,24] In our case strong coupling with JT-active e-modes is not expected because of the large noncubic crystal field in YVO_4, which will effectively quench the JT effect in the ^2E ground and $^2T_2$ excited states. This is supported by the complete polarization of the absorption band at 9000 cm^{-1}. There remain two possible assignments for the 400 cm^{-1} mode. In the D_{2d} point symmetry of the host material, the ν_2 mode has a totally symmetric component. It is thus a likely candidate for the ν_b progression forming mode in Figure 2. Unfortunately, this vibration could not be identified in the vibrational spectra of $YCrO_4$[20] and $NdCrO_4$.[21] There is an alternative assignment, however, which cannot be excluded. In the EPR spectra of YVO_4:Cr(V) some evidence was found that the actual point symmetry of CrO_4^{3-} is C_{2v} and not D_{2d}, i.e., a slight axial distortion destroying S_4. A component of the t_2 (ν_3) bending vibration of CrO_4^{3-} would then become totally symmetric and could couple to the d–d excitation. In the IR spectra of $YCrO_4$[20] and $NdCrO_4$[21] the ν_3 vibration is observed at 395 and 420 cm^{-1}, respectively, i.e., close to the observed ν_b in Figure 2.

The 130 cm^{-1} mode in the absorption and the luminescence spectrum is assigned to a local, totally symmetric stretching vibration of the two Y^{3+} ions along the *c*-axis relative to the CrO_4^{3-} unit. External modes in YVO_4 in which the Y^{3+} ions vibrate relative to the VO_4^{3-} unit have similar energies.[25] It is not unexpected that this totally symmetric vibration involving the Y^{3+} "ligands", which have such a strong influence on the energy of the ground state of Cr(V), is prominent in the d–d spectra of YVO_4:Cr(V) and thus contributes to the excited-state distortion.

A final comment concerns the fact that the internal progression forming mode ν_b has a lower energy of 400 cm^{-1} in emission than 440 cm^{-1} in absorption. We ascribe this exceptional observation to a strong coupling of the bending mode with the external Cr–Y stretching mode. This coupling is strong in the electronic ground state with the electron in the d_{z^2} orbital and weak in the excited state.

Conclusions

For the interpretation of optical spectra of metal ions in solids it is common to consider only the first coordination sphere of the metal ion, formed by the ligand atoms. In most cases this gives a satisfactory description of the electronic structure of the metal ion. In this paper we have presented the crystal system YVO_4:Cr(V) for which the optical spectra can only be understood if the second coordination sphere is taken into consideration. It is found that the presence of two positive Y^{3+} ions in the second coordination sphere of Cr(V) in YVO_4:Cr(V) drastically changes the energy level scheme of the CrO_4^{3-} unit and also affects the vibrational structure and thus the excited-state distortion. Polarized crystal spectra are essential to reach these conclusions. The unpolarized luminescence spectra of YPO_4:Cr(V) can then be interpreted by analogy.

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