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Observation of the ^1E state of Cr^{4+} in yttrium aluminum garnet

Y. R. Shen

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

U. Hömmerich

Department of Physics, Hampton University, Hampton, Virginia 23668

K. L. Bray

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

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High-pressure studies of the near-infrared fluorescence of Cr^{4+}:yttrium aluminum garnet (YAG) at 40 K have been used to induce a $^3T_2$-^1E crossover above 200 kbar and have permitted the observation of $^1E \rightarrow {}^3A_2$ emission. The $^1E \rightarrow {}^3A_2$ emission band is narrow, occurs near 1100 nm, and shows a small red shift expected for a spin-flip transition. The energy of the emission is similar for different Cr^{4+} centers present in YAG. A preliminary lifetime measurement of the $^1E \rightarrow {}^3A_2$ emission of the principle Cr^{4+} site at $\sim$270 kbar and 40 K yields a value of $\sim$250 μs, and an $\sim$eightfold increase relative to the value at ambient pressure and 40 K. [S0163-1829(97)50826-5]

The search for new solid-state laser materials with better and more diverse properties has been ongoing since the discovery of lasing in ruby. A continuing goal has been to identify and design materials that lase at new wavelengths and with high efficiency. Broadly tunable laser materials have been a particular focus since the advent of the alexandrite ($\sim$700–825 nm) and, more recently, the Ti:sapphire ($\sim$660–1180 nm) lasers. Current work in this area is focusing on materials that luminesce in the near infrared (NIR) in an attempt to develop broadly tunable NIR lasers for applications in optical communication and medicine.

The tetravalent chromium (Cr^{4+}) ion is currently the most promising near-infrared lasing center. Tunable laser emission of Cr^{4+} was originally discovered in forsterite.[1–3] Later work on forsterite has shown that tunable Cr^{4+} lasing extending from 1170 nm to 1350 nm is achievable.[4] At almost the same time, laser operation of Cr^{4+}-doped yttrium aluminum garent (YAG) was observed over the range 1309–1596 nm.[5,6] Tunable room temperature Cr^{4+} lasing has also been observed in the garnets $Y_3Sc_xAl_{5-x}O_{12}$ (Ref. 7) and $Lu_3Al_5O_{12}$ (Ref. 8). In addition, Koetke *et al.*[9] demonstrated a room-temperature laser operation in Cr^{4+}-doped Y_2SiO_5. The success to date of the Cr^{4+} ion as a near-infrared lasing center has prompted studies of the spectroscopic properties of Cr^{4+} in a variety of host materials[10–17] as well as studies of the isoelectronic Mn^{5+} (Refs. 18 and 19) and Fe^{6+} (Ref. 20) ions.

It is now well accepted that the optically active ion responsible for the NIR laser emission in Cr^{4+}-doped materials is tetragonally coordinated Cr^{4+}, with varying degrees of distortion from pure tetrahedral symmetry. Cr^{4+} is a $3d^2$ ion and its crystal-field energy levels in ideal tetrahedral geometry are represented by the Tanable-Sugano diagram.[21] The emission observed for Cr^{4+} occurs from the first excited state to the $^3A_2$ ground state. The emitting level of Cr^{4+} can be either the $^3T_2$ or the ^1E state, depending on its crystal-field strength (Dq) in the host material. In weak crystal fields, the $^3T_2$ state is lower in energy and in strong crystal fields, the ^1E state becomes the first excited state. The $^3T_2 \rightarrow {}^3A_2$ and $^1E \rightarrow {}^3A_2$ transitions are spin allowed and spin forbidden, respectively. Typical fluorescence features for spin-allowed transitions are fast (μs range) and have

broad emission due to a strong electron-phonon coupling. In contrast, narrow-band emission and long lifetimes (ms range) due to a weak electron-phonon coupling are observed for spin-flip transitions.

The observed NIR fluorescence spectrum of Cr^{4+} in all host systems studied to date consists of a broad band with a short decay time (a few μs or less) at room temperature. These are the expected spectroscopic features for an optically active d^2 center in a weak crystal field and it has accordingly been proposed that the room-temperature NIR fluorescence arises from the spin-allowed $^3T_2 \rightarrow {}^3A_2$ transition, in the tetrahedral approximation, or from a $^3T_2$ orbital component to $^3A_2$ when lower symmetries are considered. However, the low-temperature fluorescence spectra are quite different from those at room temperature, consisting of sharp lines accompanied by a structured or structureless sideband in different host materials. The appearance of the sharp lines at low temperature leads to a controversy in assignment since sharp lines could be consistent with a $^1E \rightarrow {}^3A_2$ transition. The experimental results currently available for these systems, however, favors the assignment to the $^3T_2$ state.[14,22,23] However, an unambiguous identification has not yet been achieved because the energy position of the ^1E state has not been found clearly in any of the Cr^{4+}-doped laser materials studied to date.

Our work focuses on high-pressure studies of luminescent solid-state materials. The primary effect of high pressure is to decrease volume and increase crystal-field strength through bond-length compression. An important feature of high pressure is its ability to continuously vary crystal-field strength and to distinguish energy states that are sensitive to crystal-field strength from those that are not. Cr^{4+} is an excellent ion from the point of view of high-pressure studies because the $^3T_2$ energy is highly sensitive to crystal-field strength, while the ^1E energy is nearly independent of crystal-field strength. Thus, it should be possible to use pressure to induce a $^3T_2$-^1E crossover in Cr^{4+} and to unambiguously establish the energy of $^1E \rightarrow {}^3A_2$ emission. Expected relative sensitivities of the $^3T_2$ and ^1E states of Cr^{4+} to pressure are similar to those of the $^4T_2$ and ^2E of Cr^{3+}. We therefore expect the high-pressure behavior of Cr^{4+} to be analogous to the high-pressure behavior of Cr^{3+}.[24–27]

In this paper we describe the results of high-pressure NIR fluorescence studies of Cr^{4+}:YAG, a member of the important garnet family of host lattices. Garnets are cubic crystals with the stoichiometric formula $A_3B_2(CO_4)_3$ where A, B, and C refer to cations at dodecahedral, octahedral, and tetrahedral lattice sites. The optically active Cr^{4+} ions enter the tetrahedrally coordinated C sites and have D_{2d} site symmetry.[14,22]

NIR fluorescence experiments were conducted on two groups of Cr^{4+}:YAG crystals provided by the University of Georgia (0.1 mol %, 0.2 mol %, and 0.3 mol %) and the University of Hamburg (0.05 mol %). All samples used were codoped with Ca^{2+} for charge compensation. The crystal-growth conditions are given in detail in Refs. 22 and 23. High-pressure fluorescence experiments were performed using a modified Merrill-Bassett diamond anvil cell (DAC). For low-temperature fluorescence measurements, the DAC was mounted on the coldfinger of a closed-cycle helium refrigerator which provided cooling down to ~40 K. A 4:1
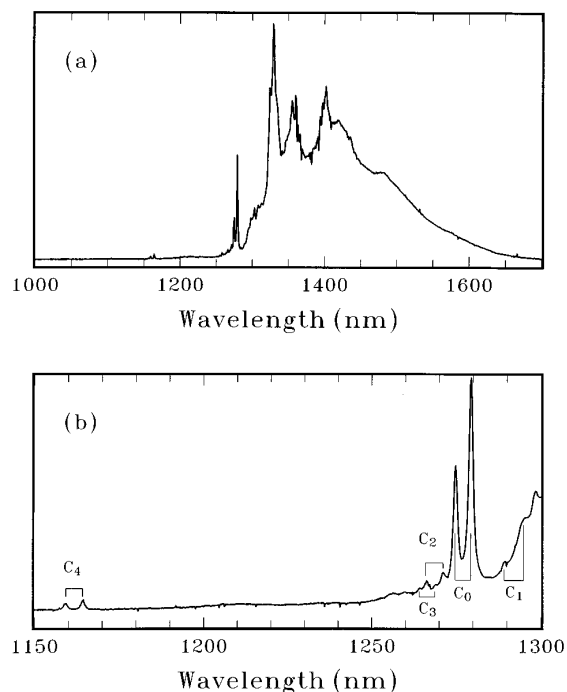

FIG. 1. Ambient-pressure NIR fluorescence spectra of the 0.1 mol % Cr^{4+}:YAG bulk crystal at 22 K.

methanol:ethanol mixture was used as a pressure transmitting medium. Pressure determinations were made by the ruby fluorescence technique.[28,29] The NIR fluorescence was dispersed by an 1 m monochromator (SPEX 1000M) and detected with a liquid nitrogen cooled Ge detector (ADC 403L) using a standard lock-in technique. All spectra were corrected for the spectral response of the system. The excitation source for the NIR fluorescence was a dye laser (Spectra Physics model 375 B) pumped by an argon ion laser (Coherent Innova Series model 70-5). Since Cr^{4+} exhibits a strong visible absorption band (580–700 nm)[14,30] in YAG, wavelengths in the range 580–620 nm from a RG 590 dye were selected for excitation.

The room-temperature, ambient-pressure fluorescence spectrum of Cr^{4+}:YAG consisted of a broad band centered near 1375 nm. As the temperature was lowered, the spectrum developed sharp zero-phonon lines and a structured phonon sideband. Similar results have been reported by others.[14,22,23,30] All crystals used in this study exhibited similar behavior, with the exception that no sharp zero-phonon lines were observed for 0.3 mol % Cr^{4+}:YAG. A typical low-temperature spectrum is shown in Fig. 1(a). An enlargement of the spectrum in the range 1150–1300 nm is shown in Fig. 1(b). Several spectral lines were observed. The two strong zero-phonon lines at 1279.4 nm (7816 cm^{-1}) and 1274.8 nm (7844 cm^{-1}) labelled C_0 originate from the main Cr^{4+} center and are assigned to the two spin-orbit coupling components of the transition from the $^3B_2(^3T_2)$ excited state to the $^3B_1(^3A_2)$ ground state.[14,22,23] Additional pairs of weak lines, C_1 [1284.4 nm (7786 cm^{-1}) and 1294.0 nm (7728 cm^{-1})], C_2 [1266.2 nm (7898 cm^{-1}) and 1271.2 nm (7867 cm^{-1})], and C_3 [1264.2 nm (7910 cm^{-1}) and 1268.8 nm (7881 cm^{-1})] were observed near the two lines of the main center and are associated with low-concentration

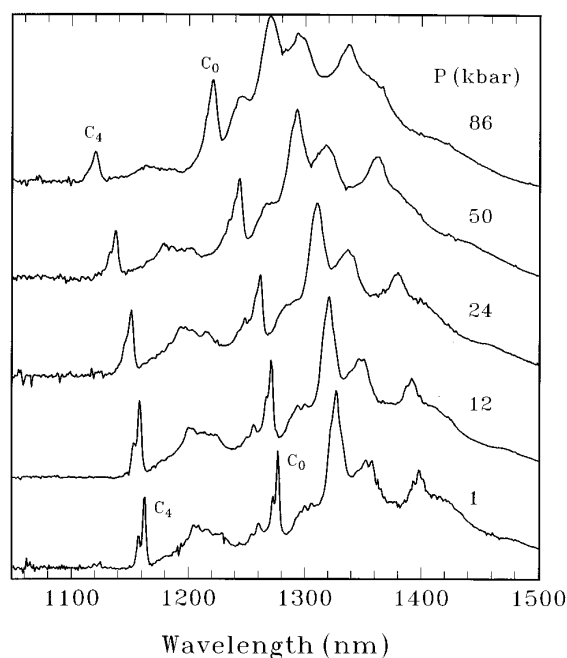FIG. 2. 40 K NIR fluorescence spectra of 0.2 mol% Cr^{4+}:YAG at several pressures below 100 kbar.

FIG. 3. 40 K NIR fluorescence spectra of 0.2 mol% Cr^{4+}:YAG at several pressures above 100 kbar.

Cr^{4+} multisites. Detailed studies on the multiple sites of Cr^{4+} multisites in YAG (Ref. 31) has shown that the different centers have different polarization behavior and lifetimes, and are independent of the charge-compensating codopants. We also observed another pair of sharp lines (labelled C_4) at 1159.2 nm (8627 cm^{-1}) and 1164.3 nm (8589 cm^{-1}) with a broad sideband centered at 1210 nm. These features have been observed previously,[32] but have not been definitively assigned. The large shift (800 cm^{-1}) of the lines relative to the principle C_0 lines suggests that the Cr^{4+} center responsible for them is fundamentally different from the minority centers C_1, C_2, and C_3. The C_4 lines are most likely due to a strongly distorted tetrahedral Cr^{4+} site and may be due to a site perturbation induced by the charge compensating Ca^{2+} codopants present in the crystals. Such a phenomenon was observed in the system Cr^{4+}:$LiAlO_2$ by Kück et al.[10] who observed that codoping with Mg^{2+} led to the observation of strong zero-phonon lines (8684 and 8657 cm^{-1}) due to an additional Cr^{4+} center that were ~400 cm^{-1} higher in energy than those of the Cr^{4+} center in Cr^{4+}:$LiAlO_2$ without Mg^{2+} codoping.

High-pressure NIR fluorescence experiments were performed at 40 K up to ~270 kbar. The NIR fluorescence spectra at several pressures below 100 kbar are shown in Fig. 2. In the pressure region shown in Fig. 2, the pair of zero-phonon lines for the main C_0 center and the minority C_4 center were well resolved. A large blue shift [~4.3(2) cm^{-1}/kbar] with pressure was observed for both pairs of lines. The blue shift is consistent with the low-temperature assignment of the lines to the spin-allowed $^3B_2(^3T_2) \rightarrow {}^3B_1(^3A_2)$ transition. With increasing pressure a gradual decrease in the intensity of the zero-phonon lines was also observed.

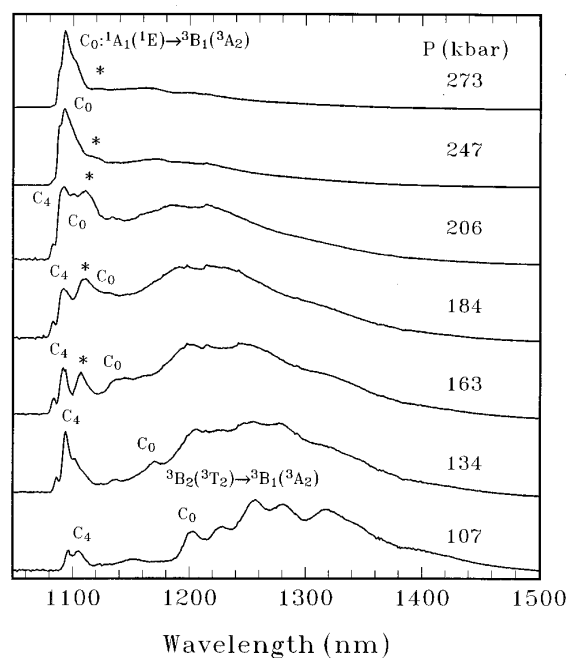As the pressure was increased above 100 kbar, the

blue shift ceased and the NIR fluorescence spectra of Cr^{4+}:YAG showed a spectral transformation (Fig. 3). The transformation was first observed at ~100 kbar for the minority C_4 sites and then near ~200 kbar for the main C_0 sites. At 107 kbar, the $^3B_2(^3T_2) \rightarrow {}^3B_1(^3A_2)$ zero-phonon lines of the C_0 site were located near 1200 nm. The blue shift of the lines was evident up to 163 kbar. At 184 kbar, the lines overlapped strongly with a line (denoted with an asterisk in Fig. 3) that was shifting red and originated from the C_4 site portion of the spectrum. At 206 kbar, the C_0 feature appeared to have crossed the line denoted with the asterisk. Simultaneously, the C_0 feature sharpened, gained intensity, and a decrease in the relative intensity of the phonon sideband intensity was observed. At 247 kbar, these changes continued and the C_0 feature became the dominant feature in the spectrum. Above 247 kbar, the phonon sideband intensity decreased further, and a small red shift of the C_0 feature was observed (1094 nm at 273 kbar).

We attributed the spectral changes observed for the C_0 center to a pressure induced $^3B_2(^3T_2)$-^1E crossover. The cessation of the blue shift, development of a red shift above 200 kbar, loss of phonon sideband intensity, and strong intensity increase are consistent with the proposed crossover. In addition, a preliminary lifetime measurement at 273 kbar and 40 K provided a value of ~250 μs. This value is much longer than the ~30 μs value at ambient pressure and low temperature and is similar to values observed for the well established $^1E \rightarrow {}^3A_2$ emission in isoelectronic Mn^{5+}-doped systems.[33–35]

An analogous crossover was also observed for the minority C_4 site near 100 kbar. At 107 kbar, a new line at 1046.4 nm was observed in the vicinity of the $^3B_2(^3T_2)$ lines of the C_4 center. We attribute the new line to the $^1E \rightarrow {}^3A_2$ transition of the C_4 center. At 134 kbar, the new line gained considerable intensity and exhibited essentially no shift, while

the $^3B_2(^3T_2)$ feature receded. At higher pressure, the new C_4 line continued to show no shift and was observed until it was above 200 kbar by the more intense ^1E line of the main C_0 sites. The similarity of the ^1E energy for the main and minority sites, despite the large difference in energy at ambient pressure, is consistent with the expected weak sensitivity of the ^1E energy to crystal-field strength and host lattice and supports the proposed electronic crossover.

The feature denoted by the asterisk in Fig. 3 is less certain at this time. It is most likely due to a $^1E \rightarrow {}^3A_2$ transition for the minority C_2 and C_3 centers. Given the slightly higher $^3B_2(^3T_2) \rightarrow {}^3A_2$ energies of the C_2 and C_3 sites, we would expect these sites to exhibit an electronic crossover at a lower pressure than in the main C_0 site. The observation of the feature at 163 kbar as well as its slight red shift and intensity loss relative to the main C_0 site at high pressure are consistent with the proposed $^1E \rightarrow {}^3A_2$ assignment.

In conclusion, the low-temperature NIR fluorescence of Cr^{4+}:YAG as a function of pressure up to ~ 270 kbar has been measured. In the low-pressure range, we observed large blue shifts of the fluorescence lines originating from the $^3T_2$ state. At high pressure, a $^3T_2$-^1E crossover was induced and $^1E \rightarrow {}^3A_2$ emission in Cr^{4+} was observed for the first time. The crossover was accompanied by an $\sim$ eightfold increase in lifetime. A similar ^1E energy position was observed for the different Cr^{4+} centers in YAG, consistent with the expected insensitivity of the ^1E energy to crystal-field strength. Our results will be important for a deeper understanding of the energy-level structure and spectroscopic properties of Cr^{4+} and other d^2 ion systems.

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