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Manganate(VI): A Novel Near-Infrared Broadband Emitter

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The Ti^{3+}: sapphire laser is undoubtedly the most important laser light source in the near infrared (NIR) between 700 nm and 1 μm. Its tuning range far exceeds that of dye lasers, it is not photodegradable, and it can be mode locked with pulse widths down to 10 fs. Research in the area of new solid-state lasers is very active at present. Among the groups investigating potential new laser materials there are only a few worldwide exploring new metal ions exhibiting spontaneous emission. We are using a chemical approach, and in recent years we have found and investigated a number of novel NIR luminescent ions with a $(3d)^2$ electron configuration in various hosts.[1−4]

Mn^{6+} is isoelectronic with Ti^{3+}, i.e., a $(3d)^1$ ion. Although the MnO_4^{2-} ion, in which Mn^{6+} is stabilized in a well-defined tetrahedral oxo coordination, has been known for more than 330 years,[5] no luminescence has been reported so far. Polarized single-crystal absorption spectra have been presented for MnO_4^{2-}-doped $BaSO_4$,[6] K_2CrO_4, and various alkali-metal sulfates.[7,8] In all host lattices a weak broad absorption band with a maximum around 12 500 cm^{-1} is observed. It corresponds to the $^2E \rightarrow {}^2T_2$ ligand-field transition (T_d notation) in which the single d electron is excited from the lower lying π antibonding set of e orbitals to the π and σ antibonding set of t_2 orbitals. The $^2E-{}^2T_2$ splitting directly corresponds to the ligand field strength Δ, and the value $\Delta \approx 12\,500$ cm^{-1} is comparable to the Δ values found for the tetraoxo-coordinated Mn^{5+} and Fe^{6+} ions.[4,9]

We have prepared MnO_4^{2-}-doped crystals of K_2SO_4, K_2CrO_4, and K_2SeO_4 by slowly evaporating aqueous 10 M KOH solutions saturated with the appropriate potassium salt. The solutions were initially 1×10^{-3} M in MnO_4^-, which is rapidly reduced to MnO_4^{2-} in the presence of OH^-, leading to a change in color from purple to green. Single crystals of Mn^{6+}-doped $BaSO_4$ were grown from a NaCl−KCl flux in a temperature-controlled furnace by slow cooling from 750 to 650 °C at 1.5 °C/h using a platinum crucible, as described in ref 6. The $KMnO_4$ concentration in the starting material was 0.1 mol % with respect to $BaSO_4$.

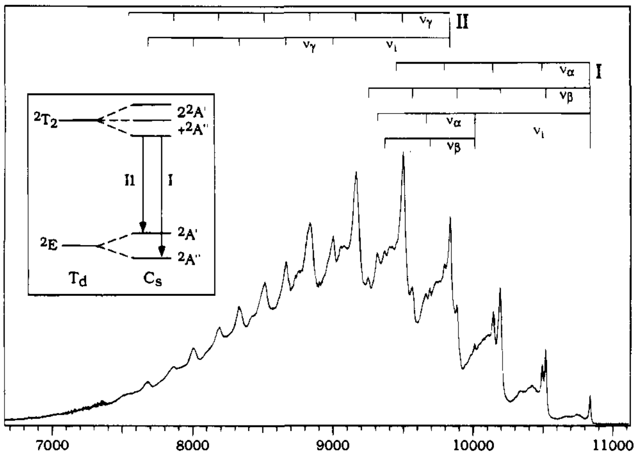

Figure 1. Unpolarized luminescence spectrum at 10 K of MnO_4^{2-}-doped K_2SO_4 upon excitation at 17 600 cm^{-1} with a Kr^+ laser (Coherent CR 500 K), dispersed with a single monochromator (3/4m Spex 1702) and detected with a Ge-IR detector cooled to 77 K (Applied Detector Corporation ADC 403 L). The spectrum is corrected for system response and shows the number of photons emitted per unit time plotted against energy. The two electronic transitions I and II are indicated in the Figure and assigned in the inset. The vibrational progressions are labeled ν_α, ν_β, ν_γ, and ν_1 (see text).

Spontaneous emission between 11 000 and 7000 cm^{-1} at 10 K was observed from all the samples upon photoexcitation at 17 600 cm^{-1} with a krypton ion laser. In Figure 1 we present the 10 K luminescence spectrum of a MnO_4^{2-}-doped crystal of K_2SO_4 as an example. At this temperature the spectrum shows a rich structure that can be fully analyzed. The band is very broad, reflecting a significant change in the geometry of the MnO_4^{2-} ion between ground state and excited state. Two electronic transitions, I and II, are observed, whose origins and sidebands are indicated in the upper part of Figure 1. The two transitions are from the lowest orbital component of the $^2T_2$ excited state to the two orbital components $^2A''$ and $^2A'$, respectively, of the ^2E ground state. This orbital splitting is due to a $T_d \rightarrow C_s$ distortion of the MnO_4^{2-} ion replacing SO_4^{2-} in the K_2SO_4 structure.[10] In the K_2CrO_4 and K_2SO_4 host lattices the ground state of MnO_4^{2-} has been shown by EPR[11] and polarized single-crystal absorption spectroscopy[8] to be $^2A''$ with the single unpaired electron in the $e(d_{x^2-y^2})$ orbital. From our luminescence spectrum it follows that the $^2A'$ state (unpaired electron in $e(d_{z^2})$ orbital) lies 1024 cm^{-1} above the ground state since this splitting corresponds to the separation of the two electronic origins at 10 857 and 9833 cm^{-1}. Similar splittings at 10 K are observed in the other host lattices. The MnO_4^{2-} ion occupies a site with C_s symmetry in K_2CrO_4 and $BaSO_4$,[10] which is reduced to C_1 in K_2SeO_4 below 125 K.[14] The very pronounced vibrational progressions in the luminescence spectrum of both electronic transitions are dominated by Mn−O bending modes, whereas the Mn−O stretching mode with $\nu_1(a_1) = 830$ cm^{-1} has a much smaller Huang−Rhys factor S. The energies of the bending modes of the MnO_4^{2-} ion in K_2MnO_4 are $\nu_2(e) = 325$ cm^{-1} and $\nu_4(t_2) = 332$ cm^{-1}.[15] Both the e and t_2 modes acquire some totally symmetric character upon distortion to C_s, $e \rightarrow a' + a''$ and $t_2 \rightarrow 2a' + a''$, and can

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(1) Ti^{2+} in octahedral coordination: (a) Jacobsen, S. M.; Güdel, H. U.; Daul, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 7610. (b) Jacobsen, S. M.; Güdel, H. U. *J. Lumin.* **1989**, *43*, 125.

(2) Octahedrally coordinated V^{3+}: (a) Reber, C.; Güdel, H. U. *J. Lumin.* **1988**, *42*, 1. (b) Reber, C.; Güdel, H. U.; Meyer, G.; Schleid, T.; Daul, C. A. *Inorg. Chem.* **1989**, *28*, 3249.

(3) Mn^{5+} in tetrahedral oxo coordination: (a) Herren, M.; Güdel, H. U.; Albrecht, C.; Reinen, D. *Chem. Phys. Lett.* **1991**, *183*, 98. (b) Herren, M.; Riedener, T.; Güdel, H. U.; Albrecht, C.; Kaschuba, U.; Reinen, D. *J. Lumin.* **1992**, *53*, 452.

(4) Fe^{6+} in tetrahedral oxo coordination: (a) Herren, M.; Güdel, H. U. *Inorg. Chem.* **1992**, *31*, 3683. (b) Brunold, T. C.; Hauser, A.; Güdel, H. U. *J. Lumin.* **1994**, *59*, 321. In this reference a MnO_4^{2-} luminescence in FeO_4^{2-}-doped K_2CrO_4 which originated from a small manganese impurity was erroneously attributed to the FeO_4^{2-} ion.

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thus couple to the electronic transitions. This explains the existence of the progressions in $\nu_\alpha = 350$ cm^{-1} and $\nu_\beta = 320$ cm^{-1} built on the first origin I and the one in $\nu_\gamma = 330$ cm^{-1} built on the second origin II, see Figure 1. Since the first members of all these progressions are very well resolved, we can estimate the corresponding Huang–Rhys factors S which are a measure of the distortion between the initial and the final state along these normal modes. For transition I to the $^2A''(^2E)$ ground state we find $S(\nu_\alpha) \approx 2$ and $S(\nu_\beta) \approx 3$, whereas $S(\nu_1)$ is only ≈ 0.2 for the a_1 stretching mode. The values found for transition II to the $^2A'(^2E)$ lowest excited state, $S(\nu_\gamma) \approx 2.5$ and $S(\nu_1) \approx 0.6$, differ somewhat from the above values, indicating that the MnO_4^{2-} ion has a slightly different geometry in this state than in its ground state. The site symmetry of the MnO_4^{2-} complex in the present host lattices is so low that all orbital degeneracy is lifted. Hence, all the spectral features reported here can be interpreted by assuming coupling to totally symmetric modes only. This is very different in Ti^{3+}-doped crystals, in which evidence for strong Jahn–Teller effects has been found.[12] In fact, the enormous luminescence bandwidth of Ti^{3+}: sapphire is the likely result of simultaneous distortions along totally symmetric and Jahn–Teller coordinates.[13] In our MnO_4^{2-} systems the strong progressions in Mn–O bending modes may also be the result of Jahn–Teller coupling. In this case the $S(\nu_\alpha)$, $S(\nu_\beta)$, and $S(\nu_\gamma)$ values would be a measure of distortions along Jahn–Teller modes ν_α, ν_β, and ν_γ, respectively. Without an unambiguous identification of the three modes involved we cannot discriminate between the two possibilities.

The luminescence lifetimes observed at 10 K are between 1.91 and 2.75 μs for the four host lattices investigated here. They are essentially radiative. For K_2CrO_4 the lifetime and the total intensity of the luminescence remain constant up to 90 K. Above this temperature we observe a similar decrease for both quantities due to the onset of multiphonon relaxation processes. At 200 K the lifetime is reduced to 280 ns and the intensity amounts to 10% of its 10 K value.

Figure 2 compares the origin region and the onset of the vibrational progressions of the 10 K absorption and luminescence spectra of MnO_4^{2-}-doped K_2SeO_4. In K_2SeO_4 the MnO_4^{2-} ion occupies three crystallographically inequivalent sites below 125 K, the temperature of the phase transition from the *Pnma* to the *Pna*2$_1$ low-temperature space group.[14] Consequently both spectra consist of a superposition of three very similar spectra corresponding to the three sites. The luminescence lifetimes at 10 K, obtained from the decay curves detected at the spectral positions of the three origins, are (in the order of increasing energy) 1.91, 2.05, and 2.18 μs.

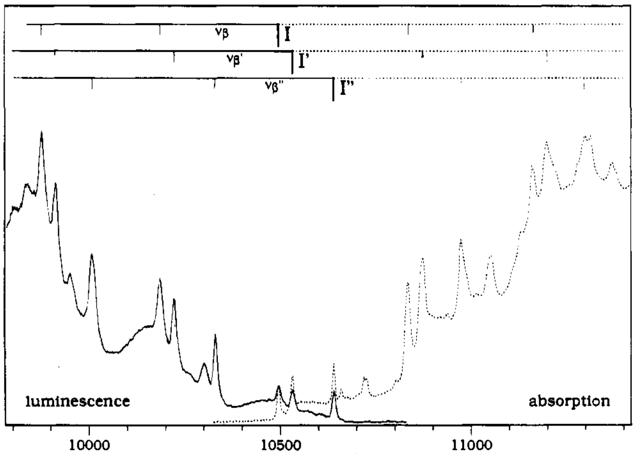

Figure 2. Crystal absorption and luminescence spectra of MnO_4^{2-}-doped K_2SeO_4 at 10 K in the overlap region. Three electronic origins I, I′, and I″ due to three crystallographic sites are identified, and the progressions in Mn–O bending modes are indicated.

The luminescence observed at 10 K from the manganese-doped crystals of $BaSO_4$ is less structured. In addition, the MnO_4^{2-} spectrum is superimposed by a sharp-line luminescence centered at 8500 cm^{-1} which carries about one-third of the total intensity. From its spectral position and bandshape it is assigned to the MnO_4^{3-} ion.[3] The existence of Mn^{5+} in this host lattice is undoubtedly the consequence of the different preparation. It is generally known that lower oxidation states are favored at higher temperatures of preparation. This evidence for MnO_4^{3-} in manganese-doped $BaSO_4$ from luminescence spectroscopy is very important since it brings out a new aspect for the interpretation of the absorption spectrum[16] which has been assigned differently so far.[6,17]

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