Volume 31
Number 18
September 2, 1992

Inorganic Chemistry

Communications

Ferrate(VI), a Novel Near-Infrared Luminophore

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Received April 29, 1992

The ferrate(VI) ion has been known for 150 years,[1] and here we report the first observation of its luminescence spectrum. Upon photoexcitation in the visible or near-infrared (near-IR) region, crystals of K_2CrO_4 doped with 0.05% FeO_4^{2-} exhibit a sharp-line luminescence around 1.6 μm. Its lifetime is 1.3 ms at 10 K, decreasing to 0.6 ms at room temperature. There is a potential use of luminophores of this kind as near-IR solid-state laser materials.

We have been engaged in a systematic study of the luminescence properties of transition metal ions with $(3d)^2$ electron configurations in recent years.[2-4] Whereas Ti^{2+} and V^{3+} prefer octahedral lattice sites, the best characterized Mn^{5+} and Fe^{6+} species are the tetrahedral tetraoxo anions. The situation is much less clear for Cr^{4+}. In chromium-doped forsterite, a tunable near-IR laser material,[5,6] Cr^{4+} ions in tetrahedral or octahedral coordination are supposed to play an important role in the stimulated emission process.[7,8]

We have used literature procedures to prepare aqueous FeO_4^{2-} solutions.[1,9] The visible and near-IR absorption spectrum of the ferrate ion is characterized by two bands at about 500 and 800 nm, leading to a purple color.[10] Doped crystals were obtained from FeO_4^{2-} solutions saturated with K_2CrO_4.[11] Luminescence was excited at 900–1000 nm with a filtered tungsten lamp, dispersed by a $^3/_4$-m Spex 1702 monochromator with a grating blazed at 1.6 μm and detected with a cooled germanium photodetector (ADC 403L). For luminescence decay measurements, the crystals were excited by a pulsed N_2 laser (337 nm), and the luminescence was detected by a germanium photodetector with 1-μs response (ADC 403 HS) in combination with a Tektronix digital 2432A oscilloscope.

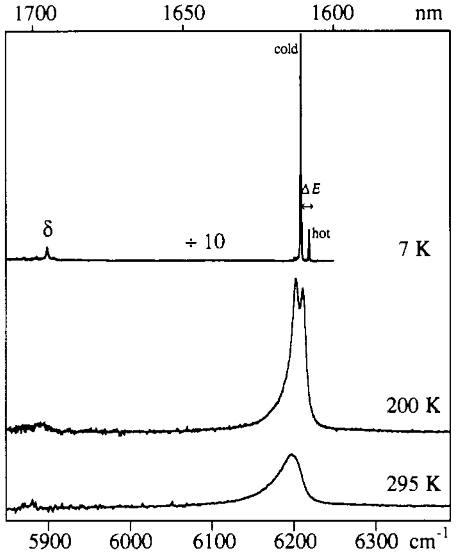

Figure 1. Luminescence spectra of 0.05% FeO_4^{2-}-doped K_2CrO_4 at three temperatures, with broad-band excitation at 900–1000 nm. The ordinate scale of the 7 K spectrum is compressed by a factor of 10. The spectra are corrected for detector sensitivity, which steeply drops between 6200 and 5850 cm^{-1}. The energy difference between cold and hot lines denoted ΔE refers to Figure 2. The vibrational sideband denoted δ refers to the bending mode of FeO_4^{2-}.

Figure 1 shows the luminescence spectrum at three temperatures between 7 K and room temperature. The prominent lines at 6209 and 6219 cm^{-1} (7 K) are identified as electronic origins. Their assignment, as shown in Figure 2, is straightforward from a comparison with the analogous MnO_4^{3-} spectrum.[4] The emitting state ^1E is split into two orbital components in the C_s site symmetry of K_2CrO_4,[12] thus leading to a cold and a hot line, respectively. The ^1E splitting ΔE, which reflects the geometrical distortion from a regular tetrahedron, is only 10 cm^{-1} in the K_2CrO_4 host, whereas it is an order of magnitude larger in MnO_4^{3-}-doped apatites and spodiosites.[4] We notice that the luminescence intensity is strongly concentrated in the origins, with less than 10% altogether in vibrational sidebands. The line denoted δ in

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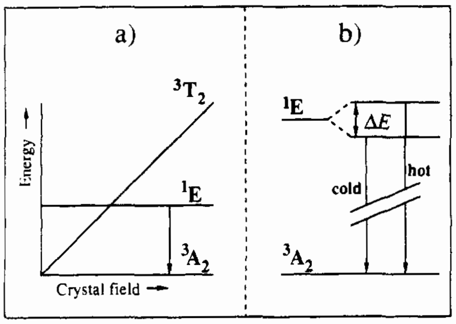

Figure 2. Relevant part of the energy level scheme of a tetrahedral d^2 ion: (a) ground and first excited states; (b) orbital splitting of ^1E in C_s site symmetry and spectroscopic transitions.

Figure 1 is separated by 310 cm^{-1} from the cold origin line. This energy difference corresponds to the energy of a bending mode in the FeO_4^{2-} unit.[9]

The measured luminescence lifetime τ = 1.3 ms at 10 K is in good agreement with the radiative lifetime estimated from the intensity of the $^3A_2 \rightarrow {}^1E$ absorption lines.[13] Since there is no noticeable drop in τ up to 100 K, we conclude that the quantum yield is close to 1 in this temperature range. At 295 K, the lifetime and the quantum yield have dropped to about 50%. This is comparable to the behavior of Mn^{5+}-doped $Sr_5(PO_4)_3Cl$ and Ca_2PO_4Cl, in which stimulated emission could be observed around 1.2 μm up to room temperature.[14] We are presently studying the absorption and emission properties of FeO_4^{2-}-doped systems in more detail.

Acknowledgment. We are grateful to the Swiss National Science Foundation for financial support.

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