Unusual Luminescence of $Ca_8[Al_{12}O_{24}](WO_4)_2$: Tb^{3+}

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The luminescence properties of aluminate sodalite $Ca_8[Al_{12}O_{24}](WO_4)_2$ (CAW) undoped and doped with Tb^{3+} are reported and discussed. At room temperature the emission of tetrahedral WO_4^{2-} in CAW showed an abnormally small Stokes shift ($9060\ cm^{-1}$), which is related to the crystal structure of CAW. A strong absorption band in the excitation spectrum of the Tb^{3+}-activated CAW is ascribed to the absorption of the charge transfer state Tb^{4+}-W^{5+}, into which the excitation resulted in the efficient emission from the $^5D_4$ level of Tb^{3+}, but not from the $^5D_3$ level.

Keywords   aluminate sodalite, terbium ion, tungstate, charge transfer, Stokes shift, luminescence

Introduction

The luminescence of tungstates unactivated and activated with trivalent rare-earth ions has been the subject of extensive investigations.[1-5] We are interested in the luminescence of WO_4^{2-} and Tb^{3+} in $Ca_8[Al_{12}O_{24}]$-$(WO_4)_2$ (CAW) for the following two reasons. First, different from those compounds which have been investigated before, CAW has a so-called sodalite framework.[6,7] Will it give rise to an unusual luminescence behavior of WO_4^{2-}? Second, when Tb^{3+} ions and some high-valence transition metal ions with a d^0 configuration (*e.g.*, W^{6+} and V^{5+}) coexist in a compound, the luminescence of the Tb^{3+} ions is often quenched due to the formation of the charge-transition (CT) state (e.g., Tb^{4+}-W^{5+} and Tb^{4+}-V^{4+}).[8,9] However, if a Tb^{3+} is substituted for a Ca^{2+} in a lattice and thus bears an effectively positive charge, the quenching is weakened, and even the efficient luminescence can be observed.[10] Will the situation occur in CAW? We have observed that the emission of tetrahedral WO_4^{2-} has a much smaller Stokes shift in CAW than in other compounds containing WO_4^{2-} tetrahedra. In addition Tb^{3+} showed an efficient green emission in CAW when excited to the charge transition state Tb^{4+}-W^{5+}, usually giving rise to the quenching of the Tb^{3+} luminescence. In this paper, we report and discuss these results.

Experimental

The samples were prepared by firing the mixtures of $CaCO_3$ (A.R.), Al_2O_3 (S.P.), WO_3 (A.R.), Tb_4O_7 (99.95%) and Na_2CO_3 (A.R.) in air at 1200 ℃ for 6 h and then at 1380 ℃ for 17 h. The crystal structure of the products were checked by X-ray powder diffraction analysis with a Rigaku 2028 diffractometer using Cu Kα radiation. The emission and excitation spectra of the samples were recorded on an SPEX Fluorolog-2 spectrofluorometer with a 450 W xenon lamp as an excitation source. The IR absorption spectrum of CAW was measured with a Perkin-Elemer 850B infrared spectrophotometer. All measurements were carried out at room temperature (r.t.).

Results and discussion

Spectral properties of CAW

The X-ray powder diffraction analysis (Figure 1) showed that the prepared samples are orthorhombic with space group *Aba*2 and $a=2.618$, $b=1.306$, $c=0.934$ nm.
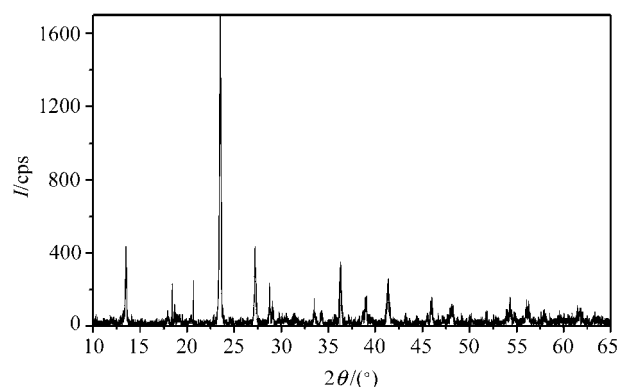

Figure 1   X-ray diffraction pattern of CAW.

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Figure 2 is the excitation and emission spectra of CAW. The emission spectrum consists of a broad band, the maximum of which is located at 431 nm. The excitation spectrum is composed of a relatively narrow band peaking at 310 nm. The Stokes shift of the emission and the half-width of the emission band are about 9060 cm^{-1} and 5580 cm^{-1}, respectively. The tungstate WO_4^{2-} exists as a tetrahedron in CAW[6,7] and its excitation and emission arise from internal WO_4^{2-} CT transition. As far as we know, the Stokes shift is the smallest one reported so far for the emission of WO_4^{2-} tetrahedra, the Stokes shifts of WO_4^{2-} ion emission exceeding generally 15000 cm^{-1}.[11]
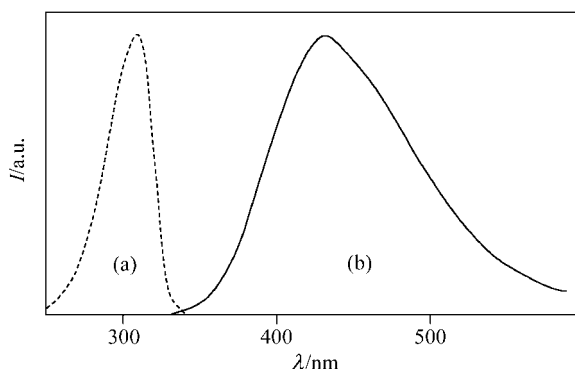
Figure 2 (a) Excitation ($\lambda_{em}=431$ nm) and (b) emission ($\lambda_{ex}=310$ nm) spectra of $Ca_8[Al_{12}O_{24}](WO_4)_2$ at r.t..

The small Stokes shift is probably related to the structure of CAW. The structure of CAW is characterized by corner-sharing AlO_4 tetrahedra forming the so-called sodalite framework. The framework encloses relatively large cages, the centers of which are occupied by the tetrahedral cage anions WO_4^{2-}.[6,7] When excited, the WO_4^{2-} group is in the anti-bonding excited state, and the W—O distance is larger than in the ground state. In general, because the W^{6+} ion is too large for a tetrahedral hole in oxides, the expansion is large, resulting in a large Stokes shift.[2] However, the expansion is now hindered by the rigid framework of CAW, resulting only in a small offset of the potential energy curve of the excited state and thus in the small Stokes shift.

Tb^{3+}-activated CAW

Under UV light excitation, the Tb^{3+}-activated CAW samples showed efficient green emission. The excitation and emission spectra of $Ca_{8-2x}Tb_xNa_x[Al_{12}O_{24}](WO_4)_2$ with $x=0.008$, 0.02, 0.08 are similar. For $x=0.008$, the spectra are shown in Figure 3. The excitation spectrum consists of a strong absorption band peaking at 277 nm and some weak lines ranging from 330 to 400 nm, the lines arising from intra-$4f^8$ configuration transitions of Tb^{3+}. Upon excitation into the band ($\lambda_{ex}=277$ nm), the emission of the sample came entirely from the $^5D_4\rightarrow^7F_J$ ($J=3$, 4, 5, 6) transitions of the Tb^{3+}, whereas the emission of the $^5D_3\rightarrow^7F_J$ transition could not be observed. Besides, no WO_4^{2-} emission was observed in the emission spectrum, even if the excitation wavelength was changed to 310 nm.
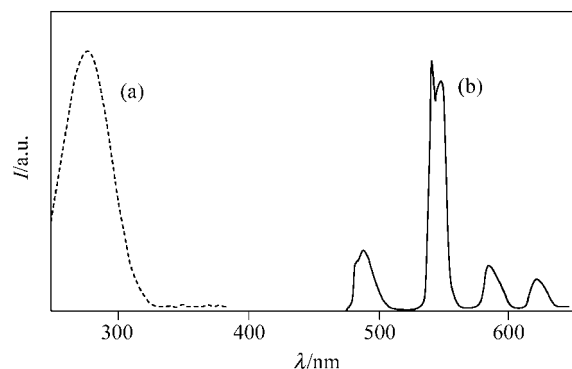
Figure 3 (a) Excitation ($\lambda_{em}=542$ nm) and (b) emission ($\lambda_{ex}=277$ nm) spectra of $Ca_{7.984}Tb_{0.008}Na_{0.008}[Al_{12}O_{24}](WO_4)_2$ at r.t..

It is remarkable that the emission from the $^5D_3$ level of the Tb^{3+} is so strongly quenched in the sample. The occurrence of this situation is generally explained in references by the followings:

(i) Cross relaxation:[12,13] In concentrated terbium systems, the average distance between Tb^{3+} ions is small, and the $^5D_3$ state can be relaxed nonradiatively to the $^5D_4$ state via the "cross relaxation" processes such as $Tb^{3+}(^5D_3) + Tb^{3+}(^7F_6) \rightarrow Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0)$. This transfer spans some 1.3 nm.[14] As a result, the $^5D_3$ emission decreases (concentration quenching), whereas the $^5D_4$ emission increases. The phenomenon can be observed in most compounds. In some cases, although the Tb^{3+} concentration is small, there is still a considerable amount of cross relaxation, because the Tb^{3+} ions are incorporated into a host lattice in pairs, as can be seen in $CsCdBr_3$-Tb^{3+},[15,16] the cross relaxation occurs between the Tb^{3+} ions in pairs.

(ii) Multi-phonon emission:[10,17] If there exist high-frequency phonons in a host lattice, the radiationless relaxation process $^5D_3\rightarrow^5D_4$ can take place accompanied by the excitation of a few of such phonons. It has been shown[18] that if the energy gap (viz. the energy difference between the $^5D_3$ and $^5D_4$ levels) is equal to or less than five times of the phonon energy, the radiationless relaxation process can effectively compete with the radiative transitions $^5D_3\rightarrow^7F_J$ ($J=3$, 4, 5, 6). In $LnMgB_5O_{10}$ (Ln=La, Gd),[19,20] for example, the maximum phonon energy is about 1400 cm^{-1} (about a quarter of the energy difference between the $^5D_3$ and $^5D_4$ levels), and no emission from the $^5D_3$ state could be observed even for a low Tb^{3+} concentration.

Besides, if a phosphor is doped with a Tb^{3+} and a sensitizer, and the emission spectrum of the sensitizer overlaps much more favorably with the $^5D_4$ level of Tb^{3+} than with the $^5D_3$ level, the $^5D_4$ emission is much stronger than the $^5D_3$ emission. Examples are $CaSO_4$-Tb^{3+}, V^{5+} [10] and $La_3WO_6Cl_3$-Tb^{3+}.[2] This situation is equivalent to that in which the Tb^{3+} is directly excited to the $^5D_4$ level.

According to our experimental results, the radiationless decay of the $^5D_3$ state of the Tb^{3+} arising from a cross relaxation does not occur in $Ca_{7.984}Tb_{0.008}Na_{0.008}[Al_{12}O_{24}](WO_4)_2$. First, there is a low Tb^{3+} concentration in the sample. Second, in many compounds, a cross relaxation can also occur between Sm^{3+} ions: $Sm^{3+}(^4G_{5/2})+Sm^{3+}(^6H_{5/2})\rightarrow 2Sm^{3+}(^6F_{9/2})$. This transfer can occur over about 2 nm.[14] The transfer distance is comparable with that for Tb^{3+} ions (1.3 nm). For the sake of comparison, we prepared the sample $Ca_{7.84}Sm_{0.08}Na_{0.08}[Al_{12}O_{24}](WO_4)_2$ (note that the concentration of Sm^{3+} in the sample is ten times that of the Tb^{3+} in $Ca_{7.984}Tb_{0.008}Na_{0.008}[Al_{12}O_{24}](WO_4)_2$). In the sample, we did not find appreciable quenching of the emission from the $^4G_{5/2}$ level of Sm^{3+}. Therefore, we conclude that the quenching of the $^5D_3$ emission of Tb^{3+} in CAW is not the result of the concentration quenching, and also not of the pair effect of Tb^{3+} ions, because we have no reason to believe that the Tb^{3+} ions have been incorporated into CAW in pair, but Sm^{3+} ions have not been.

Multi-phonon emission does not give rise to so strong decay of the $^5D_3$ state of the Tb^{3+} in CAW. The maximum vibration frequency of CAW, obtained from the IR spectrum, is 985 cm^{-1}. Silicates and phosphates usually have about the same vibration frequency as this. For example, the maximum frequencies of the phonons in $Mg_2Y_8(SiO_4)_6O_2$[21] and $LaPO_4$[22] are 970 and 1080 cm^{-1}, respectively. It was observed that the $^5D_3$ and the $^5D_4$ emissions have comparable intensities in these two compounds.[21,23]

The strong absorption band in the excitation spectrum of the Tb^{3+} emission (see Figure 3(a)) is not ascribed to the absorption of the WO_4^{2-}, because it seems impossible that the incorporation of such a small amount of Tb^{3+} and Na^+ ions could lead to so large a shift of the position of the WO_4^{2-} absorption. This means that the luminescence of the Tb^{3+}, different from that in $CaSO_4$: V, Tb,[10] is not due to the energy transfer from the WO_4^{2-} to the Tb^{3+}, and the inefficiency of the $^5D_3$ state emission not to the poor overlap of the WO_4^{2-} emission band with the $^5D_3$ level of Tb^{3+}.

We ascribed the above-mentioned absorption band to the absorption of the CT process between the Tb^{3+} and the W^{6+}, viz. Tb^{3+}-$W^{6+}\rightarrow Tb^{4+}$-$W^{5+}$. The CT process as such (metal-to-metal) usually quenches the luminescence of the relevant species, as can be seen in YVO_4-Tb^{3+},[9] $SrTiO_3$-Ce^{3+}[24] and $La_3WO_6Cl_3$-Ce^{3+}.[2] However, the process does not necessarily lead to the quenching of all possible luminescences, as was pointed out by Blasse and Sabbatini.[17] In order to explain the luminescence of the Tb^{3+} in CAW, a configurational coordination diagram is shown in Figure 4. The parabola representing the potential energy of the CT state has a large offset relative to the ground state due to the weak bond in the CT state. The equilibrium position of the CT state is close to the intersection of the curves of the CT state and the $^5D_4$ state. When excited to the CT state, the system relaxes rapidly to the equilibrium position fol-

lowed by a nonradiative relaxation to the $^5D_4$ state, from which the radiative transitions $^5D_4\rightarrow ^7F_J$ (J=3, 4, 5, 6) occur. Consequently, the efficient emission from the $^5D_4$ state can be observed, but that from the $^5D_3$ state can not.
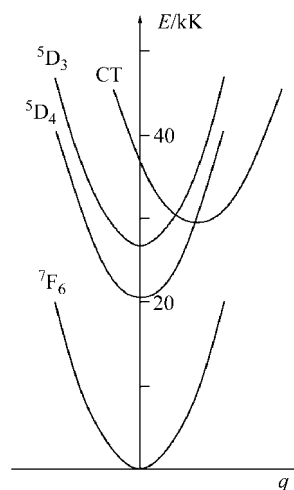
Figure 4 Schematic configuration coordinate diagram with energy E and configuration coordinate q for Tb^{3+} in $Ca_8[Al_{12}O_{24}](WO_4)_2$. For simplicity, only a few of parabolas of the Tb^{3+} $4f^8$ configuration are drawn.

According to the model, upon excitation into a certain Tb^{3+} level between the $^5D_3$ state and the CT state, the $^5D_3$ and the $^5D_4$ emission with about the same intensity should be observed. This situation occurs indeed. Figure 5 is the emission spectrum of $Ca_{7.984}Tb_{0.008}Na_{0.008}[Al_{12}O_{24}](WO_4)_2$ under the excitation of 352 nm (the $^5L_9$ level of Tb^{3+}).
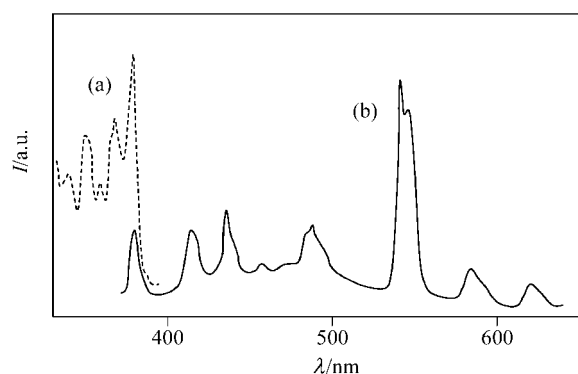
Figure 5 (a) Excitation (λ_{em}=542 nm) and (b) emission (λ_{ex}=352 nm) spectra of $Ca_{7.984}Tb_{0.008}Na_{0.008}[Al_{12}O_{24}](WO_4)_2$ at r.t. (see also the text).

Finally we explain why we do not assign the strong absorption band to the $4f\rightarrow 5d$ transition of the Tb^{3+}. Because $4f\rightarrow 5d$ transition is the so-called Rydberg transition[25] and the Tb^{3+} (on a Ca^{2+} site) in CAW bears an effectively positive charge, we expect that the excited 5d state will lie at a high energy level and has a poten-

tial energy parabola with a small offset. In other words, the minimum of the 5d state curve will fall inside the $^5D_3$ state curve. Therefore, we could observe the stronger emission from the $^5D_3$ state. But it was not true.

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