Radiative decay of self-trapped excitons in $CaMoO_4$ and $MgMoO_4$ crystals

Radiative decay of self-trapped excitons in CaMoO$_4$ and MgMoO$_4$ crystals

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Abstract
Spectroscopic properties of CaMoO$_4$ and MgMoO$_4$ crystals were studied in view of their application to cryogenic scintillation detectors. Luminescence spectra and the luminescence decay kinetics were measured over a wide range of temperatures (8–300 K). For the first time we measured time-resolved luminescence spectra of CaMoO$_4$. In addition to the green emission arising from the triplet state of self-trapped excitons (STEs), a new band at around 430 nm with a decay time constant 10 ± 3 ns was observed at $T = 8$ K. This emission is assigned to the radiative decay of a singlet STE.

The relaxation of electronic excitations in the crystals under study is discussed on the basis of our current understanding of their electronic structures and a configuration coordinate model for the radiative decay of STEs. The model includes adiabatic potential energy surfaces (APESs) associated with singlet and triplet states and explains the variation of the luminescence kinetics with temperature as a result of a re-distribution in the population of these states. Thus, judging from the change of the singlet STE emission due to temperature variation, we infer the existence of an energy barrier between the singlet and triplet APESs. The multi-exponential character of the decay of the triplet emission can be understood assuming that the relevant radiative transitions originate from different minima of the triplet APES. Non-radiative energy transfer processes control the population of these states, resulting in thermal variation of the intensities of the different emission components.

1. Introduction

Luminescence properties of CaMoO$_4$ have been studied intensely in view of applications of this material as a phosphor and laser host [1–5]. The results of these examinations, when combined

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with experiments on EPR studies [6], measurements of other spectroscopic properties, such as refraction [7], reflectivity [8], photoconductivity [9], excited-state absorption [10] and latest computations of the electronic structure [11], provide a good basis for our understanding of the features of the emission processes in the crystals. It is generally accepted that the intrinsic green emission of $CaMoO_4$ is due to the radiative decay of a self-trapped exciton (STE) localized at the $(MoO_4)^{2-}$ oxyanion complex [4, 6, 12]. The luminescence is characterized by a decay time of the order of tens of microseconds at 300 K and is interpreted as a triplet emission of STE.

On the other hand, as far as we are aware, there is no dedicated investigation of the luminescence properties of $MgMoO_4$. This compound has been the subject of few structural and chemical studies, and as part of these studies computation of the electronic structure has been carried out recently [13].

The interest in molybdates has increased again recently due to the need of providing different scintillation targets for cryogenic particle physics experiments searching for rare events [14]. The scintillating crystal is a key element of these experiments [15] and a high light yield of these materials at low temperatures is a crucial selection criterion. Nonetheless, other criteria, such as radio-purity, surface properties and thermodynamic properties of the lattice, can be equally important. Molybdate crystals, exhibiting good mechanical and surface properties and appropriate isotopic abundance, may offer a suitable choice for this application if the principal luminescence characteristics (light yield and decay time) prove to be adequate.

In view of the special interest in these materials there is a need for expanding the knowledge with particular emphasis on the investigation of the temperature dependences of the luminescence characteristics. Here we present the results obtained from a series of experiments aiming to investigate the electronic excitations and the luminescence kinetics of $CaMoO_4$ and $MgMoO_4$ over a wide range of temperatures (8–300 K). Preliminary results have been published recently [16]. The present study represents an attempt at improving the understanding of the features in the emission process in this technologically important class of materials. The results should provide the basis for an assessment of the practical merit of the crystals when being used as cryogenic scintillation detectors.

2. Experimental technique

The single crystals of $CaMoO_4$ and $MgMoO_4$ investigated in this study were grown by the Czochralski technique. The sample of $CaMoO_4$ was polished to optical quality, while the $MgMoO_4$ sample was cleaved from a large ingot.

The emission spectra were measured using a 0.4 m VUV monochromator and a 150 W D_2 lamp with an MgF_2 window as an excitation source. The primary monochromator resolution was 2 nm. The samples were mounted on the copper holder of a closed-cycle cryogenic refrigerator. Luminescence from the samples was observed at right angles to the exciting UV light by means of a Nikon G250 monochromator and a photomultiplier (Hamamatsu R106UH or R4220). The band pass of the G250 monochromator was 12 nm or less.

The measurements of the luminescence decay kinetics were carried out using the fourth harmonics (4.66 eV; 0.7–0.9 mJ; 10 Hz) from a Q-switched Nd:YAG laser as a pulsed excitation source. The emission passed through a Jobin Yvon HR320 monochromator was detected with a R106UH photomultiplier, the signal from which was fed into a Tektronix 2440 digital storage oscilloscope. For measurements of time-resolved luminescence spectra, a gated ICCD camera (Hamamatsu C5909-06) was coupled to the monochromator.
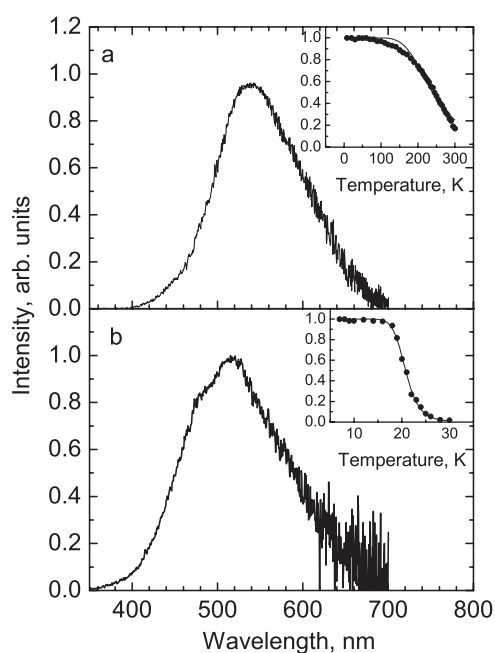
Figure 1. Luminescence spectra of CaMoO$_4$ (a) and MgMoO$_4$ (b) measured under excitation with 7.7 eV photons at 8 K. Insets show the variation of the integrated light yield as a function of temperature. Lines are the best fit of the Mott formulae to the data points.

3. Crystal structure

CaMoO$_4$ has scheelite-type structure and belongs to the space group $I4_1/a$ with four molecules per unit cell [17]. In this structure four oxygen ions are arranged about molybdenum in an insulated tetrahedron, which is slightly compressed along the c-axis. A Ca^{2+} ion is surrounded by eight oxygen ions. The lattice constants are $a = 5.222$ and $c = 11.425$ Å. Single crystals of MgMoO$_4$ exhibit monoclinic symmetry and at normal temperature and pressure adopt the $C2/m$ space group [18]. In this structure, each Mo ion is surrounded by four oxygen ions with approximately tetrahedral coordination having different Mo–O distances. Mg^{2+} ions occupy the sites with octahedral coordination. The crystal cell parameters are $a = 10.278, b = 9.291$, $c = 7.021$ Å and $\beta = 106.9°$.

It needs to be emphasized that the existence of the same geometrical arrangement, i.e. isolated MoO$_4$ tetrahedrons, is an important common feature of the crystal structures in both compounds. To a large extent, this makes their electronic structures very similar in the low-energy part, as is confirmed by theoretical calculations of the band structures of CaMoO$_4$ [11] and MgMoO$_4$ [13].

4. Results and discussion

4.1. Luminescence properties

Figure 1 shows emission spectra of CaMoO$_4$ and MgMoO$_4$ measured for excitation with 7.7 eV photons at $T = 8$ K. The luminescence spectra are located in the green spectral

range, exhibiting the main maxima at 540 (CaMoO$_4$) and 520 nm (MgMoO$_4$). As the temperature increases, CaMoO$_4$ shows almost constant light yield up to 100 K and then it gradually decreases (see inset in figure 1). The quenching temperature T_q, at which the emission intensity exhibits half of its initial value, is found to be 250 K. In MgMoO$_4$ the thermal quenching manifests itself at very low temperature ($T_q = 20$ K). In the framework of a simple configuration coordinate model the temperature dependence of the light yield can be expressed using the canonical Mott equation: $I(T) = 1/(1 + C \exp(-\Delta E/k_B T))$ [19]. Analysis of experimental results gave the value of the energy barriers as $\Delta E = 112 \pm 5$ and 26 ± 1 meV for CaMoO$_4$ and MgMoO$_4$, respectively.

The luminescence spectra shown in figure 1 clearly point to a composite structure. There are a number of factors that can account for this complexity. Given the similarity of the crystal structure of CaMoO$_4$ and CaWO$_4$, as well as the analogous tetrahedral configuration of the oxyanion molecular complex in molybdate crystals, it is assumed that the energy structure of these compounds should be very similar. The computations by Zhang *et al* [11] have shown that the top of the valence band and the bottom of the conduction band, whose states are directly involved in the process of radiative relaxation, have almost identical energy structure in CaMoO$_4$ and CaWO$_4$. It is therefore accepted that the emission characteristics of these crystals are interpreted in terms of the same model. It should be noted that further consideration specifically refers to CaMoO$_4$ while the situation in MgMoO$_4$ is more complex owing to the availability of two crystallographically different types of emitting centres. This can lead to a quantitative difference in the resultant emission originating from these centres. With such a caveat taken into account, the concept of this approach can also be applied to MgMoO$_4$ that exhibits a similar energy structure of the highest occupied and lowest unoccupied states (see [13]).

In the molybdate and tungstate crystals with scheelite structure, optical transitions occur within the oxyanion molecular complex MO$_4^{2-}$ (M = W, Mo) between the $^1A_1$ ground state and the singlet ($^1T_1$, $^1T_2$) and triplet ($^3T_1$, $^3T_2$) levels. The electric dipole allowed $^1A_1 \rightarrow {}^1T_2$ transitions account for the excitation while the radiative transitions arise from the closely located lower-lying triplet states [4, 9, 12]. These transitions are spin forbidden. The lowering of the site symmetry of the oxyanion complex makes the $^3T_2 \rightarrow {}^1A_1$ transition orbitally allowed while the $^3T_1 \rightarrow {}^1A_1$ transition remains forbidden [4, 12, 20]. Therefore, the prevailing opinion is that the high-energy band in the luminescence spectrum is associated with the radiative recombination of electron–hole pairs localized at the MoO$_4^{2-}$ group [4]. Consequently the low-energy part of the spectrum is tentatively assigned to defect emission, being most likely an oxygen-deficient complex [4, 21].

In addition there are considerations indicating that Jahn–Teller interaction might have an effect on the structure of the lowest emitting states of the crystals with scheelite structure [9, 22]. According to theoretical works by Bacci *et al* [22, 23], pseudo Jahn–Teller (PJT) interaction enables a coupling between $^3T_1$ and $^3T_2$ states and hence allows the two adiabatic potential energy surfaces (APESs) to contribute to the overall emission. When the spin–orbit (SO) and Jahn–Teller (JT) interactions are considered, the structure of the lowest excited state becomes more complex, with a few APESs contributing to the emission spectrum. This makes the emission spectrum composed of several emission bands.

Very recently this prediction has been confirmed through experimental studies of time-resolved luminescence spectra of PbWO$_4$ [24]. It was shown that the main luminescence band consists of four emission bands with different decay times. The long-lived (millisecond) green band is the emission of defect centres, while the three other resolved sub-bands constituting the blue emission represent the transitions from different APESs. These bands exhibit different
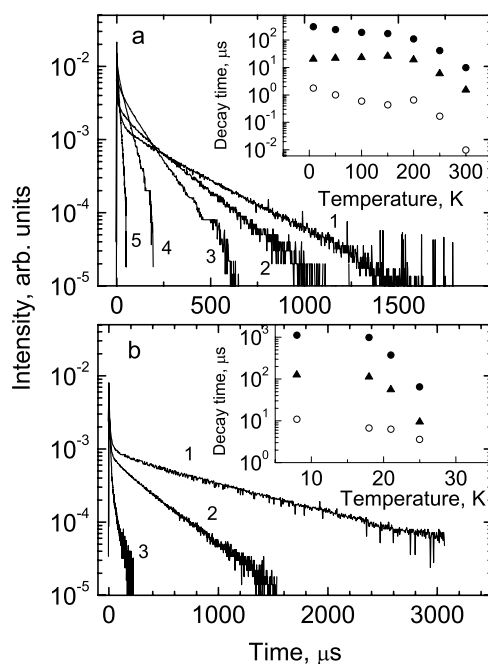
Figure 2. Decay kinetics of the luminescence of CaMoO$_4$ (a) and MgMoO$_4$ (b) measured under excitation with 4.66 eV photons. Temperature is 8 (1), 100 (2), 200 (3), 250 (4) and 300 K (5) for CaMoO$_4$ and 8 (1), 21 (2) and 25 K (3) for MgMoO$_4$. Insets show the temperature variation of the slow (●), medium (▲) and fast (○) decay time constants obtained using a three-exponential decay function.

decay times and their peak positions are shifted by ∼100 meV; altogether, this causes changes of the spectrum with time.

4.2. Kinetics of luminescence decay and time-resolved luminescence

The APES minima which originate from different triplet levels give rise to radiative transitions with different probabilities, and therefore this should result in complex character of the luminescence decay. Measurements of the luminescence kinetics of CaMoO$_4$ and MgMoO$_4$ have been carried out at different temperatures using pulsed UV excitation. The measured decay curves (see figure 2) demonstrate well defined fast slopes at the beginning of the luminescence pulse and slow exponential tails. The best fit of the experimental results was obtained using a sum of three exponentials. By this, the luminescence kinetics of the crystals under study differ significantly from that of CaWO$_4$, which exhibits a single exponential decay under optical excitation [25]. The variations of the decay time constants with temperature obtained from this fit are presented in the inset of figure 2. As the temperature increases one can notice an interesting effect in the luminescence kinetics of CaMoO$_4$, namely the increase of the initial intensities of all components. This effect is especially prominent for the slow component, that exhibits a gain by an order of magnitude in the temperature range between 8 and 300 K. This is a fairly unusual peculiarity of the luminescence kinetics, indicating that the initial population of the emitting states of CaMoO$_4$ depends on temperature.

Overall these findings favour the interpretation that several different states are involved in the luminescence process. To gain better insight into the features of the radiative relaxation
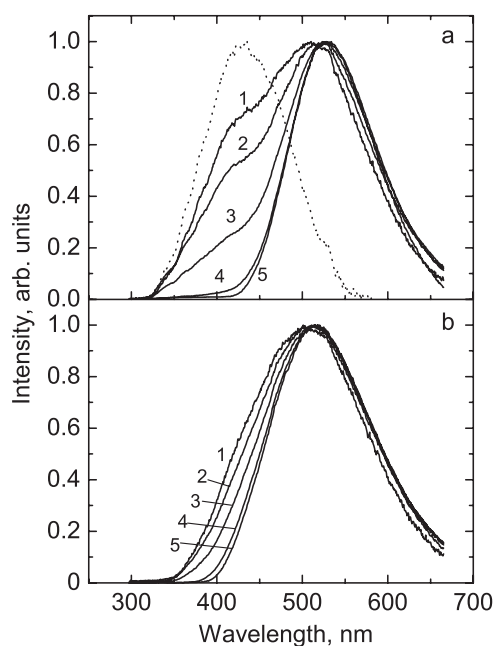
Figure 3. Time-resolved luminescence spectra of $CaMoO_4$ measured under excitation with 4.66 eV photons at 8 (a) and 300 K (b). The time delay is 0 ns (1), 5 ns (2), 20 ns (3), 40 ns (4) and 1 μs (5). The dotted line in (a) represents the spectrum of the fast emission obtained by subtracting the slow component.

of the molybdate crystals, we measured time-resolved luminescence spectra of $CaMoO_4$. The spectra taken at 8 and 300 K with different delay times after the excitation pulse are shown in figure 3. The most interesting feature is shown in figure 3(a), where the early stage of the evolution of the emission spectrum at 8 K is presented. Immediately after the excitation pulse one can clearly see a short-wavelength emission that vanishes in a few tens of nanoseconds. Subtraction of the slow emission from the total luminescence signal allows the fast emission band, peaking at 430 nm, to become clearly resolved. This emission decreases with temperature and at 300 K the only indication of this fast luminescence band is the change of the short-wavelength side of the main emission band that has millisecond decay time constant (see figure 3(b)). When delay times exceed 50 ns the emission spectrum exhibits no further change: only the usual green emission of $CaMoO_4$ is observed for a delay within the range between 50 ns and 500 μs.

Figure 4 shows the decay time spectrum of the newly observed short-wavelength luminescence. The best fit to the experimental results obtained with the single-exponential function gives decay time constant 10 ± 3 ns, that is characteristic of a spin-allowed transition. Taking into account additionally the spectral position and temperature dependence of the fast emission, we infer that this luminescence is most likely due to the radiative decay of a singlet STE originating from the higher-lying $^1T_{1,2}$ states. As can be seen in figure 3(a), the detected intensity of the fast emission at 8 K is comparable with that of the slow component. Provided that the decay time constant of the slow component is of the order of 100 μs, this effectively means that the fast emission contributes $\sim$0.1% or less to the total luminescence yield of the crystal. Furthermore, the emission strongly overlaps with the ordinary slow emission of triplet STE. This explains why this emission has not been detected hitherto; the only indication of
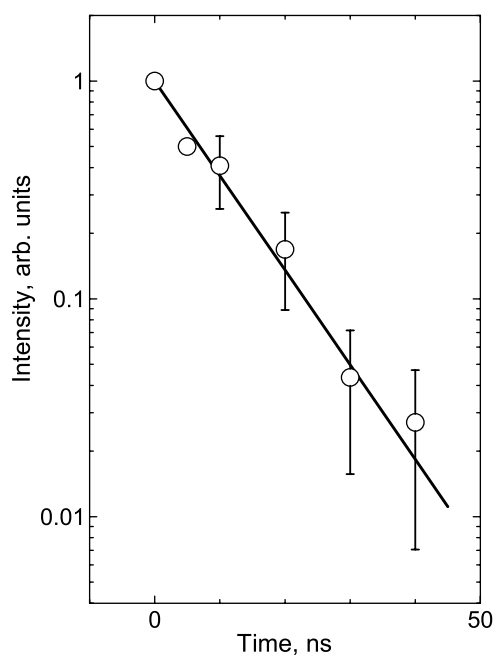
Figure 4. Decay time spectrum of the fast emission of CaMoO$_4$ at 8 K measured under excitation with 4.66 eV. The line shows the best fit to the experimental results using a single-exponential decay function with $\tau = 10 \pm 3$ ns.

the nanosecond emission component in CaMoO$_4$ has been observed in the integrated mode at x-ray excitation [26].

4.3. Model of decay of intrinsic excitations in CaMoO$_4$

The results of the time-resolved luminescence studies of CaMoO$_4$ are central to the understanding of the features of the emission processes in molybdates. First of all, the observation of the emission from a singlet STE has an important consequence because it can explain the variation of the luminescence kinetics with temperature. According to the conventional model, the singlet $^1T_1$ and $^1T_2$ levels in tungstates and molybdates are involved exclusively in the excitation process while all radiative transitions occur from the lower-lying $^3T_1$ and $^3T_2$ triplet states. This is thought to be due to very efficient non-radiative singlet–triplet relaxations that provide a channel for population of the emitting states. The findings presented here show that in CaMoO$_4$ this conventional process of triplet state feeding is temperature dependent and suppresses the instantaneous non-radiative relaxation of singlet states at low temperatures. This is possible if there is an energy barrier between the singlet and triplet APESs. The existence of such an energy barrier is in fact a quite common feature of the STE emission [27, 28], which leads to the appearance of the singlet emission at low temperatures and to the appreciable variation in the initial population of triplet states with temperature. Both effects are observed clearly in the spectral and kinetic characteristics of CaMoO$_4$ luminescence.

Another factor that affects the population of the triplet states is the phonon-assisted non-radiative transition between different APESs constituting the triplet states [22, 23]. The non-radiative transition rate is a complex function of temperature and energy separation of the levels. The temperature dependence of non-radiative transition rates between the levels controls the
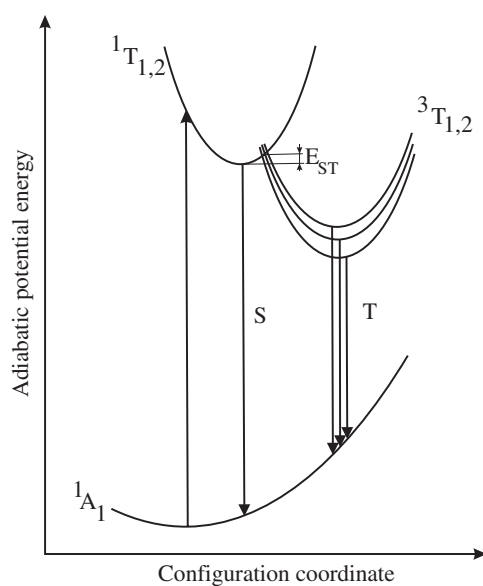
Figure 5. A configuration coordinate diagram and scheme of radiative transitions in CaMoO$_4$. E_{ST} indicates the energy barrier between singlet (S) and triplet (T) states.

decay time constants and the initial intensities of the emission components. They are thus the result of the thermodynamic balance established between these levels. Quantitative analysis of the dynamics of the emission process in the Jahn–Teller active system is quite a sophisticated task (see e.g. [29, 30]) and this is beyond the scope of the present paper. Nonetheless, the main message is that in a certain temperature range the kinetics of the radiative decay consists of a few decay components, and this indeed is observed in the crystals under study. The scheme in figure 5 shows the suggested energy diagram of singlet and triplet states as well as relevant radiative transitions in CaMoO$_4$.

The results of the present study of the luminescence kinetics of CaMoO$_4$ as a function of temperature can be understood in terms of the suggested scheme of radiative processes. First of all, the singlet–triplet transitions are responsible for the change of the initial population of the triplet levels with temperature. Then, temperature dependent re-distribution in the population of the triplet levels occurs. The temperature increase stimulates the re-distribution of the initial population of the emitting levels, thereby providing the increase in population of lower APESs. Consequently, the intensity of the corresponding emission should increase, being consistent with the variation in the initial intensity of the slow component. The process of re-distribution between the emitting states does not affect the total balance of energy emitted and therefore the total light yield of the emission should not change before the thermally induced non-radiative quenching starts.

Finally, it should be noted that for the sake of simplicity we did not include in this consideration a metastable level originating from the lower $^3T_1$ term, the presence of which causes an order of magnitude increase of the decay time in tungstates and molybdates at very low temperatures [31]. Due to a small separation in energy between this level and the emitting one ($\sim$0.5 meV), it plays a noticeable role only at temperatures less than 10 K and does not much affect the features of the radiative decay process in the temperature range examined here.

5. Conclusions

In this work we carried out detailed investigations of the features of the relaxation processes in $CaMoO_4$ and $MgMoO_4$ crystals. It was found that the emission spectra exhibit a complex character, and the decay kinetics of the luminescence consists of a few components. Moreover, an appreciable variation in the initial intensity of the decay components with temperature was observed in $CaMoO_4$. In order to gain better insight into the nature of the radiative relaxation in the molybdates, time-resolved luminescence measurements were carried out for $CaMoO_4$. These measurements revealed a new emission band at 430 nm with a decay time of 10 ± 3 ns at 8 K on the high-energy side of the main green band. This observation gave a first clear experimental evidence of the existence of the emission from a singlet STE in the tungstate and molybdate family. Thus, the results of our study allowed us to present a unified model for the luminescence processes in $CaMoO_4$. This model includes APESs associated with singlet and triplet states, and considers the emission as a final product of a dynamic equilibrium established between these states with the actual balance of populations controlled by temperature. We believe that this finding should provide a good testing ground for furthering our understanding of the principal features of the emission of molybdate and tungstate crystals. The latter is particularly important, given the future prospects of these materials as cryogenic scintillation detectors of ionizing radiation.

Acknowledgments

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