Emission decay kinetics in a CaWO$_4$:Bi crystal

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Abstract

The decay kinetics of the 2.88 eV emission of pure and Bi-doped CaWO$_4$ crystals has been studied in the temperature region of 4.2–300 K. The decay components connected with the radiative transitions from the triplet excited states of regular WO$_4^{2-}$ oxyanionic complexes and WO$_4^{2-}$ complexes perturbed by Bi^{3+} ions (WO$_4^{2-}$(Bi^{3+}) centres) have been identified. It is shown that WO$_4$(Bi^{3+}) centres can be excited directly above the edge of the fundamental absorption of CaWO$_4$, or due to the energy transfer from the metastable state of a Bi^{3+} ion at the excitation in the Bi^{3+} absorption band at 4.4 eV. At temperatures $T > 170$ K, the excited state of the WO$_4^{2-}$(Bi^{3+}) centre is thermally ionised, giving rise to phosphorescence in the blue spectral region. These processes are compared with those known for excitons in PbWO$_4$ crystals.
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1. Introduction

Based on a comparative study of PbWO$_4$ and CaWO$_4$:Bi crystals, we have suggested that relaxation processes between cationic and anionic states make an essential contribution to the relaxation of electronic excitations in these materials [1]. The CaWO$_4$:Bi crystal was used as a model system for studying the role of cationic states (cation excitons) in the relaxation of electronic excitations in PbWO$_4$. It has been assumed that in CaWO$_4$:Bi,

an efficient energy transfer from cationic impurity states to the WO$_4$ complex takes place even at the excitation within the Bi^{3+} states situated in the forbidden gap of the CaWO$_4$ crystal. Our recent investigation of the decay kinetics of the main emission of pure and Bi-doped CaWO$_4$ crystals allowed us to confirm this model.

2. Experimental methods

Single CaWO$_4$:Bi crystals were grown by the flux method at Chalmers University of Technology, Gothenburg, Sweden. During the growth,

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Na^+ ions were introduced into the crystals to provide a local compensation of the Bi^{3+} extra charge.

Time-resolved spectra were measured by using a Perkin-Elmer FX-1152 Flashtube (pulse duration $1\,\mu s$) and an Ortec MCS-PCI Card with $100\,ns$ time resolution. Two double-quartz monochromators were used to select the excitation and the emission wavelength. Each measured decay curve was decomposed into exponential components with characteristic decay times τ_i. The light sum (integral intensity) of each component was calculated as $S_i = A_{0i}\tau_i$, where A_{0i} is the corresponding initial amplitude. Temperature dependences or spectra of S_i and τ_i were analysed.

3. Results and discussion

It has been shown that Bi^{3+} centres possess an absorption band peaking at $4.4\,eV$ in the transparency region of $CaWO_4$ [1]. Optical excitation in this band at $4.2\,K$ produces an emission band at $2.75\,eV$ that is spectrally close to the main $2.88\,eV$ emission of the crystal. To verify the suggestion that the new emission band originates from the WO_4 oxyanionic complexes perturbed by Bi^{3+} ions [1], we compared the decay kinetics of the emission near $2.8\,eV$ of a $CaWO_4$:Bi crystal at three excitation energies: within the fundamental absorption region at $5.5\,eV$, slightly above the fundamental absorption edge at $5\,eV$ and in the Bi^{3+} absorption band at $4.4\,eV$. The decay curves measured at the specified excitation energies at $4.2\,K$ and the results of their decomposition into single exponential components are shown in Fig. 1. From excitation at $5.5\,eV$, we find the value of the decay time (τ_1) of the $2.8\,eV$ emission of $CaWO_4$:Bi to be equal to $360\,\mu s$ (curve 1,1′) and it coincides with that of the main emission in pure $CaWO_4$. At the excitation at $5.0\,eV$, the $360\,\mu s$ component (we label it C_1) is observed along with a shorter one (C_2) with the decay time $\tau_2 = 74\,\mu s$ (curves 2, 2′, 2″). At the excitation in the Bi^{3+} absorption band the same C_2 decay component is observed, whereas it is preceded by a $9\,\mu s$ rise in the decay curve (curve 3, 3″). The spectrum of the

light sum of the rise component coincides with that of the C_2 component.

As the temperature rises the decay time τ_1 sharply shortens to about $25\,\mu s$ at $60\,K$ (Fig. 2, curve 1), while the light sum of this component remains nearly constant. Starting from $60\,K$ there is a plateau in the temperature dependence of τ_1,
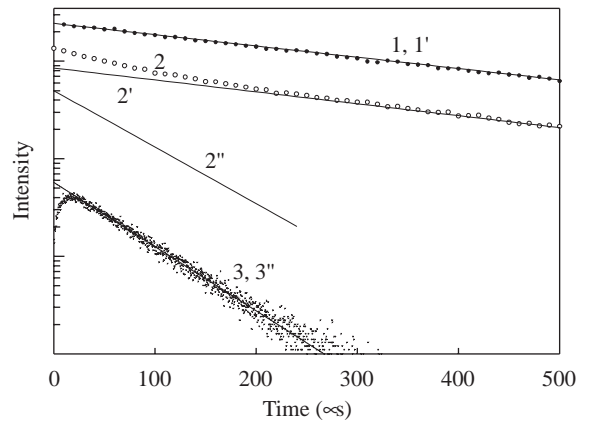

Fig. 1. Decay curves of the $2.88\,eV$ emission of $CaWO_4$:Bi measured at $T = 4.2\,K$ for excitation energies $E_{exc.} = 5.5\,eV$ (1), $E_{exc.} = 5.0\,eV$ (2), $E_{exc.} = 4.4\,eV$ (3). The solid lines 1′, 2′, 2″ and 3″ represent the C_1 (1′, 2′) and C_2 (2″, 3″) decay components calculated using parameters obtained from decomposition of the corresponding decay curves into single exponential components.
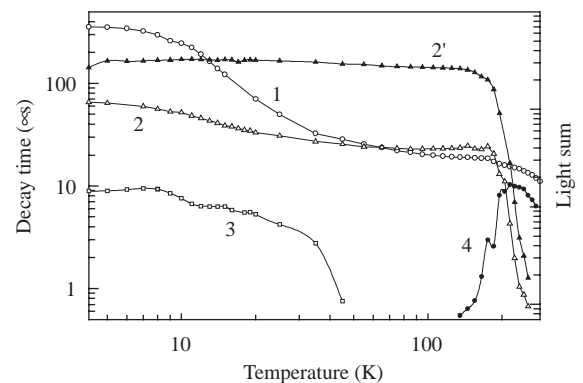

Fig. 2. Temperature dependences of the decay time (1, 2) and the light sum (2′) of the C_1 (1) and C_2 (2, 2′) components and of the rise time (3) of the $2.8\,eV$ emission of $CaWO_4$:Bi for the excitation energies 5.0 (1) and $4.4\,eV$ (2, 2′, 3). Curve 4 gives the temperature dependence of the background under the decay curve at $4.4\,eV$ excitation (see the text for details).