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Thermally and optically stimulated processes in X-irradiated scheelite type crystals

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Résumé. — Des centres électrons et trous peuvent être produits dans les tungstates et molybdates ayant une structure scheelite par l'irradiation X à la température de l'azote liquide. Plusieurs de ces centres ont été étudiés au moyen de la méthode d'électron paramagnétique de résonance (EPR). Nous attribuons la décroissance thermique et le blanchiment optique aux pics de thermoluminescence et de conductivité stimulée thermiquement ou optiquement ainsi qu'aux changements caractéristiques de la bande d'absorption. Pour le cas du CaWO_4 dopé avec du plomb, plusieurs processus des centres et des transferts sont discutés. L'information en détail sur la structure électronique peut être déduite de l'analyse EPR, de la polarisation, de la composition spectrale de thermoluminescence, de l'absorption optique ainsi que de la réponse spectrale de conductivité et de la thermoluminescence réexcitée.

Abstract. — In tungstate and molybdate crystals having scheelite structure various (intrinsic and extrinsic) hole and electron centres are created by X-irradiation at liquid nitrogen temperature. Several of these centres have been thoroughly investigated by electron paramagnetic resonance (EPR) measurements. Their thermal decay and optical bleaching, resp., can be related to glow peaks of thermoluminescence and thermally resp. optically stimulated conductivity as well as characteristic changes in optical absorption. For the case of CaWO_4 doped with lead some of these centres and typical transport processes are discussed. From analysis of EPR data, polarization and spectral composition of thermoluminescence, optical absorption, spectral response of optically stimulated conductivity and re-excited thermoluminescence detailed information about electronic structure can be obtained.

1. Introduction. — Scheelite type crystals such as CaWO_4 have a tetragonal structure [1] (space group C_{4h}^6). Among the about 50 compounds crystallizing in this structure there are some tungstates and molybdates which have found attention as luminescent materials. They are ionic systems $A^{2+}B^{2-}$ with cations $A = \text{Ca, Sr, Ba, Pb, (Cd), and (Eu)}$. The tungstate or molybdate anions are mainly covalent bonded, nearly tetrahedral oxocomplexes. Since there are significant differences if the electronic structure of the free cation deviates from the rare gas configuration properties discussed in the following should be generalized only with respect to earth-alkaline tungstates and molybdates with scheelite structure.

2. Experimental results and discussion. — Among thermally stimulated processes observed in substances such as CaWO_4 occurrence of thermoluminescence (TL) after excitation with energetic radiation ($\lambda < 150 \text{ nm}$) at low temperatures has been known for a long time [2]. As an example in figure 1 the TL glow curve of CaWO_4 nominally doped with 10^{-4} Pb is shown. From glow measurements on various CaWO_4 crystals three major glow maxima are found to appear near $T = 160 \text{ K}$, 220 K , and 300 K [3], but their intensities and spectral composition vary

Fig. 1. — TL glow curve of a $\text{CaWO}_4 : 10^{-4} \text{ Pb}$ crystal X-irradiated at $T \approx 90 \text{ K}$ (dose $\approx 10\,000 \text{ R}$).

strongly from sample to sample. So for an analysis of the recombination processes one needs further experimental data.

As a first result one finds from electrical glow measurements three peaks of thermally stimulated current correlated to the respective TL peaks. Beyond that the EPR spectrum of the sample is altered by the X-irradiation, and one gets detailed informations

from the changes in the concentration of paramagnetic centres during the TL emission. In the case of $\text{CaWO}_4 : 10^{-4} \text{ Pb}$ (Fig. 2) one finds a certain amount

Fig. 2. — Temperature dependence of radiation-induced paramagnetic centres in $\text{CaWO}_4 : 10^{-4} \text{ Pb}$.

of Nd^{3+} ions to be present in the crystal as an unintended dopant. Their concentration is strongly reduced by X-irradiation at low temperatures due to trapping of an electron near the rare earth site. In addition electron centres $(\text{MoO}_4)^{3-}$ and hole centres $(\text{WO}_4)^{2-}$ and Pb^{3+} are created in this sample [4]. After heating the crystal to 185 K, the intrinsic hole centres $(\text{WO}_4)^{2-}$ have vanished, the concentration of $(\text{MoO}_4)^{3-}$ centres is strongly reduced, the concentration of Pb^{3+} hole centres strongly enhanced. Within the second glow peak near 220 K we obviously have a thermal activation of electrons trapped at the rare earth sites; these electrons are partially retrapped at Mo impurities. During the third glow peak at about room temperature a thermal bleaching of the remaining electron and hole centres occurs.

These results may be illustrated in a very simplified energy band scheme (Fig. 3), even though a localized description seems to be more adequate to these crystals (since for instance no photoconductivity has been found until now). In this picture we have a *valence* and a *conduction* band both formed by molecular states of the oxocomplexes, and a gap of about 6 eV. Near the conduction band the electron centres, near the valence band the $(\text{WO}_4)^{2-}$ and the Pb^{3+} hole

Fig. 3. — Simplified energy level scheme for the recombination processes.

centres are located. The latter are more correct seen as $[\text{Pb}^{3+}(\text{WO}_4)_4^{8-}]$ complexes since they show a pronounced superhyperfine interaction with four neighbouring tungstate tetrahedra [5]. The intrinsic hole centres [6, 7, 8] are to some extent similar to V_k centres in alkali halides. Since they exhibit in their EPR line width and hyperfine splitting marked motional effects already at low temperatures we assume these holes to move through the crystal during the first glow peak, most probably by a polaronic hopping process [9]. They are then either captured again by Pb^{2+} hole traps, or recombine at a $(\text{MoO}_4)^{3-}$ centre under emission of green light ($\lambda_{\text{max}} \approx 540 \text{ nm}$). Whereas the intrinsic hole centres and their participation in the TL process are found to be a characteristic feature of the scheelites in question [10], there are a lot of different electron centres in other samples [11]. Some of them are indicated in the insert. This variety of similar electron centres seems to be one reason for the differences in spectral composition of the first glow peak. Considering the large Stokes shift in the luminescence of these materials [12], we expect remarkable relaxation effects in the thermoluminescence process too.

For the $\text{CaWO}_4 : 10^{-4} \text{ Pb}$ sample we are discussing here, the EPR results indicate $(\text{MoO}_4)^{3-}$ to be the recombination centre. Further arguments for this assumption are the green emission and its high degree of polarization of about 0.48, both results also known from pure CaMoO_4 crystals [13]. The importance of Pb for the green emission discussed in the literature [14] can be excluded by comparison with another sample nominally doped with 10^{-3} Pb . Here the glow emission at 160 K is in the blue region ($\lambda_{\text{max}} \approx 460 \text{ nm}$) although the same conversion of $(\text{WO}_4)^{2-}$ into Pb^{3+} occurs. In that sample, however, electrons trapped near a $(\text{WO}_4)^{2-}$ complex are mainly involved in the recombination process.

At higher temperatures trapped electrons become mobile. Since there is probably a hole mobility too, determination of nature and site of recombination is difficult.

The influence of the lead dopant becomes evident in the optical absorption of the crystal. In figure 4 the results after irradiation respectively partial annealing are shown. One finds two absorption bands at about 3.4 and 4.15 eV following the change in Pb^{3+} concentration measured by EPR. Although a definitive assignment of these absorptions is difficult due to others being superposed they are at least partially caused by charge-transfer transitions in the $\text{Pb}(\text{WO}_4)_4^{5-}$ complexes, similar as in $\text{KCl} : \text{Pb}$ [15]. This can be seen from figure 5. After annealing the first glow peak and the $(\text{WO}_4)^{2-}$ hole centres can be re-excited by light. The spectral response of this process as well as the spectral response of the observed optically stimulated conductivity and the bleaching rate of Pb^{3+} centres are similar to the observed absorption. They can be explained by a transition of the hole located mainly

Fig. 4. — Radiation induced polarized optical absorption of $\text{CaWO}_4 : 10^{-4} \text{ Pb}$ at $T = 100 \text{ K}$. a) After X-irradiation at $T = 100 \text{ K}$. b) After heating up to 185 K . $\alpha_b - \alpha_a$: Change in absorption accompanying first TL glow peak.

in the Pb^{3+} -6s state to another state of the $\text{Pb}(\text{WO}_4)_4^{5-}$ complex located more at the oxocomplexes. From there the hole may be transferred by radiationless processes to neighbouring $(\text{WO}_4)^{2-}$ tetrahedra where it can be stabilized again.

3. Conclusion. — Although the problems concerning thermally stimulated processes in earth-alkali scheelites are not understood in all details until now some general features become more and more evident. This is particularly true for the importance of the intrinsic hole centres and their motional effects to these processes. In addition it seems to be obvious that any reliable interpretation of experimental results obtained from these rather complex ternary com-

Fig. 5. — Spectral response of re-excited thermoluminescence and bleaching constant of Pb^{3+} centres (reciprocal time constant of exponential decay).

pounds is possible only with detailed knowledge about the defect structure of the sample investigated.

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