Identification of Thermoluminescence Traps in CaWO₄ and BaWO₄ by EPR Measurements

A. Hofstaetter, J. Planz *, and A. Scharmann
I. Physikalisches Institut der Universität Giessen

(Z. Naturforsch. 32 a, 957 — 963 [1977]; received June 20, 1977)

In calcium- and barium tungstate crystals both containing molybdenum and phosphorus, paramagnetic centres are created by X-ray irradiation at room temperature. Two kinds of centres are identified by EPR measurements; an electron trapped at a molybdate complex and a hole trapped at a phosphate complex. The EPR parameters of the hole centres are temperature dependent indicating motional effects. A connection of these two traps with the observed thermoluminescence is found for both crystals.

I. Introduction

The thermoluminescence (TLu) of calcium tungstate (CaWO₄) and other scheelite type crystals has been the subject of many investigations for the past twenty years¹−⁸. In general after irradiation with X-rays at liquid nitrogen temperature one finds three prominent peaks in the glow curve accompanied by similar maxima of the thermally stimulated conductivity. Various attempts have been made to determine the influence of impurities on the thermoluminescence of the scheelites, but no definite identification of trapping centres has been possible from Tlu measurements alone. This situation has been much improved during the last years by combining electron paramagnetic resonance (EPR) and Tlu measurements⁹−¹³. So for instance Gurvich et al.⁸ concluded from Tlu investigations that lead ions in CaWO₄ produce electron traps, whereas combined EPR and Tlu measurements have unambiguously shown that lead acts as a hole trap which is involved in a glow peak at about room temperatureⁱ⁴.

Such combined experiments established especially the importance of an intrinsic hole centre of the form (WO₄)₂⁻ for the Tlu of these crystals, but provided also a lot of information about the influence of various dopants. In this paper we wish to report on X-ray induced paramagnetic centres in CaWO₄ and BaWO₄ which are related to the high temperature glow peak (at about 340 K) of these crystals.

* Part of thesis, Giessen 1977 (D 26).
Reprint requests to Prof. Dr. A. Scharmann, I. Physikalisches Institut der Universität, Heinrich-Buff-Ring 16, D-6300 Giessen.

II. Experimental

Both CaWO₄ and BaWO₄ crystallize in the scheelite structure (tetragonal system, space group C₄ᵥ) with four molecules in the unit cell having the dimensions a = b = 5.24 Å, c = 11.38 Å for CaWO₄¹⁴,¹⁵, and a = b = 5.60 Å, c = 12.69 Å for BaWO₄¹⁶. Each molecule consists of a Ca²⁺- or Ba²⁺-ion and a slightly distorted WO₄²⁻-tetrahedron.
The single crystals we used in this investigation were grown in our institute by the Czochralski method. The calcium tungstate crystal was made from nominally pure CaWO₄ powder (obtained from Cerac pure Inc.), the barium tungstate made from BaCO₃ andWO₃-powder (Fa. Merck) was doped with 10⁻⁴ P and 10⁻⁴ Mo. The specimen were oriented by X-ray Laue patterns and cut in pieces of about 2 × 2 × 6 mm³.

The EPR measurements were performed with an AEG 20X-T spectrometer using a bath cryostat in the temperature range from 1.8 to 4.2 K, a variable gas flow from 80 to 380 K. TLu was investigated in a self-constructed cryostat using a copper block as cooling resp. heating device and a RCA 6217 photomultiplier for registration of the emitted light. X-rays of 50 to 150 keV were used for excitation.

III. Experimental Results

1) Thermoluminescence (TLu)

After X-ray excitation at a temperature of about 95 K CaWO₄ shows a thermoluminescence which is given in Figure 2 a. It is characterized by three glow maxima at 170 K, 266 K, and 322 K. In this investigation we were especially interested in the third glow peak above room temperature. As is shown in Figure 2 b, this part of the TLu can also be excited by X-ray irradiation at room temperature. By this method it can easily be separated.

The BaWO₄ crystal exhibits a similar glow curve having three main peaks with maxima at 115 K, 180 K, and 360 K (Figure 3). Again it is possible to create only the third glow peak by irradiation at room temperature.

2) Electron paramagnetic resonance (EPR)

Since we were mainly interested in the nature of this third peak all the EPR results reported here refer to crystals which have been irradiated at room temperature. When investigating such a specimen at 4.2 K one finds two groups of EPR signals, from now on called α and β.

2 a) Group α consists of one strong central line and two times six partially overlapping hyperfine components. From this hyperfine splitting and the...
observed intensity ratio it is readily identified as due to a molybdenum impurity, since the two isotopes $^{95}\text{Mo}$ and $^{97}\text{Mo}$ both have a nuclear spin $I = \frac{5}{2}$, slightly different hyperfine constants and a natural abundance of 15.8% resp. 9.6%. The spectrum is characterized by axially symmetric $g$- and hyperfine tensors, the symmetry axis coinciding with the crystallographic $c$-axis. This corresponds to the assumption that Mo due to the similar structure of $\text{CaW}_4\text{O}_4$ and $\text{CaMo}_4\text{O}_4$ resp. $\text{BaW}_4\text{O}_4$ and $\text{BaMo}_4\text{O}_4$ will occupy the tungsten site having symmetry $S_4$. The measured $g$-values

$$g_{||} = 1.987, \quad g_\perp = 1.887$$

for $\text{CaW}_4\text{O}_4$ and

$$g_{||} = 1.976, \quad g_\perp = 1.881$$

for $\text{BaW}_4\text{O}_4$.

are in good agreement with results of Azarbayejani and Merlo and Soltsev et al. To explain the observed negative $g$-shift one has to start with Mo replacing W to form $(\text{MoO}_4)^{2-}$ tetrahedra which are slightly compressed along the $c$-axis. Within these tetrahedra the highest orbital occupied is a $t_1$ state followed by an $e$- and a $t_2$-orbital. The distorted tetrahedra have the reduced symmetry $D_{2d}$; by that one gets a splitting $e \rightarrow a_1, b_1$ and $t_2 \rightarrow b_2, e$. An additional electron, forming a $(\text{MoO}_4)^{3-}$ complex, will occupy the $a_1$ state and shows a negative shift for $g_\perp$ due to spin-orbit-coupling with the $e$-orbital lying some eV above. In this model one would expect $g_{||} = g_e = 2.0023$, whereas the experiment yields a slight negative shift for $g_{||}$ too. The difference should be due to admixtures of other states of the crystal via binding effects. This explanation is supported by the fact that the same $(\text{MoO}_4)^{3-}$ centre in $\text{PbW}_4\text{O}_4$ shows a significantly larger $g$-shift ($g_{||} = 1.898, \quad g_\perp = 1.789$) obviously caused by the “lone pair” $s$-electrons of lead.

Summarizing, the group $\alpha$ spectrum can be explained by an additional electron ionized by X-raying and trapped at a molybdenum impurity to form a $(\text{MoO}_4)^{3-}$ complex. The temperature dependence of this spectrum is different in $\text{CaW}_4\text{O}_4$ and $\text{BaW}_4\text{O}_4$ due to different spin-lattice relaxation. While in $\text{CaW}_4\text{O}_4$ at 80 K the lines are already too broad to be detected, one can observe them up to about 100 K in $\text{BaW}_4\text{O}_4$.

2 b) The group $\beta$ spectrum is a little bit more complicated since it strongly depends on temperature and orientation. To start with the simplest case we first discuss the results obtained at temperatures between 80 K and 120 K (above this temperature the resonance lines become too broad to be detected). In this temperature range the group $\beta$ spectrum consists of two lines separated by about 2.7 mT (Figure 4). It originates from a $S = 1/2$ system interacting with a 100% abundant spin $I = 1/2$. The analysis of the angular dependence (Fig. 5) yields axial $g$- and hyperfine tensors with

$$g_\parallel = 2.0109, \quad g_\perp = 2.0138, \quad A_{\parallel} = 25.63 \cdot 10^{-4} \text{ cm}^{-1}, \quad A_{\perp} = 26.05 \cdot 10^{-4} \text{ cm}^{-1}$$

for the $\text{CaW}_4\text{O}_4$ crystal. The symmetry axes of both tensors coincide with the crystallographic $c$-axis.

Since these results are very close to those obtained by Edwards et al. for phosphorus incorporated in
CaWO₄ one tends to assign the group β spectrum to a (PO₄)²⁻ centre too, which is formed by the X-ray irradiation from an impurity complex (PO₄)³⁻. To check this assignment we doped the BaWO₄ specimen with Ba₃(PO₄)₂. This leads to the same type of radiation induced spectrum with the parameters

\[ g_\parallel = 2.0125, \ g_\perp = 2.0141 \]

and

\[ A_\parallel = 26.4 \times 10^{-4} \text{ cm}^{-1}, \ A_\perp = 26.8 \times 10^{-4} \text{ cm}^{-1}. \]

Lowering the temperature to 4.2 K results in a further splitting of the group β spectrum so that for an arbitrary direction of the magnetic field \( B \) with respect to the crystallographic axes one gets two groups of four lines each (Figure 6). These collapses into two times two lines for \( B \) lying in the ab-plane of the crystal and into two lines for \( B \) parallel to the c-axis. The angular dependence of the \( g \)-factor of the (PO₄)²⁻ centre at 4.2 K shown in Fig. 7 is rather similar to that of the intrinsic hole centres in CaWO₄. So at liquid helium temperature we again assume a hole centre located at one of the oxygen ligands of a PO₄ tetrahedron formed by removing an electron from the highest occupied orbital of the PO₄ complex. This is again a \( t₁ \) state (resp. \( a₂ \) state in \( D_{3d} \) symmetry) made up only from oxygen \( p_z \) orbitals. The splitting into four lines is then due to the four magnetically distinct sites such a hole centre can occupy at one of the four ligands. These four ligand sites and thereby the corresponding \( g \)- and \( A \)-tensors are related to each other by fourfold rotations around the c-axis. The numerical results for one of those \( g \)- and \( A \)-tensors are given in Table 1, \( \theta \) and \( \varphi \) being the angles between their principal directions and the c- resp. a-axis of the crystal.

Since the intrinsic hole centres in CaWO₄ interact with two tungsten nuclei we looked for a hyperfine interaction of the (PO₄)²⁻ hole centre with a neighbour W¹⁸³ nucleus having \( I = 1/2 \). In fact such a hyperfine structure can be partially resolved by lowering the temperature to about 1.8 K. This is shown in Fig. 8 for the low field part of the group β spectrum.

The different behaviour of the (PO₄)²⁻ resonances at 4.2 K and 80 K is easily understood as a motional effect. Contrary to the intrinsic hole centre where one has to assume an increasing hopping of the hole between two neighbouring WO₄ tetrahedra the hole trapped at the impurity complex PO₄ obviously is more located and performs some kind of rotation around the four ligand sites at higher temperatures. This leads to a motional averaging giving the observed \( g \)- and \( A \)-values at 85 K.
IV. Correlations Between EPR and TLu

The TLu investigations have shown that X-ray excitation at room temperature in CaWO₄ resp. BaWO₄ containing the impurities molybdenum and phosphorus leads to the occurrence of one thermoluminescence glow peak. At the same time one finds in the EPR spectrum one radiation induced paramagnetic centre formed by electrons trapped at a MoO₄ complex and another one formed by holes trapped at a PO₄ complex. To answer the question if these two traps are connected with the observed TLu peak we compared their saturation behaviour relative to the irradiation dose. This is shown for the TLu intensity in Figure 9. A comparison of the TLu intensity and the concentration of (PO₄)²⁻ centres as determined from the EPR spectrum of a CaWO₄ crystal irradiated in the same manner reveals the linear correlation illustrated in Figure 10. With the BaWO₄ crystal the situation is a little bit more complicated since there after the first irradiation a

<table>
<thead>
<tr>
<th>PO₄²⁻</th>
<th>g₁</th>
<th>g₂</th>
<th>g₃</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaWO₄</td>
<td>85 K</td>
<td>2.0139</td>
<td>2.0112</td>
<td>2.0130</td>
</tr>
<tr>
<td>4.2 K</td>
<td>2.0124</td>
<td>2.0064</td>
<td>2.0212</td>
<td>2.0133</td>
</tr>
<tr>
<td>4.2°</td>
<td>51.4°</td>
<td>72.6°</td>
<td>41.9°</td>
<td>179.3°</td>
</tr>
<tr>
<td>62° -27.8°</td>
<td>73.4°</td>
<td>179.3°</td>
<td>25.9</td>
<td></td>
</tr>
<tr>
<td>128.9°</td>
<td>2.0064</td>
<td>2.0133</td>
<td>2.0135</td>
<td></td>
</tr>
<tr>
<td>BaWO₄</td>
<td>85 K</td>
<td>2.0141</td>
<td>2.0125</td>
<td>2.0136</td>
</tr>
<tr>
<td>4.2 K</td>
<td>2.0131</td>
<td>2.0085</td>
<td>2.0188</td>
<td>2.0135</td>
</tr>
<tr>
<td>4.2°</td>
<td>106.1°</td>
<td>140°</td>
<td>54.6°</td>
<td>64.0°</td>
</tr>
<tr>
<td>106.1°</td>
<td>54.6°</td>
<td>64.0°</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>62° -26.6°</td>
<td>38.9°</td>
<td>130.1°</td>
<td>25.9</td>
<td></td>
</tr>
<tr>
<td>62° -27.8°</td>
<td>73.4°</td>
<td>179.3°</td>
<td>25.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. g-values and hyperfine values A for (PO₄)²⁻ in CaWO₄ and BaWO₄.

Fig. 9. CaWO₄: Mo, P: Dependence of the intensity of the TLu glow peak at 322 K upon X-ray irradiation time.

Fig. 10. CaWO₄: Mo, P: Correlation between the TLu intensity shown in Fig. 9 and the concentration of (PO₄)²⁻ centres at increasing X-ray irradiation dose.
constant amount of \((PO_4)^{2-}\) centres remains which cannot be removed even by heating to about 450 K. This rest amount stabilizes at about 40\% of the saturation concentration (Figure 11). Subtracting this constant contribution, the linear correlation between TLu intensity and the concentration of the \((MoO_4)^{3-}\), as well as the corrected concentration of the \((PO_4)^{2-}\) centres, again is satisfied as can be seen from Figure 12.

### V. Conclusions

From all the experimental results given one can deduce that phosphorus and molybdenum impurities play an active part in the thermoluminescence process of X-rayed CaWO_4 and BaWO_4 acting as rather deep hole resp. electron traps. The \((PO_4)^{2-}\) hole centres thereby are in line with a lot of other centres (e.g. \(NbO_4^{2-}, VO_4^{2-}\)) analogous to the intrinsic hole centre \((WO_4)_2^{3-}\). \((MoO_4)^{3-}\) seems to be a very characteristic electron trap in the tungstate scheelites since MoO_4 very easily replaces a tungsten complex. As long as the molybdenum concentration is not too high this trap in all cases we know causes a TLu glow peak at about room temperature (for instance the counterpart for the \(Pb^{3+}\) hole centre in CaWO_4 described by us in an earlier paper\(^1\) is also a MoO_4^{3-} electron trap). At higher Mo concentration (>1\%) the maximum temperature of the glow peak due to \((MoO_4)^{3-}\) decreases\(^2\). Such effects complicate the assignment of TLu glow peaks to certain traps but little by little a systematic description seems possible. To that end this investigation was to give a further contribution.

### Acknowledgements

We wish to thank Mr. R. Biederbick, Mr. B. Cord, and Mr. B. Vitt for their helpful assistance and many fruitful discussions and Mr. R. Oeder and Dr. D. Schwabe for growing the crystals. We are also indebted to the Deutsche Forschungsgemeinschaft for financial support.
3. V. V. Levshin, V. B. Guman, and E. N. Karzhivina, Opt. Spectr. VI, 234 [1959].
22. R. Biederbick, G. Born, A. Hofstaetter, and A. Scharmann, phys. stat. sol. (b) 69, 55 [1975].