EFFECTS OF STRUCTURE MICRODEFECTS ON SCINTILLATION AND PHOTOSTIMULATED PROPERTIES OF CdWO₄ CRYSTALS

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ABSTRACT

CdWO₄(CWO) scintillator single crystals find broad applications as detectors of ionizing radiation in tomographic and introspective devices. Scintillation characteristics of the crystals are strongly dependent upon growth conditions. In this paper the nature of the defects is studied, related to deviations from stoichiometry and presence of admixtures, for the crystals grow by the Chochralski method. Negative effects of admixtures (Fe, Cu, Bi, Ga joins) on the light yield and afterglow in CWO crystals were established. Photosensitivity of CWO crystals under UV-radiation was noted in the region of the fundamental absorption edge, causing the induced absorption ($\alpha$ up to 1.5 cm$^{-1}$) and a decrease of the light yield (to 30%). The studies have shown that the induced absorption depends upon both admixtures and non-stoichiometry. Basing on the results, preparation conditions were optimized for large-sized (55 x 250 mm) CWO crystals, allowing to obtain scintillation characteristics meeting the requirements for their use in radiation detectors for tomography and introscopy.

Keywords: cadmiun tungstate, scintillator, stoichiometry, transmission spectra, afterglow, light yield, induced absorption, photochromic effect.

2. INTRODUCTION

Scintillation single crystals of cadmium tungstate CdWO₄ (CWO) are widely used as detectors of ionizing radiation in tomographic and introspective devices [1,2]. This is due to their unique complex of properties (light yield 30-35% with respect to NaI(Tl), absorption at the luminescence maximum < 0.01 cm$^{-1}$, radiation length 1.06 cm, afterglow less than 0.05% after 20 mks). However, scintillation characteristics of these crystals are largely dependent upon condition of their preparation. During the solid-phase synthesis and the crystal growth oxide evaporation may take place, leading to violations of stoichiometry [3]. Besides this, the quality of the crystals grown is affected by possible impurities. Another point of importance is related to the coloring centres in CWO crystals, which are formed both during the growth process and under influence of light and radiation factors. In this paper we studied effects of some uncontrolled impurities and deviations from stoichiometry upon scintillation and optical characteristics of the crystals, and the character of the induced absorption resulting from photostimulated processes in them.

3. EXPERIMENTLE

For the studies four CWO crystals were chosen, 50 mm in diameter and 20 mm in length, which were grown by the Czochralski method in a "Kristall-3M" installation using platinum crucibles. The samples obtained from these crystals were cleaved plates 10 mm thick and differed in microimpurities content and stoichiometric composition.

4. RESULTS AND DISCUSSIONS

Results of chemical analysis of these samples are presented in Table 1, together with their visual characteristic.
Table 1

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Stoichiometric composition, %*</th>
<th>Content of microimpurities, 10^-2 %</th>
<th>Coloring</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CdO</td>
<td>WO_3</td>
<td>Mn</td>
</tr>
<tr>
<td>BK-1</td>
<td>35.70</td>
<td>64.30</td>
<td>2</td>
</tr>
<tr>
<td>BK-2</td>
<td>35.78</td>
<td>64.21</td>
<td>2</td>
</tr>
<tr>
<td>BK-3</td>
<td>35.84</td>
<td>64.15</td>
<td>2</td>
</tr>
<tr>
<td>BK-4</td>
<td>35.79</td>
<td>64.20</td>
<td>2</td>
</tr>
</tbody>
</table>

*theoretical stoichiometric composition: CdO — 35.65% WO_3 — 64.35%

Radioluminescence spectra of all the samples studied were identical and had a maximum of the luminescence band around 480 nm. Small differences in the short-wave part of the spectrum are presumably due to self-absorption of the intrinsic radiation in the crystal.

The light yield values were measured both by the current method (in relative units) with energy of X-ray radiation E = 100keV and by the amplitude method (in relation to NaI(Tl)) under irradiation by ^{137}Cs source. The results obtained are presented in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Crystal</th>
<th>C, rel. units</th>
<th>C, resp. to NaI(Tl)</th>
<th>Afterglow, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 ms</td>
</tr>
<tr>
<td>BK-1</td>
<td>0.95</td>
<td>0.34</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>BK-2</td>
<td>0.74</td>
<td>0.29</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>BK-3</td>
<td>0.63</td>
<td>0.17</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>BK-4</td>
<td>0.65</td>
<td>0.23</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Optical transmission spectra for the 300-700 nm region are presented in Fig.1. In the short-wave region two absorption bands were observed: max = 360 nm (BK-2 and BK-4) and =390 nm (BK-3 and BK-4). In the long-wave region there were no clearly observed absorption bands.

Fig.1. Transmission spectra of CWO samples: 1- BK-1, 2- BK-2, 3- BK-3, 4- BK-4. Sample thickness 0.1 cm

Fig.2. Differential transmission spectra between excited and initial state of CWO samples: 1- BK-1, 2- BK-2, 3- BK-3, 4- BK-4. Sample thickness 1 cm

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All the CWO samples studied were characterized by the additional induced absorption in the long-wave region, including the region of intrinsic absorption (400-600 nm) which appeared under the influence of UV-radiation in the 320-380 nm region (photochromic effect). The photochromic effect is characterized by a rapid increase of the induced absorption with subsequent saturation, the level of which does not depend upon the intensity of UV-radiation and can reach values of about 1.5 cm$^2$. Fig.2 shows spectral dependence of the induced absorption under 365 nm UV irradiation. The spectra display a broad band with maximum at 490-500 nm for BK-2, BK-3, BK-4. For the BK-1 sample a more distinguished band of the intrinsic absorption is noted at 460 nm. The light yield with is 20% lower with respect to the initial value for all the samples.

For the BK-1 sample kinetic dependence of the intrinsic absorption change at different irradiation rates in the 0.01 - 0.2 mW range is presented in Fig.3. The threshold value of the irradiation rate determining the emergence of the photochromic effect has not been noted.

![Fig.3. Change of optical transmission with time for different excitation rates for the BK-1 sample: 1-0.2 mW, 2-0.1 mW, 3-0.05 mW, 4-0.01 mW. Wavelength: 450 nm.](attachment:image.png)

The value of the photochromic effect is essentially dependent upon the oxygen content in the growth medium. The annealing of the BK-1 sample in the oxygen-poor medium for 6 hours at T=600 C lead to the complete disappearance of reaction to UV irradiation. However, the light yield became two times lower than the initial value, and light-blue coloration of the sample appeared.

Basing on the results obtained, several conclusions could be made on the influence of deviations from stoichiometry and doping ions on scintillation characteristics of CWO crystals:

a) luminescence spectrum of CWO crystals is not changed within the considered limits of deviations from stoichiometry and dopant content;

b) the afterglow (> 0.05%) observed in the BK-2 crystal is related to higher Bi or Ga content (> 10 -4%), which also gives rise to the 350 nm absorption band in the transmission spectra;

c) the light yield value depends upon deviations from stoichiometry, with higher content of excess Cd causing smaller relative effect. The 390 nm absorption band is presumably related to deviations of this kind;

d) defects related to the oxygen content in the anion sublattice of the crystal do significantly affect the light yield values.

As for the photochromic effect in CWO crystals, its nature has not yet been understood in details. However, one can assume that the main cause of this effect are colouring centres which are similar to the F-centres in the alkali halide...
crystals and are related to intrinsic defects in the anionic sublattice of the crystal. This is confirmed by the fact that the intrinsic absorption bands of CWO crystals and F-centres of alkali halide crystals are situated rather close to each other, as well as by a similar character of relaxation caused by irradiation of the crystal by light in the wavelength range of the intrinsic absorption. The mechanism of photochemical formation of colour for calcium, strontium and barium tungstates related in [4] to the isomorphic replacement of the crystal lattice ions by bismuth seems not to be probable, because, as we have shown, Bi content in the CWO crystal does not significantly affect the intrinsic absorption.

Basing on the results obtained, conditions have been optimized for preparation of large-size (55 x 250 mm) CWO crystals which allowed to use such crystals in ionizing radiation detectors for tomography and introscopy.

REFERENCES