Optical Materials 35 (2013) 2465–2472

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Trap centers in molybdates

D.A. Spassky [a,b,*], V. Nagirnyi [a], V.V. Mikhailin [b], A.E. Savon [b], A.N. Belsky [c], V.V. Laguta [d], M. Buryi [d], E.N. Galashov [e], V.N. Shlegel [f], I.S. Voronina [g], B.I. Zadneprovski [h]

[a] Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia
[b] Skobeltsyn Institute of Nuclear Physics, M.V. Lomonosov Moscow State University, Moscow 119991, Russia
[c] Institute of Light and Matter, CNRS, University Lyon1, Villeurbanne 69622, France
[d] Institute of Physics AS CR, Cukrovarnicka 10, Prague 162 00, Czech Republic
[e] Novosibirsk State University, Novosibirsk 630090, Russia
[f] Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk 630090, Russia
[g] A.M. Prokhorov General Physics Institute of RAS, Vavilov str. 38, Moscow 119991, Russia
[h] Central Research and Development Institute of Chemistry and Mechanics, Moscow 115487, Russia

ARTICLE INFO

Article history:
Received 1 June 2013
Received in revised form 21 June 2013
Accepted 30 June 2013
Available online 20 July 2013

Keywords:
Molybdate single crystals
Thermostimulated luminescence
Scintillating bolometers
Self-trapping of charge carriers

ABSTRACT

Charge carrier trapping centers have been studied in molybdates $CaMoO_4$, $SrMoO_4$ and $PbMoO_4$ with the scheelite crystal structure as well as in $ZnMoO_4$, which crystallize in a-$ZnMoO_4$ structural type. The trap parameters such as activation energies and frequency factors have been determined. It is shown for the first time that both electrons and holes are trapped by the elements of regular crystal structure in $ZnMoO_4$. The effect of the charge carrier trapping on luminescence properties is demonstrated. Potential influence of the traps on the scintillation process is discussed.

1. Introduction

The scintillation properties of crystals are commonly dependent on the presence of traps in the material. Intermediate localization of charge carriers at shallow traps may result in the appearance of slow components in scintillation decay curves while the suppression of light yield may be expected in case of deep traps when the energy of thermal vibrations is not sufficient for the release of the trapped charge carriers. Molybdate single crystals are perspective for the cryogenic scintillating bolometers that operate in ultra-low temperature conditions (tens of mK) [1]. In view of such application, a set of promising molybdate crystals including $CaMoO_4$ [2–5], $SrMoO_4$ [1], $PbMoO_4$ [1,6,7], Li_2MoO_4 [8,9], $Li_2Zn_2(MoO_4)_3$ [10] and $ZnMoO_4$ [11–13] have been recently studied. Special attention has been paid to the following two representatives of the molybdate family. Calcium molybdate is a well-studied compound for cryogenic detectors [2–5], which has already been chosen as a cryogenic scintillator for the AMoRE experiment [14]. Zinc molybdate is a new crystal and only recently it has been successfully grown in a bulk form using the conventional Czochralski technique [15,16] or the low temperature gradient Czochralski technique which allowed obtaining crystals with better optical quality [17,18]. $ZnMoO_4$ attracts enhanced attention also as a material for cryogenic experiments due to its high energy resolution and efficient α background rejection [11–13], however the light yield of this crystal is rather low. A measurement of the absolute value of a scintillation light yield at the operating temperatures of cryogenic scintillators is a complicated task. The value of energy yield was estimated at 1.1 keV/MeV only for $ZnMoO_4$ [13]. Taking into account the average energy of a single emission photon as ~2.0 eV [18] the light yield of $ZnMoO_4$ can be estimated to be 550 ph/MeV. The data on the light yield of molybdates are commonly presented with respect to the light yield of $CaWO_4$ at temperatures around 10 K. The light yield of $CaMoO_4$ is 95% of that in $CaWO_4$ [19] while it is only 34% in $PbMoO_4$ [6]. Taking into account the estimation of the absolute light yield of BGO as 23,700 ph/MeV which has been shown to be 150% of that in $CaWO_4$ at 6 K [19], one can conclude that the absolute value is about 15000 ph/MeV for $CaMoO_4$ and 5500 ph/MeV for $PbMoO_4$. Therefore, at cryogenic temperatures, the light yield of $ZnMoO_4$ is ~30 times lower than the light yield of $CaMoO_4$. Such low value of the light yield in $ZnMoO_4$ may be related to the strong decrease of luminescence intensity upon temperature decrease from 100 to 50 K, which has been observed under VUV [18,20] and X-ray [11] irradiation

* Corresponding author at: Institute of Physics, University of Tartu, 51014, Estonia.
E-mail address: deris2002@mail.ru (D.A. Spassky).

0925-3467/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2013.06.054

of the crystal in good correlation with the position of a strong peak of thermostimulated luminescence at ~70 K. Charge carrier trapping is a serious problem for cryogenic scintillators. Under the operating conditions, even shallow traps can have a strong impact on scintillation efficiency due to capturing separated charge carriers. Therefore, the study of the origin of traps in molybdates is of crucial importance for understanding their scintillation properties at low temperatures. By using the EPR and TSL techniques it has been shown for some molybdates that charge carriers are trapped by regular complexes [21–23]. Despite the quite low energy of the thermal release from intrinsic trap centers, the trapping itself will definitely worsen the scintillation properties at low temperatures. The influence may be expected even for the most perfect crystals with low content of uncontrollable impurities and crystal structure defects, which are commonly introduced during the crystal growth.

Here we discuss the origin of trap centers for the scheelite type crystals $CaMoO_4$, $SrMoO_4$, $PbMoO_4$ as well as for $ZnMoO_4$, which are considered for application as cryogenic scintillators. For the first time the origin of the traps is determined for $ZnMoO_4$ by using the EPR and TSL techniques. It is shown that the temperature dependence of the luminescence intensity under VUV and X-ray excitation is affected by the presence of traps. The influence of the traps on the scintillation process is discussed.

2. Experimental details

$CaMoO_4$, $SrMoO_4$ and $PbMoO_4$ single crystals were grown by the conventional Czochralski method in a Pt crucible in air. Samples of $ZnMoO_4$ were grown using low temperature gradient Czochralski technique that allows growing crystals with improved optical properties [17]. The concentrations of contaminating impurities were determined by atomic-emission spectral analysis. This method allows determining the presence and concentration of 72 different elements from Li to U. The atoms of Nb and Ta belong to the structural materials of the ion source used in the analysis and their concentration in the samples was not detected. The data on the impurities detected in the investigated samples is summarized in Table 1. The concentrations of other impurities were below 3 ppm. It follows from the table that the total concentration of impurities remained between 100 and 400 ppm. Tungsten impurity which is an attendant of Mo was detected in all the samples studied, whereas it was a dominating impurity in $PbMoO_4$ and $ZnMoO_4$.

X-ray excited luminescence, thermostimulated luminescence (TSL) curves and spectra were measured at the Laboratory PCML, Claude Bernard Lyon University. An X-ray source with a tungsten anode operating at $U = 30$ keV was used as an excitation source. Luminescence characteristics under excitation in UV and VUV spectral region have been measured at the SUPERLUMI station in the synchrotron radiation channel of the storage ring DORIS III (DESY, Hamburg) [24], and at the laboratory setup of the Institute of Physics, University of Tartu. All measurements have been carried out on the freshly cleaved vitreous surfaces of the samples. The EPR measurements for $ZnMoO_4$ were performed at 9.23 GHz with the standard 3 cm wavelength of the EPR spectrometer in the temperature range 10–290 K using an Oxford Instrument cryostat. The sample was directly irradiated in the spectrometer cavity by X-rays at temperature about 30 K.

Table 1
The concentration of contaminating impurities in the studied crystals according to the data of atomic-emission spectral analysis.

$CaMoO_4$	Ba (100 ppm), Sr (60 ppm), Na (30 ppm), Ag (10 ppm), W (10 ppm)
$SrMoO_4$	Si (70 ppm), Ca (20 ppm), Cl (15 ppm), W (10 ppm), Ba (10 ppm)
$PbMoO_4$	W (300 ppm), Ca (40 ppm), S (10 ppm), Bi (4 ppm), K (4 ppm)
$ZnMoO_4$	W (200 ppm), Si (40 ppm), Cd (4 ppm)

3. Experimental results

3.1. Characterization of traps in molybdates

The TSL curves and spectral composition of the TSL peaks of molybdates are presented in Figs. 1–4 for the temperature region 10–300 K. The calculated trap parameters and spectral positions of the emission bands in TSL peaks are summarized in Table 2. Almost all TSL peaks were fitted using the first order decay approximation supposing that the probability for a charge carrier released from traps to be captured by traps again is much lower than the probability of radiative recombination. In this case, we used the following fitting expression:

$$I_{lum}(t) = n(0)\omega_0 \exp\left(-\frac{E_A}{k_BT(t)} - \frac{\omega_0 k_B T^2(t)}{E_A T'(t)} e^{-E_A/k_BT(t)}\right) \quad (1)$$

where $n(0)$ is the concentration of filled traps just after the end of sample excitation (here it is in arbitrary units), E_A is activation energy of the trap, ω_0 is frequency factor of the trap, k_B is Boltzmann constant, T is the temperature and T' is heating rate [25].

However for a pronounced peak at 43 K in $PbMoO_4$ and for a peak at 166 K in $SrMoO_4$ the fitting with this formula gives unsatisfactory result (see the unsatisfactory approximation for 43 K peak in $PbMoO_4$ in Fig. 3a). The symmetric shape of these peaks without distinctive bends does not allow to suggest their complex structure and to perform fitting with several peaks in the first order decay

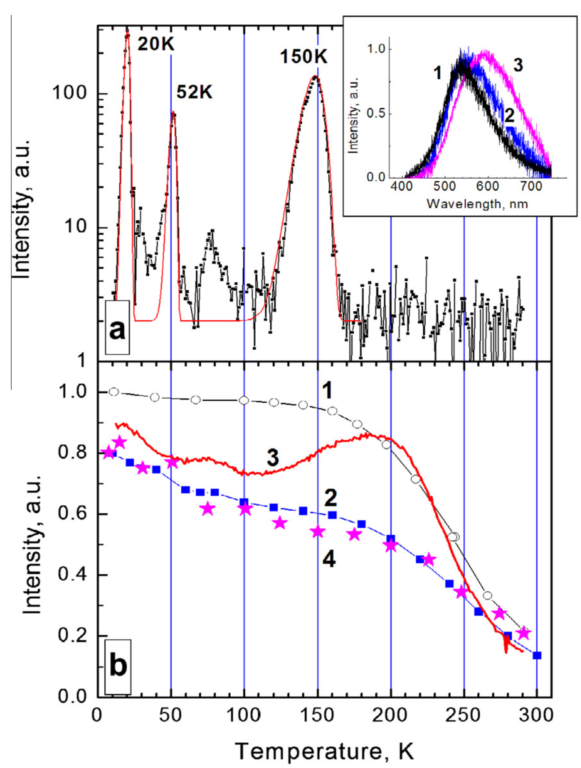

Fig. 1. (a) TSL curve of $CaMoO_4$. Thin red line represents the fitting of TSL curve with the trap parameters that are presented in Table 2. In the inset-emission under X-ray excitation and spectral composition of TSL recorded at $T = 10–30$ K (all-curve 1), $T = 40–55$ K (2) and $T = 120–160$ K (3) and (b) temperature dependence of the luminescence intensity measured at $E_{ex} = 4.1$ eV (1), $E_{ex} = 11$ eV (2), X-ray excitation (3) and of the scintillation output under excitation with α-particles (4) presented in [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)