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New cadmium and rare-earth metal molybdates with scheelite-type structure

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ABSTRACT

New cadmium and rare-earth metal molybdates with the formula $Cd_{0.25}RE_{0.50}MoO_4$ (RE = Pr, Nd, Sm–Dy) were synthesized by the solid-state reaction of $CdMoO_4$ with corresponding $RE_2(MoO_4)_3$. The obtained compounds crystallize in the scheelite-type structure. They were characterized here by XRD, DTA-TG, IR and EPR methods. The $Cd_{0.25}RE_{0.50}MoO_4$ compounds showed solubility in $CdMoO_4$ forming the $Cd_xRE_{2-2x}(MoO_4)_{3-2x}$ ($0.50 < x < 1.00$) solid solutions. It can be found from EPR measurements of the samples with volatile Gd^{3+} ions content, that Gd^{3+} ions can be located at sites of octahedral symmetry, and both temperature and gadolinium content have an influence on local magnetic interaction and relaxation processes of Gd^{3+} ions.

1. Introduction

Double molybdates and tungstates containing rare-earth ions are attractive laser host materials due to a very high stability of emission, high efficiency, long lifetime and low excitation threshold as well as excellent chemical and thermal durability in air. The diode pumped solid-state lasers based on these compounds demonstrate very high stability of emission of nano- or femtosecond pulses with high peak power. These lasers are used for optical and undersea communications, medical and eye-safe detecting, scientific researches and in military applications.

Fedorov and Tunik [1,2] examined reactivity of the $CdWO_4$ (the wolframite-type structure, space group $P2/c$ [3]) with $RE_2(WO_4)_3$. The authors obtained the following compounds in the $CdWO_4$–$La_2(WO_4)_3$ system: $CdLa_2(WO_4)_4$ and $CdLa_4(WO_4)_7$ [4]. Both compounds do not show any homogeneity region [4]. The authors [1,2] obtained two families of double tungstates with the following formulas for the RE = Pr–Ho lanthanides: $Cd_{0.40}RE_{0.40}WO_4$ (the molar ratio of $CdWO_4/RE_2(WO_4)_3$ – 2:1) and $Cd_{0.25}RE_{0.50}WO_4$ ($CdWO_4/RE_2(WO_4)_3$ – 1:1). The $Cd_{0.40}RE_{0.40}WO_4$ phases crystallize in the scheelite-type structure and melt congruently for RE = Pr-Eu or incongruently when RE = Gd-Ho [1,2]. The latter compounds crystallize in the monoclinic system, in a structure that is very similar to the one of scheelite-type. The homogeneity region of the $Cd_{0.40}RE_{0.40}WO_4$ (RE = Pr-Dy) phases is located in the range of about 40.00–60.00 mol.% of $RE_2(WO_4)_3$ and its width decreases, as the RE^{3+} radius decreases. The thermal stability of these compounds decreases analogically. [1,2,4]. The concentration tetrahedron of the CdO–WO_3–RE_2O_3–MoO_3 system with a position of the $Cd_{0.25}RE_{0.50}WO_4$ and $Cd_{0.40}RE_{0.40}WO_4$ compounds is shown in Fig. 1.

Our earlier studies on a reactivity of cadmium tungstate with some rare-earth metal tungstates ($RE_2W_2O_9$, RE_2WO_6) showed an existence of the following new cadmium and rare-earth tungstates: $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ (RE = Nd, Sm, Eu, Gd, $\square$ – statistical distributed vacancies in cation sublattice) [5], $CdPr_2W_2O_{10}$ [6], $CdRE_2W_2O_{10}$ (RE = Y, Nd, Sm–Er) [7]. The $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ compounds were prepared via the solid-state reaction of $CdWO_4$ with $RE_2W_2O_9$ and they crystallize in the scheelite-type structure [5]. $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ melt congruently for RE = Nd, Sm or incongruently when RE = Eu, Gd in the temperature range of 1391–1450 K [5]. The second type double tungstates with the general formula $CdRE_2W_2O_{10}$ were obtained from $CdWO_4$ and an adequate RE_2WO_6 trough the solid-state reaction also [6,7]. The $CdPr_2W_2O_{10}$ crystallizes in the orthorhombic system with cell parameters: $a = 0.68567(2)$ nm; $b = 1.4586(7)$ nm; $c = 0.84102(4)$ nm and is isostructural with other types of double praseodymium tungstates $MPr_2W_2O_{10}$ (M = Mn, Co) [6]. The other cadmium and rare-earth tungstates of $CdRE_2W_2O_{10}$ type crystallize in the monoclinic system and their anion sublattice is made of WO_4 tetrahedra [7]. The $CdRE_2W_2O_{10}$ compounds decompose in the solid-state above 1400 K [6,7]. EPR results obtained for $CdGd_2W_2O_{10}$ showed that an interaction between Gd^{3+} ions had mainly antiferromagnetic type [7].

As a continuation with respect to the earlier works, new families of cadmium and rare-earth molybdato-tungstates with the scheelite-type structure $Cd_{0.25}RE_{0.50}\square_{0.25}(MoO_4)_{0.25}(WO_4)_{0.75}$ (RE = Pr, Nd, Sm–Dy, $\square$ – statistical distributed vacancies in

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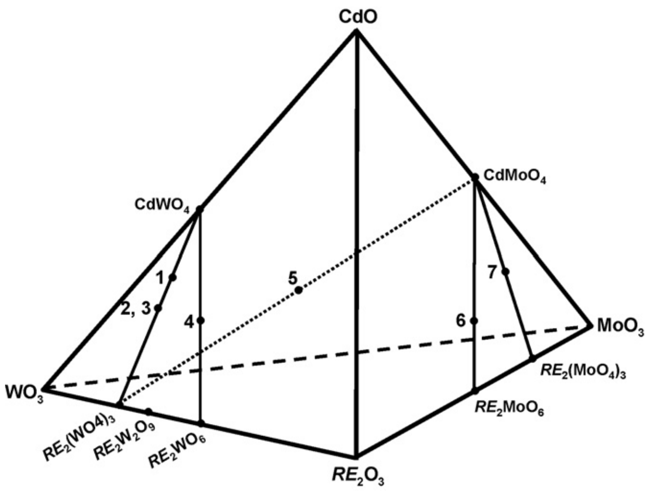

Fig. 1. Concentration tetrahedron of the CdO–WO$_3$–RE_2O$_3$–MoO$_3$ system 1 – $Cd_{0.40}RE_{0.40}WO_4$; 2 – $Cd_{0.25}RE_{0.50}WO_4$; 3 – $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$; 4 – $CdRE_2W_2O_{10}$; 5 – $Cd_{0.25}RE_{0.50}\square_{0.25}(MoO_4)_{0.25}(WO_4)_{0.75}$; 6 – $CdRE_4Mo_3O_{16}$; 7 – $Cd_{0.25}RE_{0.50}MoO_4$.

cation sublattice) [8] and the $Cd_xRE_{2-2x}(MoO_4)_x(WO_4)_{3-3x}$ solid solutions (RE = Pr, Nd, Sm–Dy) [9] were prepared and characterized by X-ray powder diffraction, infrared spectroscopy and thermal analysis techniques. It was found that the $Cd_{0.25}RE_{0.50}\square_{0.25}(MoO_4)_{0.25}(WO_4)_{0.75}$ phases melt congruently in the temperature range of 1382–1461 K [8]. The positions of the new cadmium and rare-earth tungstates and molybdatotungstates were marked in the concentration tetrahedron of the CdO–WO$_3$–RE_2O$_3$–MoO$_3$ system, seen in Fig. 1.

Cadmium and rare-earth metal molybdates $CdRE_4Mo_3O_{16}$ (RE = Y, La–Yb, Fig. 1) were prepared for the first time by Faurie and Kohlmuller who reported their XRD, IR, magnetic and luminescent data [10]. The $CdRE_4Mo_3O_{16}$ compounds were obtained by heating, in the solid-state, rare-earth metal molybdates RE_2MoO_6 with cadmium molybdate CdMoO$_4$ mixed at the molar ratio of 2:1 [10]. The compounds crystallize in the cubic space group $Pn3n$ and their structure can be described as a derivative of the fluorite type structure with a tetrahedral environment of Mo^{6+} ions [11].

In the present paper, we describe synthesis and perform characterization of new cadmium and rare-earth metal molybdates $Cd_{0.25}RE_{0.50}MoO_4$ (RE = Pr, Nd, Sm–Dy) and the $Cd_xRE_{2-2x}(MoO_4)_{3-2x}$ ($0.50 < x < 1.00$) solid solutions using XRD, DTA-TG, IR and EPR methods. In order to characterize a nature of the magnetic interaction in this type of materials, EPR studies of $Cd_xGd_{2-2x}(MoO_4)_{3-2x}$ for x = 0.50, 0.60, 0.70, 0.75, 0.80, 0.90, 0.975 and 0.995 have been carried out in the temperature conditions from the ambient one to the one of liquid nitrogen.

2. Experimental

2.1. Synthesis

CdO, MoO$_3$, Pr$_6$O$_{11}$ and other rare-earth metal oxides RE_2O_3 (all 99.9%, Aldrich) were used as starting materials. Cadmium molybdate (CdMoO$_4$) and rare-earth molybdates ($RE_2(MoO_4)_3$, RE = Pr, Nd, Sm–Dy) were prepared by the solid-state reactions. Heating was started from 823 K, stepwise increasing temperature up to 1148 K (to prepare the $RE_2(MoO_4)_3$) or 1273 K (to obtain the CdMoO$_4$) to avoid a loss of MoO$_3$ due to its evaporation. The solid-state synthesis took 84 h (7 × 12 h). The reaction mixtures were ground in an agate mortar after each 12 h period of the annealing for a better reactivity. The $RE_2(MoO_4)_3$/CdMoO$_4$ mixtures were prepared within the range of cadmium molybdate from 10.00 to 99.5 mol.%. All mixtures were heated in the atmosphere of static air, in 12 h cycles and at the following temperatures: 1023 K, 1073 K, 1123 K and 1173 K. Additionally, the $RE_2(MoO_4)_3$/CdMoO$_4$ (RE = Sm–Dy) were annealed at the temperatures: 1273 K, 1298 K and 1323 K. After each heating period, all samples were cooled slowly down to ambient temperature, ground and examined for their content by XRD method. After each heating cycle a mass of each sample was controlled.

2.2. Characterization of experimental methods

A routine phase analysis was conducted with an X-ray powder diffractometer (DRON-3) operating at 40 kV/20 mA, using Cu$K\alpha$ radiation (λ = 0.15418 nm). The powder diffraction patterns were collected within the 2Θ range 10–45°, at the stepped scan rate 0.02° per step and the count time of 1 s per step. Data suitable for indexing procedure were collected in the 2Θ range 10–100° with a step size of 0.02 (2Θ) and counting time of 10 s for each step. The POWDER [12,13] and DICVOL [14,15] programs were used for indexing procedure.

Infrared spectroscopy data were collected on a Specord M80 spectrophotometer in the range of 300–1200 cm^{-1} using KBr pellets.

Thermogravimetric analysis was performed on a TA Instruments thermoanalyzer (Model SDT 2960) at the heating rate of 10 K min^{-1} to a maximum temperature of 1673 K and in the air atmosphere (gas flow 110 mL h^{-1}).

The EPR measurements were carried out with a conventional X-band Brücker ELEXSYS E500 CW spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. Temperature dependence of the EPR spectra was registered in the range 85–295 K.

Chemical analysis of metallic elements' content was preformed for selected phases and equimolar mixtures of $RE_2(MoO_4)_3$ with CdMoO$_4$. The analyzed samples were melted with a mixture of Na$_2$CO$_3$ with K$_2$CO$_3$ (as flux). The resulting melt was dissolved in a hot dilute hydrochloric acid. The obtained precipitate of MoO$_3$ was used to determining of molybdenum content (gravimetric analysis). The filtrate obtained after separation of MoO$_3$ precipitate was used for determining of cadmium and rare-earth elements' contents by ICP-AES method (IY ULTRACE 238 spectrometer).

3. Results and discussion

3.1. Phases identification in the RE$_2$(MoO$_4$)$_3$–CdMoO$_4$ system

The XRD analysis' results of the samples obtained after the last heating cycle of $RE_2(MoO_4)_3$/CdMoO$_4$ mixtures indicate that initial compounds react with each other in the solid-state. The XRD analysis of the samples, whose initial mixtures contained up to 50.00 mol % of CdMoO$_4$, showed that two solid phases were found in the treated samples, viz. the compounds: $RE_2(MoO_4)_3$ and yet unknown $Cd_{0.25}RE_{0.50}MoO_4$. At the molar ratio 1:1 of the $RE_2(MoO_4)_3$/CdMoO$_4$ mixtures, both reactants reacted to produce a new cadmium and rare-earth metal molybdates:

$$CdMoO_{4(s)} + RE_2(MoO_4)_{3(s)} = 4Cd_{0.25}RE_{0.50}MoO_{4(s)} \qquad (1)$$

It was observed that the XRD patterns of $Cd_{0.25}RE_{0.50}MoO_4$ consisted of peaks due to the scheelite-type lattice. The scheelite-type peaks were found also on powder diffraction patterns of the samples that were obtained after heating of $RE_2(MoO_4)_3$/CdMoO$_4$ mixtures comprising initially over 50.00 mol.% of CdMoO$_4$. The positions of the scheelite-type peaks that we observed were being shifted towards higher angles as the CdMoO$_4$ content increases. This fact indicates that the $Cd_{0.25}RE_{0.50}MoO_4$ compounds can form scheelite-type solid solutions with CdMoO$_4$. The formula of these solid solutions may be written as $Cd_xRE_{2-2x}(MoO_4)_{3-2x}$.

3.2. Composition determination

The chemical analysis of metallic elements' contents was performed for $Cd_{0.25}RE_{0.50}MoO_4$ (RE = Eu and Dy) and equimolar, initial mixtures of $RE_2(MoO_4)_3$ (RE = Eu and Dy) with CdMoO$_4$. The experimental and calculated contents of Mo, Cd and RE in analyzed phases and mixtures are shown in Table 1. Very similar experimental values of metallic elements' contents for $Cd_{0.25}RE_{0.50}MoO_4$ and initial $RE_2(MoO_4)_3$/CdMoO$_4$ mixtures confirm the validity of the proposed formula for new cadmium and rare-earth molybdates.

3.3. Characterization of Cd$_{0.25}$RE$_{0.50}$MoO$_4$ and the Cd$_x$Eu$_{2-2x}$(MoO$_4$)$_{3-2x}$ solid solutions by XRD and IR methods

Powder diffraction patterns of $Cd_{0.25}RE_{0.50}MoO_4$ were subjected to indexing procedure. Table S1 (supplementary data) shows the