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New vacancied and Dy^{3+}-doped molybdates – Their structure, thermal stability, electrical and magnetic properties

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ABSTRACT

Microcrystalline samples of new $Cd_{1-3x}Dy_{2x}\square_xMoO_4$ solid solution with limited homogeneity ($0 < x \leq 0.2222$) and cationic vacancies (denoted as $\square$) were prepared by a high-temperature solid state reaction. The XRD data and SEM analysis showed that as-prepared ceramics crystallize in the tetragonal scheelite type symmetry (space group $I4_1/a$) with the crystallite size varying between ~2 and ~20 μm. A systematic change in lattice constants, *a* and *c*, as well as in lattice parameter ratio *c/a* with an increase of Dy content was observed. Dy-doped molybdates are paramagnets with the antiferromagnetic short-range interaction and spin-orbit coupling. Optical and electrical investigations proved $Cd_{1-3x}Dy_{2x}\square_xMoO_4$ solid solution to be in the insulating state of $E_g > 3$ eV at room temperature and the thermally activated conduction of the Arrhenius-type above 350 K. Moreover, the *I-V* characteristics provided the evidence of symmetrical and non-linear behavior typical of charge carrier emission weakly induced by the temperature. Relative dielectric permittivity ε_r below 10 as well as loss tangent $\tan\delta$ below 0.15 do not substantially depend both on the temperature in the range of 76–400 K and the frequency in the range of $5 \cdot 10^2$–$1 \cdot 10^6$ Hz. These results are interpreted in the framework of the acceptor and donor vacancy centers.

1. Introduction

For several decades inorganic materials doped with rare earth ions have been extensively studied and used in phosphors. Molybdates and tungstates are intensively considered to be very good candidates hosts for luminescent materials due to the diversity of structures (*e.g.* scheelite, wolframite) [1–12]. All these structures are suitable hosts for many rare earth ions doping due to their advantageous properties like high thermal and chemical stability, short decay time as well as high light yield [5,6,8,9,12–15]. Dy^{3+} is a promoted active ion for phosphors because it can be excited by commercial near-UV LEDs [16–27]. This ion has two intensive emission bands in blue and yellow regions related with the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively [16–18,24,25,27]. This second *4f–4f* transition is a hypersensitive and strongly influenced by the crystal field. Therefore, it is possible to adjust the intensity ratio of yellow to blue emission via choosing different kind of hosts. Laser materials with yellow and blue laser emission spectra have attracted a great interest by their wide applications in medicine, oceanic communication, and military [18,22,24,27]. Blue and yellow lasers pumped directly by LEDs would be smart, compact and user-friendly.

Our earlier studies on a reactivity in the solid state of cadmium molybdate or tungstate ($CdMoO_4$ or $CdWO_4$) with various type of rare-earth molybdates or tungstates (*e.g.* $RE_2(XO_4)_3$, where X = Mo or W) have been showed an existence of a large group of new interesting materials for potential applications in optoelectronics [13,28–32]. Scheelite-type $Cd_{1-3x}RE_{2x}\square_xMoO_4$ and $Cd_{1-3x}RE_{2x}\square_x(MoO_4)_{1-3x}(WO_4)_{3x}$ solid solutions (as ceramics and single crystals), where RE = Pr-Yb and $\square$ means cationic vacancies represent the special group of new materials [14,15,29–34]. Value of *x* parameter, *i.e.* homogeneity range of above mentioned solid solutions, strongly depends on the RE^{3+} ion radius and it can reach the maximum value of 0.25 for light lanthanides [14,15,29–32]. When trivalent rare earth ions are incorporated in $CdMoO_4$ tetragonal scheelite lattice it must be accompanied by a charge-compensating defect. The substitution of divalent Cd^{2+} ions by trivalent RE^{3+} ones leads to the formation of cationic vacancies in a framework and some disordering what in consequence leads to improving of the luminescence intensity [28–31]. Additionally, a

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slight distortion of crystal lattice around of RE^{3+} ions is manifested by an emission of broad bands associated with *f-f* transitions in such laser active ions as Nd^{3+} or Yb^{3+} and this phenomenon allows both tuning of laser radiation and generation of ultra-short pulses that could be used in pico- or femtoseconds lasers [29,31]. Recently, a superparamagnetic-like behavior and low relative dielectric permittivity of ~8 in the $CdMoO_4$:Gd^{3+} single crystal [33] as well as a colossal increase in electron emission of $Cd_{1-3x}Gd_{2x}\square_xMoO_4$ solid solution [35] and the diode-like behavior of $CdMoO_4$:Nd^{3+} single crystal [34] were found.

In the present paper, results on $Cd_{1-3x}Dy_{2x}\square_xMoO_4$ ($0 < x \leq 0.2222$) new ceramic materials with potential laser applications have been presented. In particular, the optical, magnetic and electrical studies were made to obtain insights into the nature of their insulating and paramagnetic properties.

2. Experimental

2.1. Solid state synthesis

Dysprosium molybdate ($Dy_2(MoO_4)_3$) and cadmium molybdate ($CdMoO_4$) were used as the starting reactants for synthesis. These compounds were separately prepared by annealing of stoichiometric metal oxide mixtures in air, *i.e.* mixture of Dy_2O_3 with MoO_3 (both 99.95%, Alfa Aeasar) and CdO with MoO_3 (both 99.95%, Alfa Aeasar) according to the procedures used by us in previous studies [14,15,29–32,35]. Microcrystalline samples of new cadmium and dysprosium molybdates have been successfully synthesized by a high-temperature annealing of $CdMoO_4$ with $Dy_2(MoO_4)_3$ mixed at different molar ratios. The concentration of dysprosium molybdate in each initial $CdMoO_4/Dy_2(MoO_4)_3$ mixture is shown in Table 1. All initial mixtures were heated in corundum crucibles and in the atmosphere of static air. The samples were sintered in the six 12 h stages and at temperatures in the range of 1223–1333 K. After each the heating stage, all samples were cooled to room temperature, ground in an agate mortar and followed by examined for their content by XRD method.

2.2. Characterization of experimental methods

Powder X-ray diffraction patterns were collected in the 10–100° 2Θ range with the scanning step 0.013^0 on a EMPYREAN II diffractometer (PANalytical) using CuK$\alpha_{1,2}$ radiation ($\lambda = 0.15418$ nm). XRD patterns were analyzed by a *HighScore Plus 4.0* software and lattice parameters were calculated using the least squares refinement procedure and a *POWDER* software [36]. The density was measured on a Quantachrome Instruments Ultrapycnometer (model Ultrapyc 1200 e) using argon (99.99%) as a pycnometric gas. Morphology and grain size of samples under study were examined using JEOL scanning electron microscope (model JSM-1600). Ceramic samples in form of tablets were coated with thin gold-palladium alloy layer to facilitate conductivity measurements. Simultaneous DTA and TG measurements were carried out on a TA Instruments thermoanalyzer (model SDT 2960) at the heating rate of 10 K min^{-1}, in air (the maximum temperature of 1473 K, the air flow 110 mL h^{-1}), and using alumina crucibles. The mass of each sample for DTA-TG measurements was ~30 mg. The UV–vis diffuse reflectance spectra were recorded within the range of 200–1000 nm using JASCO-V670 spectrophotometer equipped with an integrating sphere.

Static magnetic susceptibility, $\chi(T)$, was measured in the temperature range of 2–300 K and in the magnetic field $H = 1$ kOe as well as recorded both in zero-field-cooled (ZFC) and field-cooled (FC) mode. Because of the strong spin-orbit coupling, contributions of magnetic susceptibility independent on the temperature were not estimated [37]. Magnetization isotherms, $M(H)$, were measured at 2, 4.2 and at 300 K in the static magnetic field up to 70 kOe. For these measurements, a Quantum Design System (MPMS XL) was used. The effective magnetic moment was calculated from the high-temperature expansion of magnetic susceptibility using equation: $\mu_{eff} = 2.83\sqrt{C}$, where C is the Curie constant, and its temperature dependence from the equation: $\mu_{eff} = 2.83\sqrt{\chi \cdot T}$. Landé factor, g, was determined from the Curie constant [38] given by:

$$C = \frac{Ng^2\mu_B^2 J(J+1)}{3k}, \quad (1)$$

where N is the number of magnetic ions, μ_B is the Bohr magneton, J is the angular momentum and k is the Boltzmann constant.

The electrical conductivity, σ(T), and the *I-V* characteristics of the molybdates under study have been measured with the aid of the DC method using a KEITHLEY 6517B Electrometer/High Resistance Meter. The activation energy, E_a, was determined in the temperature range of 350–400 K from the formula $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$, where σ_0 is the reference conductivity. The thermoelectric power S(T) was measured in the temperature range of 300–600 K with the aid of a Seebeck Effect Measurement System (MMR Technologies, Inc., USA). Broadband dielectric spectroscopy measurements were carried out using pellets, polished and sputtered with (~80 nm) Ag electrodes in a frequency range from $5 \cdot 10^2$ to $1 \cdot 10^6$ Hz with use a Novocontrol Alpha Impedance Analyzer and in the temperature range 76–400 K. For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and then they were sintered during 2 h at 1073 K. The electrical and thermal contacts were made by a silver lacquer mixture (Degussa Leitsilber 200).

Table 1
$Dy_2(MoO_4)_3$ content in initial $CdMoO_4/Dy_2(MoO_4)_3$ mixtures, results of XRD analysis of samples obtained after the last annealing stage (the formula of $Cd_{1-3x}Dy_{2x}\square_x$, MoO_4 was calculated on phase compositions of initial mixtures), calculated lattice constants and *c/a* ratio of an adequate solid solution, calculated as well as experimental values of density, and determined band gap energy E_g.

$Dy_2(MoO_4)_3$ content [mol%]	Formula of solid solution		Lattice constants [nm]		*c/a*	Density [g cm^{-3}]		*Eg* [eV]
			a	*c*		d_{cal}	d_{exp}	
0	*x=0*	$CdMoO_4$ (pure matrix)	0.515749	1.12011	2.17181	6.07	6.07	3.42
0.05	*x=0.0005*	$Cd_{0.9985}Dy_{0.0010}\square_{0.0005}MoO_4$	0.515842	1.12034	2.17187	6.07	6.07	3.42
1.00	*x=0.0098*	$Cd_{0.9706}Dy_{0.0196}\square_{0.0098}MoO_4$	0.515887	1.12025	2.17150	6.06	6.05	3.43
2.50	*x=0.0238*	$Cd_{0.9286}Dy_{0.0476}\square_{0.0238}MoO_4$	0.516005	1.12065	2.17178	6.05	6.04	3.44
5.00	*x=0.0455*	$Cd_{0.8635}Dy_{0.0910}\square_{0.0455}MoO_4$	0.516487	1.12184	2.17206	6.03	5.99	3.45
10.00	*x=0.0839*	$Cd_{0.7483}Dy_{0.1678}\square_{0.0839}MoO_4$	0.516952	1.12403	2.17434	6.00	5.96	3.47
25.00	*x=0.1667*	$Cd_{0.4999}Dy_{0.3334}\square_{0.1667}MoO_4$	0.517771	1.12997	2.18237	5.93	5.76	3.52
33.33	*x=0.2000*	$Cd_{0.4000}Dy_{0.4000}\square_{0.2000}MoO_4$	0.517868	1.13367	2.18911	5.90	5.67	3.52
40.00	*x=0.2222*	$Cd_{0.3334}Dy_{0.4444}\square_{0.2222}MoO_4$	0.517841	1.13558	2.19291	5.88	5.60	3.45

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