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New cadmium and rare earth metal tungstates with the scheelite type structure

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Abstract: New cadmium and rare earth metal tungstates with the formula $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ ($RE=Nd, Sm, Eu, Gd$, \square -statistical distributed vacancies in cation sublattice) were synthesized by the solid-state reaction between $CdWO_4$ and corresponding $RE_2W_2O_9$. The obtained phases crystallize in the scheelite type structure. The $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ compounds were characterized by X-ray diffractometer (XRD), (DTA-TG), infrared (IR) and EPR methods.

Keywords: rare earth metal tungstates; scheelite type structure; XRD; DTA-TG; EPR

Cadmium tungstate ($CdWO_4$) is an attractive material because of its optical, chemical and structural properties. It is well known that $CdWO_4$ crystals have high X-ray absorption coefficient, high average refractive index, low radiation damage and low afterglow to luminescence. Single crystals of $CdWO_4$ can be used in spectroscopic and radiometric devices, for creation of small-sized detectors with photodiodes and multielement detecting assemblies for computer tomography^[1-8]. Cadmium tungstate crystals doped with the different valence ions (La^{3+} ^[9], Sm^{3+} ^[10], Li^+ , Na^+ and Cs^{+} ^[9,11], B^{3+} as well as Bi^{3+} ^[11]) were investigated by many authors in order to create new heavy and fast scintillators.

In the present paper the new cadmium and rare earths tungstates with the formula $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ ($RE=Nd, Sm, Eu, Gd$) and the scheelite type structure were synthesized by the solid-state reaction. The obtained phases were characterized by XRD, DTA-TG, IR and EPR techniques.

1 Experimental

1.1 Synthesis

$RE_2W_2O_9$ ($RE=Nd, Sm, Eu, Gd$) and $CdWO_4$ were used as the starting materials. Rare earth metal tungstates were obtained by the solid-state reaction at high temperature between an adequate RE_2O_3 (all oxides with the purity degree of 99.9%, Aldrich) and WO_3 (99.9%, Fluka). The RE_2O_3/WO_3 mixtures were heated in analogous conditions as in RE_2WO_6 synthesis^[12-14]. For the synthesis of cadmium

tungstate, a stoichiometric mixture of $3CdSO_4 \cdot 8H_2O$ (99%, Aldrich) with WO_3 was homogenized and heated in 12 h periods, at the following temperatures: 1073, 1173, 1273 and 1373 K. The $CdWO_4/RE_2W_2O_9$ mixtures were prepared with the range of cadmium tungstate from 10.00 mol.% to 90.00 mol.%. Initially, all mixtures were heated in air in the following cycles: 1273 K (12 h), 1323 K (12 h), 1348 K (12 h), 1373 K (2×12 h). Additionally, the $CdWO_4/RE_2W_2O_9$ mixtures ($RE=Nd, Sm$) were heated in the following temperatures: 1398 K (12 h) and 1408 K (2×12 h). After each heating cycle, all samples were cooled slowly to room temperature, weighed, ground and examined their contents by XRD method.

1.2 Characterization

Routine phase analysis was conducted with a DRON-3 diffractometer using the $Cu K\alpha_{aver}$ radiation ($\lambda=0.15418$ 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° – 92° with a step size of 0.02 (2θ) and counting time of 10 s for each step. The diffraction patterns were indexed using POWDER and DICVOL programs to calculate the accurate unit cell dimensions.

Thermograms of obtained samples were recorded on a TA Instruments thermoanalyzer (Model SDT 2960), recording both differential thermal analysis (DTA) and thermogravimetric (TG) curves simultaneously. The samples were heated in corundum crucibles at the heating rate of 10 K/min up to

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1773 K and in a nitrogen atmosphere (gas flow 110 ml/h).

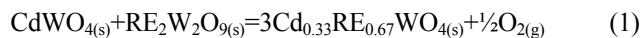
The IR spectra were recorded on a Specord M-80 spectrometer. The samples were pressed in pellets with KBr in the mass ratio of 1:100.

The EPR measurements were performed with a conventional X-band Brücker ELEXSYS E500 CW spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. Samples of selected compounds (~30 mg) were placed into 4 mm diameter quartz tubes. The first derivative of the power absorption spectra has been recorded as a function of the applied magnetic field. Temperature dependence of the EPR spectra was registered using an Oxford Instruments ESP helium-flow cryostat in the 8–295 K temperature range.

2 Results and discussion

The XRD analysis results of samples obtained after the last heating period of the $\text{RE}_2\text{W}_2\text{O}_9/\text{CdWO}_4$ mixtures point out that these compounds were not inert mutually. XRD analysis made for the samples, the initial mixtures of which contained less than 50.00 mol.% $\text{RE}_2\text{W}_2\text{O}_9$, showed that two solid phases occurred in the samples by treatment, viz. the compounds: CdWO_4 and phases characterised by the powder diffraction patterns very similar to diffraction pattern of CaWO_4 (the scheelite type structure^[15]). At the molar ratio 1:1 of the $\text{RE}_2\text{W}_2\text{O}_9/\text{CdWO}_4$ mixtures, both reactants react to completion. In the other concentration range, i.e. over 50.00 mol.% of $\text{RE}_2\text{W}_2\text{O}_9$, the compounds to remain in equilibrium within the subsolidus area will be: $\text{RE}_2\text{W}_2\text{O}_9$ and the mentioned above phases with probably the scheelite type structure. The mass change investigations of all samples showed mass decreases in all $\text{RE}_2\text{W}_2\text{O}_9/\text{CdWO}_4$ mixtures after each heating period. The biggest values of total mass loss (calculated by adding the mass losses observed after each heating cycle) were recorded for the samples comprising initially 50.00 mol.% of $\text{RE}_2\text{W}_2\text{O}_9$ and 50.00 mol.% of CdWO_4 and they equalled: (Nd)–1.396%; (Sm)–1.378%;

(Eu)–1.373% and (Gd)–1.359%. The values of mass losses for equimolar $\text{RE}_2\text{W}_2\text{O}_9/\text{CdWO}_4$ mixtures, calculated on a base of the equation (1), equal: (Nd)–1.379%; (Sm)–1.364%; (Eu)–1.361% and (Gd)–1.349%. The observed values of total mass losses are in good agreement with the calculated ones.



The formula of new cadmium and rare earth metal tungstates obtained by the reaction (1) should be written as follows: $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ (\square -statistical distributed vacancies in cation sublattice). The calculated parameters of unit cells, the values of experimental (obtained by degassing of samples and hydrostatic weighing in pycnometric liquid- CCl_4) and calculated density for $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ and CaWO_4 are tabulated in Table 1. The very big similarities in the powder diffraction patterns and the cell parameters of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ with CaWO_4 ^[15] suggest that these compounds crystallize in the scheelite type structure.

Fig. 1 shows DTA curves of the $\text{RE}_2\text{W}_2\text{O}_9$ (RE=Nd, Sm, Eu, Gd) compounds. The endothermic effects recorded on the DTA curve of $\text{Nd}_2\text{W}_2\text{O}_9$ with their onsets at 1512 and 1611 K are connected with polymorphic transition and melting this phase, respectively. Yoshimura et al.^[16] found that this compound undergoes polymorphic transition to β - $\text{Nd}_2\text{W}_2\text{O}_9$ and melts incongruently at 1528 and 1626 K, respectively. On each DTA curve of $\text{RE}_2\text{W}_2\text{O}_9$ (RE=Sm, Eu, Gd) only one endothermic peak was recorded up to 1773 K. The effects with their onsets at: 1527 K (Sm), 1487 K (Eu) and 1475 K (Gd) are associated with melting $\text{RE}_2\text{W}_2\text{O}_9$. Fig. 2 shows the DTA curves of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$. On each DTA curve one or two endothermic effects were recorded up to 1773 K. No mass losses were recorded on the TG curves (not presented) up to the onsets of the first observed effects on the DTA curves. On the base of DTA studies for $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ (RE=Nd, Sm) and observations of the residues obtained in crucibles after the DTA-TG experiments it was found that the peaks with their onsets at:

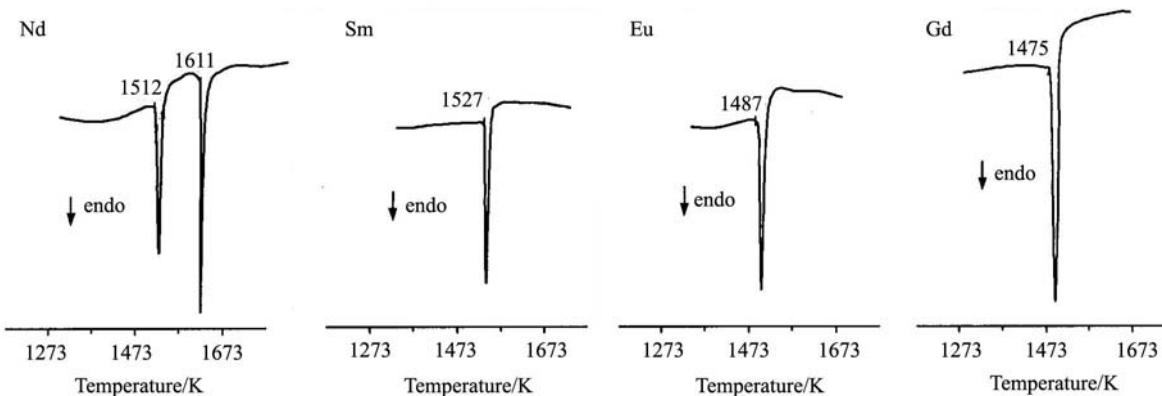
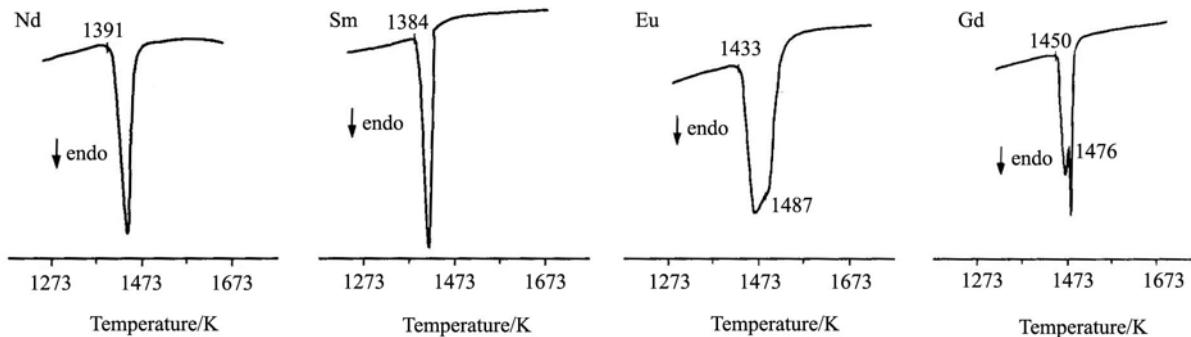


Fig. 1 DTA curves of $\text{RE}_2\text{W}_2\text{O}_9$

Table 1 Parameters of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ unit cells and the values of experimental and calculated density

| Compound (colour) | a/nm | c/nm | c/a | Z | V/nm^3 | $\rho_{\text{exp}}/(\text{g}/\text{cm}^3)$ | $\rho_{\text{cal}}/(\text{g}/\text{cm}^3)$ | Ref. |
|---|---------------|---------------|--------|-----|-----------------|--|--|-----------|
| $\text{Cd}_{0.25}\text{Nd}_{0.50}\square_{0.25}\text{WO}_4$ (blue) | 0.52760(8) | 1.1495(2) | 2.1787 | 4 | 0.31999(3) | 7.46 | 7.92 | This work |
| $\text{Cd}_{0.25}\text{Sm}_{0.50}\square_{0.25}\text{WO}_4$ (cream-colored) | 0.52534(9) | 1.1449(4) | 2.1794 | 4 | 0.31599(4) | 7.69 | 8.10 | This work |
| $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ (white) | 0.52297(3) | 1.1409(4) | 2.1816 | 4 | 0.31204(7) | 7.88 | 8.23 | This work |
| $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ (white) | 0.52182(8) | 1.1323(8) | 2.1700 | 4 | 0.30835(2) | 8.07 | 8.40 | This work |
| CaWO_4 | 0.524294(6) | 1.1373(7) | 2.1692 | 4 | 0.31263 | 6.100 | 6.117 | [15] |

Fig. 2 DTA curves of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$

1391 K (Nd); 1384 K (Sm) are connected with congruent melting these phases. Thus, separate samples of these compounds were heated above their melting points, i.e. at 1433 K for 4 h, removed from a furnace and then rapidly quenched to 263 K. The results of XRD analysis for the samples obtained this way showed that they contained the initial phases. The first endothermic effects observed on the DTA curves of the $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ phases (RE=Eu, Gd) with their onsets at 1433 K (Eu) and 1450 K (Gd) are characterized by melting these compounds. The melting behavior of these phases was also confirmed by XRD method. Consequently, samples of the mentioned compounds were heated in a furnace above their melting point, i.e. at 1463 K for 4 h and then quickly “frozen”. On the base of XRD method it was found that the samples obtained this way contained an adequate $\text{RE}_2\text{W}_2\text{O}_9$. Thus, the incongruent melting of the $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ compounds (RE=Eu, Gd) can be described by the following equation:

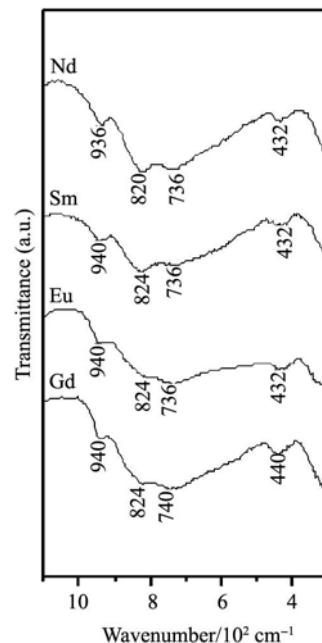


The endothermic effects with their onsets at 1487 K (Fig. 2, RE=Eu) and at 1476 K (Fig. 2, RE=Gd) are associated with melting $\text{Eu}_2\text{W}_2\text{O}_9$ and $\text{Gd}_2\text{W}_2\text{O}_9$, respectively.

The fundamental frequencies for WO_4^{2-} anion in an aqueous solution are centered around^[14]: ν_1 -931 cm^{-1} ; ν_2 -318 cm^{-1} ; ν_3 -833 cm^{-1} and ν_4 -405 cm^{-1} . For solid tungstates with the scheelite type structure (isolated WO_4 tetrahedra) the stretching multiplets ν_1 and ν_3 appear in the 930–750 cm^{-1} range as well as the bending modes in the 420–250 cm^{-1} range^[17–19]. Fig. 3 shows IR spectra of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$. In the light of literature information^[17–19] the broad absorp-

tion bands observed in the IR spectra of these compounds with their maxima at: 940 and 936 cm^{-1} are due to the symmetric stretching modes of W-O bonds in WO_4 . However, the broad absorption bands with their maxima located at 824 and 820 cm^{-1} as well as at 740 and 736 cm^{-1} could be related to the asymmetric stretching vibrations of W-O bonds in WO_4 ^[17–19]. Turn, the absorption bands centered around 440 cm^{-1} or 432 cm^{-1} can be assigned as the asymmetric deformation modes of W-O in WO_4 ^[17–19].

The EPR spectra of the $\text{Gd}_2\text{W}_2\text{O}_9$ and $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$

Fig. 3 IR spectra of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$

compounds consist of very wide, single, intense line visible at whole temperature range.

The EPR signal has got Gaussian shape probably due to strong inhomogeneous broadening characteristic for compounds where charge compensation is needed (a lot of vacancies). Denotation of the curves presented in Fig. 4, e.g. 1;4.73 K, indicates EPR line of $\text{Gd}_2\text{W}_2\text{O}_9$ compound (number 2 marks $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ compound) measured at a temperature of 4.73 K. The low signal observed at about 12000 Gs we assigned to oxygen. The integral intensity of the EPR line as a function of temperature reveal significant antiferromagnetic interaction of gadolinium magnetic species, with Curie-Weiss constant equal to about -6.6 K for $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ and -1.6 K for $\text{Gd}_2\text{W}_2\text{O}_9$ (Fig. 5(a)). Solid lines in this figure indicate Curie-Weiss relation. As one can see from Fig. 5(a) and (b), a departure of the integral intensity relation versus temperature from Curie-Weiss relation is observed between 10 and 80 K being much higher for $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ compound. Calculated effective spectroscopic parameter g_{eff} strongly decreases with increasing

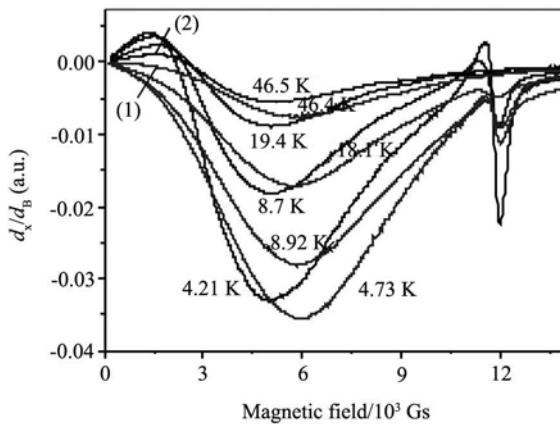


Fig. 4 EPR spectra of $\text{Gd}_2\text{W}_2\text{O}_9$ (1) and $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ (2) compounds for several temperatures

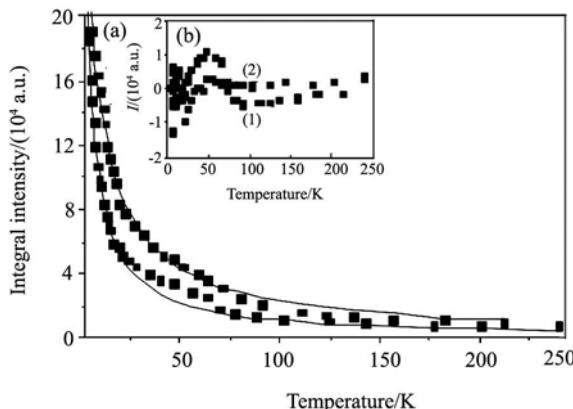


Fig. 5 (a) Total integral intensity of EPR signal for $\text{Gd}_2\text{W}_2\text{O}_9$ (1) and $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ (2) compounds (solid lines indicate Curie-Weiss relation) and (b) A departure from Curie-Weiss relation in both compounds

temperature, being minimal at about 50 K, whereas above this temperature g_{eff} significantly increases. In the same range of temperature the total magnetic moment and linewidth have got a maximum. These variations can be attributed to specific contribution of the internal magnetic field arising from the thermally fluctuating magnetic moments, which change resonance conditions.

The results indicate on the existence of strongly interacting paramagnetic Gd^{3+} centers located at the positions of high point symmetry in both studied materials.

3 Conclusion

New cadmium and rare-earths tungstates with the formula $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ ($\text{RE}=\text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$, \square -vacancies in cation sublattice) were prepared by the solid-state reaction route. The obtained phases are isostructural and crystallize in the tetragonal system, in the scheelite type structure. The lattice parameters and cell volume of the $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ phases decreased with decreasing RE^{3+} radius. Big difference between the calculated and experimental value of density for each obtained compound confirms a presence of statistical distributed vacancies in cation sublattice. In an inert atmosphere $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ melt congruently ($\text{RE}=\text{Nd}, \text{Sm}$) or incongruently ($\text{RE}=\text{Eu}, \text{Gd}$). The EPR measurements indicated that in the $\text{Gd}_2\text{W}_2\text{O}_9$ and $\text{Cd}_{0.25}\text{Gd}_{0.5}\square_{0.25}\text{WO}_4$ compounds, strong interaction between gadolinium ions had got mainly antiferromagnetic type, excluding 20–80 K region, where a strong departure from the Curie-Weiss relation is observed.

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