Investigation of the Heterovalent Substitution Cadmium for Lanthanum in Molybdate La$_2$MoO$_6$

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This paper presents the investigation of the heterovalent substitution of cadmium for lanthanum in the La$_{2-x}$Cd$_x$MoO$_{6-x/2}$ system. The samples were synthesized by the solid state reaction method at 1000°C. The samples were characterized by X-ray powder diffraction with Rietveld refinements, scanning electron microscopy with energy-dispersive X-rays spectroscopy, and Fourier transform infrared spectroscopy methods. The study results revealed that cadmium incorporation in the lanthanum molybdate leads to the transformation of the tetragonal structure of La$_2$MoO$_6$ to a cubic fluorite-like one. The content of the cubic phase reaches 94% in the La$_{1.4}$Cd$_{0.6}$MoO$_{5.7}$ sample. The unit cell parameter of the fluorite-like phase decreases with cadmium content rising. The preferred location of cadmium ions in the cubic structure was established by the Rietveld refinement method. The heterovalent substitution cadmium for lanthanide in tetragonal La$_2$MoO$_6$ molybdate leads to the cubic fluorite phase stabilization in a similar way as it occurs in the process of reduction.

1. Introduction

Molybdates of rare-earth elements (REE) have various compositions depending on the ratio of cations, for example, Ln$_2$(MoO$_4$)$_3$, Ln$_2$MoO$_6$, Ln$_5$Mo$_3$O$_{16+\delta}$, and Ln$_5$Mo$_3$O$_9$. Among them, Ln$_2$MoO$_6$ compounds attract attention for potential use in luminophores, catalysts, ionic conductors, and so forth [1–3]. Structures of REE molybdates Ln$_2$MoO$_6$ may change resulting from a value of lanthanide ionic radii and synthesis conditions. The monoclinic structure (space group C2/c, $z = 8$) is typical for REE molybdates Ln$_2$MoO$_6$, where Ln = La to Lu as well as Y [4, 5]. Besides this, REE molybdates with lanthanides from La to Sm can crystallize in the tetragonal structure (space group I41/acd, $z = 4$) [6]. The low-temperature modification of neodymium molybdate (space group I2/c, $z = 8$) was described. It was formed at 800°C by a solution-melt method from a mixture of 25 mole % Nd$_2$O$_3$ + 55 moles% MoO$_3$ + 10 moles% PbO [7], where lead oxide was used to decrease the melting point of the mixture.

Compounds Ln$_3$Mo$_3$O$_{16+\delta}$ with cubic fluorite-like structure (space group Pn-3n) are known for Nd and Pr [8]. Molybdenum content in such compounds is slightly higher than that in Ln$_2$MoO$_6$ molybdates (calculated value for MoO$_3$ is 54.5 mole%). The value of $\delta$ may range from 0 up to 0.5 because some of molybdenum ions may be reduced to a lower oxidation state during synthesis [6]. Isostructural molybdates Ln$_5$Mo$_3$O$_{16+\delta}$ ($\delta = 0$) for REE from La to Tbf with cubic fluorite–like structure were obtained in reducing conditions [9, 10].

Lanthanum molybdate La$_3$Mo$_3$O$_{16+\delta}$ ($\delta = 0.5$) is unstable in oxidizing conditions and decomposes into the mixture of compounds La$_3$Mo$_6$O$_{12}$ and La$_2$Mo$_2$O$_9$ [9]. Molybdates Ln$_5$Mo$_3$O$_{16+\delta}$ with the monoclinic structure were synthesized for REEs following after Nd in oxidizing conditions. The latter molybdates are obviously a part of the homogeneity region of Ln$_3$Mo$_3$O$_6$ compounds (space group C2/c, $z = 8$).

It is noteworthy that all crystal structures of REE molybdates and close compounds by composition are
derivatives from the fluorite structure and differ by a manner of its distortion. Compounds with the general formula MLn4Mo3O16 with a cubic structure for REE from La to Lu are stabilized by the substitution of a double-charged metal ion, M^{2+} for the lanthanide ion [11]. The temperature of synthesis increases as the REE atomic number increases and also depends on the nature of the double-charged metal ion. The incorporation of cadmium or lead ions leads to a decrease in temperature of the cubic structure formation while alkaline earth ions increase it.

The cubic molybdates Ln2MoO6 with fluorite structure for Ln = Gd, Tb, Dy, Ho, and Y were prepared by reduction of Ln2MoO6 with hydrogen [12]. In recent years due to increased interest in ionic oxygen conductors with high conductivity at medium temperatures (200–900°C), compounds Ln2MoO6-x with fluorite structure, where Ln = Tb–Yb, were studied in the systems Ln2O3–MoO3 [13]. The fluorite-like structure of La2MoO6 was also obtained by hydrogen reduction of tetragonal lanthanum molybdate La2MoO6 [14]. It has high conductivity, which makes using it as anode materials in solid oxide fuel cells possible.

The compounds Ln2MoO6 with the structure derived from fluorite can also be modified by a heterovalent substitution of the double-charged metal ion for lanthanide ion. It presumably enables obtaining a similar material with the vacancies in the oxygen sublattice but without the electronic component of conductivity.

The solid solutions (PbO)x(La2MoO6) (x=0.025) with constant La:Mo ratio synthesized by the solid state method were described in work [15]. The solid solutions were isostructural to lanthanum molybdate La2MoO6 with tetragonal structure and the heterovalent substitution did not cause transformation of the structure.

Earlier, we reported the heterovalent substitution of cadmium for REE in monoclinic gadolinium and holmium molybdates Ln2MoO6 resulted in the formation of cubic fluorite-like phases [16]. For these compositions, the Ln:Mo ratio varies but the (Ln + Cd):Mo ratio remains constant.

At the same time, there is no information about the possibility of the cubic fluorite-like structure stabilization upon substitution cadmium for REE in Ln2MoO6 molybdates with the tetragonal structure. The aim of this study is the investigation of Lax2MoO6 x molybdate transformation to the cubic structure by substitution of cadmium for lanthanum.

2. Materials and Methods

The samples with a composition that corresponds to the following ratio of reagents (1−x/2)LaxO3−xCdO·MoO3 (0 ≤ x ≤ 1) were synthesized by the solid state method from the stoichiometric mixtures of oxides (analytical grade, Synbias). Apparently, the replacement of cadmium ion for triple charged ion of REE in the structure of Lax2MoO6 (x = 0) results in the removal of oxygen for charges compensation in the crystal structure and formation of solid solutions with general formula Lax2−Cd3+MoO6-x/2. The lack of oxygen in the structure leads to the transformation of the tetragonal structure to the cubic one as it takes place in the compounds Ln2MoO6−δ.

The substitution of cadmium for lanthanum in the crystal structure occurs under the suggested scheme:

\[ \text{La}^{3+} + 1/2 \text{O}^{2-} = \text{Cd}^{2+} + 1/2 \text{V}_{\text{O}} \]

The set of all synthesized samples is hereinafter mentioned as “system Lax2−Cd3+MoO6−x/2”.

The initial oxides were calcined (La2O3 at 1000°C for 1 hour; CdO and MoO3 at 500°C for 4 hours) prior to synthesis. The homogenized mixtures of oxides were annealed at 500°C for 5 hours to fully bind MoO3. Then, samples were annealed at 800°C, 950°C, and 1000°C for 10, 20, and 10 hours, respectively. The subsequent increase in temperature or increase in time of annealing results in a considerable samples composition change due to sublimation of cadmium oxide. After annealing, each sample was homogenized and studied by the XRD method. The annealing was performed at each temperature until samples’ consistent phase composition was attained.

X-ray powder diffraction patterns of the samples were recorded at room temperature using Rigaku Ultima IV and modernized electronically controlled DRON-3 diffractometers, using Ni-filtered CuKα radiation at a scanning rate of 2° (2θ)/min in the range 25° ≤ 2θ ≤ 60°. To obtain data for crystal structure refinement by the Rietveld procedure, the samples were scanned in steps of 0.05° (2θ) in the range 15° ≤ 2θ ≤ 140° with a counting time of 3s/step. The data were analyzed with the program FullProf.2k and the WinPLOTR graphical interface. As starting data in the refinement, atomic coordinates in the structure were taken [15].

A JSM-6490LV (JEOL, Japan) scanning electron microscope and INCA Penta FETx3 (Oxford Instruments, England) energy-dispersive spectrometer were used for the samples’ investigation. The data for elemental analysis were collected in 38 fragments of the sample surface.

IR spectra of the samples dispersed in KBr tablets were recorded in the wavenumber range from 400 to 4000 cm⁻¹ with a TENSOR 27 (Bruker Optics) Fourier transform infrared spectrophotometer. The materials and methods section should contain sufficient detail so that all procedures can be repeated. It may be divided into headed subsections if several methods are described.

3. Results and Discussion

The X-ray patterns of the samples Lax2−Cd3+MoO6−x/2 are represented in Figure 1. The unmodified lanthanum molybdate is the single-phase sample with a tetragonal structure (space group, I41/acd). The substitution of cadmium for lanthanum results in the formation of the cubic fluorite-like structure in the full range of compositions. The reflections of Lax2MoO6 with the tetragonal structure are observed in the X-ray patterns in the range x = 0–0.5 and their intensities decrease as x value increases. The cadmium oxide phase forms in the range x = 0.2–1.0. The X-ray patterns of the samples with x ≥ 0.8 also contain the reflections of cadmium molybdate.

The content of lanthanum molybdate with tetragonal structure linearly decreases with the increase of cadmium in
a sample (see Figure 2). At the same time, the content of the cubic fluorite-like phase reaches ≈94% in the sample with $x = 0.6$. A decrease in the cubic phase content is caused by the formation of cadmium molybdate in the samples with higher $x$ values. The phase of cadmium oxide appears in the X-ray pattern of the sample with $x = 0.2$ and its content reaches 8% at $x = 1.0$.

The substitution of cadmium for lanthanum has not caused a substantial change of unit cell parameters of La$_2$MoO$_6$ with the tetragonal structure (see Table 1). Evidently, the solid solutions with the tetragonal phase La$_2$MoO$_6$ have not formed in the system La$_{2-x}$Cd$_x$MoO$_{6-x/2}$ or the region of their existence is very narrow.

All synthesized samples contained at least two phases. It is known that a region of single-phase solid solutions expands as temperature increases. So, an increase in temperature will presumably result in the formation of the single-phase samples in this system. To prevent cadmium oxide sublimation which occurs at high temperatures, the atmosphere with greater pressure of volatile component has to be created as it was made in the study [17] for CdY$_3$Mo$_3$O$_{16}$ single crystal growing.

The samples La$_{1.4}$Cd$_{0.6}$MoO$_{5.7}$ with the highest quantity of the cubic structure were investigated using a scanning electron microscope. In the conditions of synthesis, the powders with the particles’ size of about 1 µm were produced (see Figure 3). According to the result of local energy-dispersive X-ray spectroscopic microanalysis, the general composition of the sample corresponds to the formula La$_{1.4}$Cd$_{0.58}$Mo$_{1.08}$O$_{5.86}$. So, there is a good correlation between the theoretical and the experimentally determined composition of the sample. It reveals that the sublimation of volatile components did not occur during the synthesis.

The dependence of the cubic fluorite-like structure unit cell parameter on cadmium content has three regions (see Figure 4). The parameter equals 11.248(2) Å and does not change when the quantity of cadmium is at minimum ($y = 0.1–0.2$) and then it decreases to 11.200(2) with increasing cadmium content in the range of $x$ from 0.2 to 0.8.

The value of the unit cell parameter of fluorite-like phase and La$_{5.03}$Mo$_{6.16+\delta}$ lanthanum molybdate (11.2400(3) Å [9]) is close. The substitution of lanthanum with cadmium, like reduction [9], leads to a decrease in the cell parameter.

When the unit cell parameter of the cubic structure starts declining, the reflections of the cadmium oxide phase appear in the X-ray patterns of the samples. In the region where the reflections of the cadmium molybdate phase are observed ($x > 0.8$), the unit cell parameter remains unchanged.

Lanthanum molybdate with the tetragonal structure transforms into the cubic fluorite-like phase of La$_{5.03}$Mo$_{6.16+\delta}$ in which the content of molybdenum is higher (by 4.5% if
recalculating per molybdenum anhydride) than in La2MoO6. An assumption was made earlier that, in such compounds, the atoms of cadmium [16] or REE [18] can substitute (to a small extent) for the atoms of molybdenum in the Ln2Mo3O16+δ structure. According to this, a value of the unit cell parameter in this system depends on three factors simultaneously: first, the smaller ionic radius of cadmium than lanthanum (the values of ionic radii for coordination number 8 are 1.16 Å (La3+) and 1.10 Å (Cd2+) [19], respectively); second, the decrease in the amount of stoichiometric oxygen according to the electroneutrality principle; and the last, the cadmium atoms localization in the molybdenum sites of the crystal structure. The first two factors obviously result in the decrease of the unit cell parameter, but the reduction in oxygen content has a greater influence. Only the occupation of the molybdenum sites by the cadmium atoms can influence the expansion of the unit cell.

The first region of the plot of the unit cell parameter dependence on composition corresponds to formation and stabilization of the cubic phase which probably is due to the substitution of cadmium for lanthanum or the occupation of the molybdenum sites by cadmium occurring under the following schemes:

\[
\text{La}^{3+} + 1/2\text{O}^{2-} \rightarrow \text{Cd}^{2+} + 1/2\text{V}_0 \quad (1).
\text{Mo}^{6+} + 2\text{O}^{2-} \rightarrow \text{Cd}^{2+} + 2\text{V}_0 \quad (2).
\]

A redistribution of molybdenum from the tetragonal structure to the cubic one also takes place. The edge of the top region possibly determines the limit of cadmium localization into the molybdenum sites.

The region where the unit cell parameter decreases linearly corresponds to the substitution of cadmium for lanthanum occurring in the formed cubic phase under Scheme 1. The limit of this substitution is determined by the edge of the bottom region in the dependence and the appearance of the cadmium molybdate phase.

The CdY3Mo3O16 structure was used as the initial model [17]. The crystal structure refinement shows (see Figure 5) that the cubic phase is crystallized in the space group Pn-3m with a double unit cell of fluorite.

Atomic coordinates and isotropic thermal parameters are represented in Table 2. Different atomic ratios in the molybdenum and REE sites of the crystal structure were compensated by the localization of a part of the cadmium atoms in the molybdenum sites. Then, a cadmium atoms redistribution refinement among the lanthanide sites showed that cadmium fully occupies the 8c position. After that, the occupation of the molybdenum site was refined. With an increase in cadmium content, the unit cell parameter of the cubic structure decreases, but metal-oxygen interatomic distances decrease only for the 8c position reaffirming cadmium localization in this site (see Table 3).

The longer Mo–O interatomic distances in the cubic structure in comparison with the tetragonal one (1.779(1) Å [6]) signify a partial localization of cadmium in the molybdenum site and a distortion of the tetragonal environment.

IR spectra of lanthanum molybdate with the tetragonal and stabilized cubic structures are represented in Figure 6. According to work [20], the IR-spectrum of lanthanum molybdate with the tetragonal structure displays absorptions bands which can be assigned to internal vibrations of isolated MoO4 group: asymmetric stretching ν3 mode at 872 and 779 cm⁻¹ and asymmetric bending ν4 mode at 501 cm⁻¹. In the spectrum of La1.4Cd0.6MoO5.8 with the cubic structure, the bands observed at 893 and 853 cm⁻¹, 816 and 772 cm⁻¹, and 464 cm⁻¹ correspond to symmetric stretching ν1 mode, asymmetric stretching ν3 mode, and asymmetric bending ν4 mode, respectively [20].

IR spectra of cubic lanthanum molybdate modified by cadmium are similar to spectra of neodymium molybdate Nd3Mo3O16+δ and its solid solutions [21] as well as a phase of cubic double cadmium and gadolinium molybdate [16] (see Table 4).
A larger number of active vibrations in the IR spectra of the La$_{1.4}$Cd$_{0.6}$MoO$_{5.7}$ phase compared to La$_2$MoO$_6$ are possibly due to the fact that, in the structure of the cubic phase, MoO$_4$-tetrahedra are connected in a special way through the ions of the rare-earth elements (see Figure 7).

Maximal content of the cubic phase, 94%, was found in the sample La$_{2-x}$Cd$_x$MoO$_{6-x/2}$ with $x = 0.6$. This sample also contains the cadmium oxide phase. The sample with $x = 0.5$ consists of lanthanum molybdate with cubic and tetragonal structures and cadmium oxide phase. The simultaneous existence of lanthanum molybdate with tetragonal structure and cadmium oxide makes further interaction between these phases possible. An effort to obtain single-phase samples by increasing molybdenum content was made as molybdenum content in lanthanum molybdate with the tetragonal structure is lower than that in the cubic one. For this purpose, series of samples La$_{2-x}$Cd$_x$Mo$_{1+y}$O$_{5.75+3y}$, $y = 0.1, 0.2$ were additionally investigated. According to X-ray analysis, increase in molybdenum content in the samples results in a decrease of the reflections' intensities of the phases foreign to lanthanum molybdate (see Figure 8).

With the addition of the redundant quantity of molybdenum in the samples La$_{1.5}$Cd$_{0.5}$Mo$_{1+y}$O$_{5.75+3y}$, the unit cell parameter of the cubic phase decreases from 11.2170(4) Å to 11.2011(5) Å. This change may be related to the occupation of the molybdenum sites by the bigger atoms of cadmium due to the lack of molybdenum atoms in the sample [16]. With increased molybdenum, content cadmium passes from the molybdenum sites to the lanthanum ones.

The heterovalent substitution of cadmium for lanthanide in tetragonal and monoclinic molybdates Ln$_2$MoO$_6$ leads to the cubic fluorite phase stabilization in a similar way as it occurs in the process of reduction by hydrogen. Thus, the oxygen content in the structure is crucial for the stabilization of the cubic fluorite-like phase.

The reduction of molybdenum by hydrogen in Ln$_2$MoO$_6$ molybdates leads to an increase of its ionic radius and creates prerequisites for a formation of coordination polyhedra for molybdenum ions with a larger coordination number than in the tetrahedron. It should be noted that, for reduced compositions, molybdenum in the lower oxidation states distributes statistically over the cationic positions of the fluorite structure while stabilized by heterovalent

### Table 2: Rietveld structure refinement of the La$_{2-x}$Cd$_x$MoO$_{6-x/2}$.

| Content Cd ($x$) | 0.5 | 0.6 |
|------------------|-----|-----|
| Impurity phase   | La$_2$MoO$_6$, CdO | CdO |
| Lattice parameters $a$, (Å) | 11.2170(4) | 11.2004(6) |
| Atom coordinates, $(x, y, z)$ | | |
| La1, 12(e)       | 0.0097(7); 0; 0; 0/4 | 0.0083(8); 0; 0; 0/4 |
| (La/Cd)2, 8(c)   | 0; 0; 0/4 | 0; 0; 0/4 |
| Mo/Cd, 12(d)     | 0.110(3); 0.110(3); 0.110(3) | 0.108(3); 0.108(3); 0.108(3) |
| O1, 16(f)        | 0.577(3); 0.371(2); 0.844(3) | 0.574(2); 0.375(2); 0.850(3) |

### Position occupancy

| (La/Cd)2 | La 4; Cd 4 | La 2.93; Cd 5.07 |
| Mo/Cd   | Mo 10.8(4); Cd 1.33 | Mo 10.7(2); Cd 1.33 |

### Reliability factors

|          | $x = 0.5$ | $x = 0.6$ |
|----------|-----------|-----------|
| $R_p$    | 8.76      | 10.3      |
| $R_{wp}$ | 11.7      | 14.3      |
| $R_{exp}$| 9.33      | 12.65     |
| $\chi^2$ | 1.57      | 1.28      |
| $R_B$    | 3.49      | 5.85      |
| $R_f$    | 4.44      | 6.36      |

### Table 3: Selected interatomic distances La$_{2-x}$Cd$_x$MoO$_{6-x/2}$ [Å].

| Interatomic distances | Mult. | $x = 0.5$ | $x = 0.6$ |
|-----------------------|-------|-----------|-----------|
| La1–O                 | x4    | 2.70(3)   | 2.71(3)   |
| (La/Cd)2–O            | x4    | 2.49(3)   | 2.51(3)   |
| Mo/Cd–O               | x4    | 2.09(3)   | 2.09(3)   |
| (La/Cd)2–O            | x6    | 2.43(3)   | 2.34(3)   |
| (La/Cd)2–O            | x2    | 2.14(3)   | 2.09(3)   |

Figure 6: FTIR-spectra of the La$_2$MoO$_6$ (1) and La$_{1.4}$Cd$_{0.6}$MoO$_{5.7}$ (2).
substitution compositions, molybdenum has a tetrahedral environment and locates orderly. This fact explains the absence of superstructural reflections on X-ray patterns for the reduced compositions and its formation in the case of cubic molybdates stabilized by heterovalent substitution.

4. Conclusions

(1) The cubic fluoride-like structure (space group, \( Pn-3n \)) in the system \( La_{2-x}Cd_xMoO_6 \) (0 ≤ \( x \) ≤ 1.0) was stabilized by the heterovalent substitution of cadmium for lanthanum.

(2) The content of lanthanum molybdate with the tetragonal structure decreases as the degree of the substitution increases.

(3) The maximum content, 94%, of the cubic structure was found in the sample with \( x = 0.6 \).

(4) The Rietveld refinement of the crystal structure has revealed that cadmium ions preferably occupy the lanthanum (8c) sites and to a significantly lesser degree, the molybdenum (12e) sites causing a decrease in \( La/Cd-O \) distances and an increase in \( Mo/Cd-O \) distances.

(5) The possibility of stabilizing the cubic structure of lanthanum molybdate by substitution of lanthanum with cadmium is of great importance for regulating the functional properties of the compound.

Data Availability

The XRD data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no financial and personal relationships with other people or organizations that can inappropriately influence their work; there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled "Investigation of the Heterovalent Substitution Cadmium for Lanthanum in Molybdate La_2MoO_6."

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