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Synthesis and structure investigation of ternary oxides based on molybdenum and lanthanum

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HIGHLIGHTS

- Samples of lanthanum–molybdenum pyrochlores $MgLa_2MoO_7$ and $CaLa_2MoO_7$ are synthesized.
- The X-ray diffraction study, SEM, IR and DTA investigations were carried out.
- Structural parameters of the samples at room and high temperature were determined.

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ABSTRACT

Compounds of the ternary oxides class with formulae $MgLa_2MoO_7$ and $CaLa_2MoO_7$ were synthesized by the citrate method. According to the SEM and X-ray analysis data the samples are referred to pyrochlore with a tetragonal ($MgLa_2MoO_7$) and monoclinic ($CaLa_2MoO_7$) crystal lattice. At the temperature of 900 °C the compound $CaLa_2MoO_7$ is subjected to phase transition from the monoclinic crystal system to the cubic one. According to the differential thermal analysis data, this transition occurs through the intermediate states characterized by non-monotonic changes of lattice parameters of the unit cell. In general, the compounds are characterized by minor structural distortions compared with the cubic structure of pyrochlore.

1. Introduction

Ceramic materials based on rare earths are used in various branches of modern industry. The systems of ternary oxides based on molybdenum and alkali-earth elements are among them. The compounds exhibit a number of interesting magnetic, transport and structural properties. The cubic system is typical for the crystalline structure of these substances; in this case they as a rule crystallize in the structure type of perovskite, pyrochlore, defect fluorite, etc.

Complex oxides with the structure of pyrochlore are distinguished by a diverse composition due to a substantial capacity towards different isomorphic inclusions. This circumstance allows to vary their composition in a wide range, and hence their properties, too. Rare earth, RE, pyrochlores are also used as super-ionics, solid electrolytes, efficient catalysts as well as piezo- and ferroelectrics. RE pyrochlores are a group of minerals related to niobium–tantalum complex oxides. They have a variable composition and an approximate formula $\{Ca[Na,REE,U]\}_{\Sigma=2}\{Nb[Ta,Ti]\}_{\Sigma=2}\{O_6(OH,F)\}_{\Sigma=7}$. In this case Na, Ca, rare earth elements and U are present in the form of isomorphous impurities as well as the adsorbed oxides.

The parent of the family of pyrochlores is calcium pyroniobate $Ca_2Nb_2O_7$. The structure of pyrochlore is a superstructure of

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fluorite, the parent of which is calcium fluoride CaF_2 [1]. According to the literature, pyrochlores crystallize in the cubic system with the space group symmetry $Fd\bar{3}m$ [2–12] and $Fm\bar{3}m$ [13–15]; however, sufficiently large number of them has a lower symmetry of the unit cell [16–29]. In compounds of $A_2B_2O_7$ type the belonging to the structure of pyrochlore is determined by the ratio of ionic radii of cations r_A/r_B over the range of 1.46–1.78 [30,31]. Changes of the ratio to the smaller part leads to the structure of a defective fluorite; on increasing the ratio, the compound crystallizes in the monoclinic system. In the presence of partial cation substitution the pattern can be complicated, especially when the ionic radii are significantly different. As a result of such distortions of the unit cell, pyrochlores with the trigonal [16,17], tetragonal [18–20], orthorhombic [21–24], and monoclinic system [25–29] can be formed.

This work presents the results of the synthesis and structural investigations of compounds based on molybdenum, lanthanum and alkaline earth elements having the general formula of $MeLn_2MoO_7$, where Me is an alkaline earth metal, Ca and Mg, while Ln is a rare earth element, La. This research is a part of cycle of investigations of compounds on the base of rare-earth elements (La, Ce–Nd, Sm–Lu), alkali-earth elements (Mg, Ca, Sr, Ba) and transitional metals (Mo and W). Thus, the *s*-, *d*- and *f*-elements are presented in the structure of the compounds. The molybdenum and tungsten are analogues in Periodic table but their electronic structures are different. The molybdenum has stable semi-occupied *d*-orbital due to 5*s*-electron transition to the 4*d*-sublevel. In the electronic structure of the tungsten such transition is absent as a result of the lanthanide shielding. Therefore, the compounds on the base of these metals should have different properties.

At present, the citrate method is widely used in the synthesis of the various substances on the base of molybdates [32–40]. This method allows to achieve high homogeneity and to obtain nanosized materials. The modifications with using of gel polymer matrices are applied to improve the quality of the materials.

The structural properties of the compounds $MgLa_2MoO_7$ and $CaLa_2MoO_7$ obtained in this work were not described previously. Earlier the synthesis and structure investigations of related compounds $SrLa_2WO_7$ and $BaLa_2WO_7$ were reported [41–44].

2. Materials and methods

2.1. Synthesis

For the synthesis $MgCO_3$ and La_2O_3 of “pure” quality, MoO_3 of “analytically pure” quality and $CaCO_3$ of “chemically pure” quality were used. The lanthanum oxide was purified additionally by dissolving in nitric acid and precipitation with oxalic acid. The compounds of alkaline earth and rare earth metals were precalcined before the synthesis to remove the absorbed moisture and carbon dioxide. To carry out the synthesis the citrate method was used.

The initial oxides taken in stoichiometric ratios were dissolved in distilled water by means of complexing compound (citric acid); the nitric acid was used for acidification of the medium. The obtained solution of citrates was evaporated at 473–573 K to give a solid residue which represent a resin-like product of a dark-brown colour.

Calcination of the obtained precursors was carried out in the air in several stages at controlled temperature in Nabertherm N7/H oven, each stage lasted 5–6 h at 873, 973, 1173, 1273 K, the temperature being increased gradually; and at 1423 K in three stages, 8 h each. After each stage the product of calcination was carefully triturated in an agate mortar.

2.2. Measurements

The formation of new phases at each stage of calcination was monitored by the X-ray diffractometry. Diffraction patterns of the synthesized samples at different stages of annealing were registered by means of an X-ray diffractometer DRON-2 using a cobalt anode.

The X-ray analysis of the structure of obtained compounds was carried out from room temperature in an X-ray diffractometer XRD6000 (Shimadzu) with a high-temperature add-on device HA1001 (over the temperature range of 293–1173 K, with a step of 100 K). The measurements were performed over the range of angles 2θ from 20° to 60° with a pitch of 0.02° at radiation of CuK_α, $\lambda = 1.54056$ Å. The crystal structure of the synthesized compounds was determined by the indexing and full-profile X-ray analysis with DICVOL06, TREOR90, ITO and Endeavour Crystal Impact 1.7 programs.

The scanning electron microscopy (SEM), energy-dispersive (EDS) and wave-dispersive analysis (WDS) of the samples carried out in an electron-probe microanalyzer JXA-8230 (JEOL). Most of the SEM images were made in the backscattered electron mode (COMPO mode), which minimizes deterioration of the resolution and gives pictures of powders of a better quality. The energy- and wave-dispersive analyses of characteristic X-ray radiation of the sample were performed at an accelerating voltage (25 kV) of the electron beam and currents of the probe up to 25 nA. The wave-dispersive analysis of the samples was performed at magnification ×2000 in the mode of mapping on the chemical elements. This mapping allows to evaluate the local concentration of the various elements around peculiarities of the microstructure.

The infrared spectra of the samples were measured in an infrared spectrometer Shimadzu 8400S over the wave-number range of 420–1200 cm^{-1}.

The investigation of dielectric properties (dielectric permittivity and loss-angle tangent) of the synthesized powder samples was carried out at room temperature by measurement of electrocapacity of the samples on R2M-18 apparatus with waveguide-dielectric resonator in Division of measurement of electromagnetic parameters of materials at high and superhigh frequencies of Siberian State Scientific-Research Institute of Metrology (Novosibirsk, Russian Federation).

Thermal investigations by DTA and TGA methods have been carried out in a synchronous thermal analyzer (LabSys evo, SETARAM) at a heating rate 10 deg/min in an argon atmosphere using a platinum crucible over the range of 293–1273 K.

3. Results and discussion

3.1. Structure refinements

Compounds of calcium–lanthanum molybdate and magnesium–lanthanum molybdate with formulas $CaLa_2MoO_7$ and $MgLa_2MoO_7$ were obtained. According to the X-ray investigations, the compound $CaLa_2MoO_7$ has a monoclinic (pseudocubic) system with the space group C2/c. Formation of monoclinic pyrochlores have already been observed in the compounds containing lanthanides such as $Pr_2Ti_2O_7$ [45–47], $Gd_2Zr_2O_7$ [48–50], etc., including the space group C2/c [27–29].

In Fig. 1a, diffractograms of the obtained $CaLa_2MoO_7$ sample at room temperature, at intermediate temperatures 673 K and 1073 K, and at the temperature of 1173 K are represented. It can be seen that at room temperature the peaks characteristic of the cubic system are split into a number of very closely placed peaks. Consequently, the crystal structure of the sample is slightly distorted in comparison with the cubic lattice, and can be described as a pseudocubic one. In the other diffractograms of the sample taken at an interval of 100 K,