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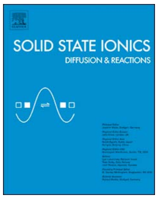

Kinetic aspects of the synthesis of $Ln_{6-x}MoO_{12-\delta}$ (Ln = Sm, Ho -Yb; x = 0, 0.5) rare-earth molybdates using mechanical activation of oxides

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A B S T R A C T

The synthesis of the Ln_6MoO_{12} (Ln = Sm, Ho - Yb) (3:1) rare-earth molybdates from binary oxides at room temperature has been studied by XRD and electron spin resonance spectroscopy (ESR). The mechanical activation of $3Ln_2O_3 + MoO_3$ (Ln = Sm, Ho, Yb) mixtures containing unmilled or premilled MoO_3 initiates the formation of Ln_6MoO_{12} (Ln = Sm, Ho - Yb) at room temperature, which is accompanied by a reduction in the ESR signal from Mo^{5+} paramagnetic ions located on the surface of the activated MoO_3 and, hence, by a reduction in the amount of MoO_3 in the mixture, due to reaction with Ln_2O_3 (Ln = Sm, Ho, Yb)·The major phase resulting from the mechanochemical synthesis is a cubic phase with the bixbyite structure ($Ia\bar{3}$, no. 206) for $Ln_{6-x}MoO_{12-\delta}$ (Ln = Dy –Yb; x = 0, 0.5) and the Sm_2O_3 type structure (*C 2/m,* no. 12) for Ln_6MoO_{12} (Ln = Gd, Sm).

The high-temperature synthesis of $Ln_{6-x}MoO_{12-\delta}$ (Ln = Ho – Yb; x = 0, 0.5) and $Ho_{10}Mo_2O_{21}$ from precursors prepared at room temperature has been studied at 1200 °C and heat treatment times of 4, 40, 80, and 160 h. The bixbyite phase disappears because it is metastable and is formed due to kinetic factors in the stability field of lower symmetry phases: tetragonal (T) and rhombohedral ($R\bar{3}$). We have located the stability range of the rhombohedral ($R\bar{3}$) phase as a function of Ln below 1200 °C using different heating time.

We have found conditions for the synthesis of the tetragonal phase T, which exists only in the case of the intermediate lanthanides. The tetragonal phase in phase-pure form has been synthesized for the first time via prolonged (160 h) heat treatment of $Ho_{10}Mo_2O_{21}$ at 1200 °C.

The electrical conductivity of the samples with different % of tetragonal phase has been measured by impedance spectroscopy in dry and wet air. The Arrhenius plot of conductivity for pure tetragonal phase has the form of straight line over the entire temperature range studied, 440–900 °C ($E_a = 1.37$ eV, $\sigma_{600^\circ C} = 1 \times 10^{-5}$ S cm^{-1}) in dry and wet air. The absence of electrode dispersions at low frequencies and conductivity growth in a wet air makes us assume the predominantly electronic conductivity type of the $Ho_{10}Mo_2O_{21}$ tetragonal phase in the temperature range 440–900 °C. In multiphase samples surface electronic conductivity is observed up to 620–650 °C in wet air, which is associated with the presence of defects at grain boundaries of crystallographically related phases (bixbyite, rhombohedral and tetragonal phases).

1. Introduction

Mixed (ionic–electronic and protonic–electronic) conductors having comparable and high ionic and electronic conductivities are important materials necessary for addressing a variety of applied issues, including the development of cathode and anode materials for solid oxide fuel cells (SOFCs), electrode materials for chemical gas sensors, and oxygen-ion- and proton-conducting membranes for oxygen and hydrogen separation from air and for the selective catalytic oxidation of hydrocarbons [1–3]. The Ln_6MoO_{12} (Ln = RE, Y) molybdates are known to differ from other molybdates of the Ln_2O_3-MoO_3 systems in that Mo^{6+} is the most stable in these compounds [4,5]. Because of this, they hold the greatest promise for the preparation of mixed conductors with the highest ionic and/or protonic conductivity among the known rare-earth molybdates.

The Ln_6MO_{12} (M = Mo, W) - based molybdates and tungstates were

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Table 1
Properties and the approximate phase compositions of the samples at 1200 °C with different heating duration.

Sample no.	Composition	Synthesis temperature, °C and heating duration, hrs	Color	Relative density, %	Phase ratios	Unit-cell parameters, Å
1	$Yb_6MoO_{12-\delta}$	1200 °C - 4	Lemon	65.86	100% R	a = 9.614(2) c = 9.170(2)
2	$Yb_6MoO_{12-\delta 1}$	1200 °C - 40	Lemon	65.53	100% R	a = 9.606(2) c = 9.163(2)
3	$Tm_6MoO_{12-\delta}$	1200 °C - 4	Lemon	–	100% R	a = 9.655(3) c = 9.204(3)
4	$Tm_6MoO_{12-\delta 1}$	1200 °C - 40	Lemon	71.48	100% R	a = 9.646(2) c = 9.205(2)
5	$Er_6MoO_{12-\delta}$	1200 °C - 4	Pink		50%B′ + 50%R	
6	$Er_6MoO_{12-\delta}$	1200 °C - 40	Pink		100% R	a = 9.695(4) c = 9.242(4)
7	$Ho_6MoO_{12-\delta}$	1200 °C - 4	Yellow		30% B′ + 40%R′ + 30% T	
8	$Ho_6MoO_{12-\delta}$	1200 °C - 40	Yellow		10% B′ + 20% R′ +70% T	
9	$Ho_6MoO_{12-\delta}$	1200 °C - 80	Yellow		50%T + 50% R	
10	$Ho_6MoO_{12-\delta}$	1200 °C - 160	Yellow		40%T + 60% R	
11	$Ho_{5.5}MoO_{11.25}$	1200 °C - 4	Yellow		60% R′+ 40% B′	
12	$Ho_{5.5}MoO_{11.25}$	1200 °C - 40	Yellow	82.1	89% T + 4% B′ + 7% R′	T: a = 5.277(3) c = 5.261(5)
13	$Ho_{5.5}MoO_{11.25}$	1200 °C - 80	Yellow		18%T + 82%R	
14	$Ho_{5.5}MoO_{11.25}$	1200 °C - 160	Yellow	75.3	15%T + 85%R	
15	$Ho_{10}Mo_2O_{21}$	1200 °C - 40	Yellow		8% B′ + 14%R′ + 78%T	
16	$Ho_{10}Mo_2O_{21}$	1200 °C - 80	Yellow		4% B′ + 7%R′ + 89%T	
17	$Ho_{10}Mo_2O_{21}$	1200 °C - 160	Yellow	74.7	100%T	a = 5.277(2) c = 5.261(4)

R - rhombohedral phase ($R\bar{3}$).
T - tetragonal phase.
B′ - metastable bixbiyte ($Ia\bar{3}$).
R′- metastable rhombohedral phase ($R\bar{3}$).

studied previously as materials for dyes and phosphors [6–12], but in recent years more attention focused on the electrochemical properties of these materials. In particular, La_6WO_{12} - based solid solutions, which are known to be mixed protonic–electronic conductors with high protonic conductivity, were discovered by Shimura et al. [13] rather long ago, in 2001, and have been most intensely studied in the last decade [14–22]. At present, it is these materials that offer the highest protonic conductivity among the Ln_6MO_{12} (M = Mo, W) mixed conductors studied so far. Unfortunately, the La_6WO_{12} - based materials have relatively low stability [23,24], so there is currently great practical interest in a search for new compositions based on rare-earth molybdates and tungstates, including multiphase materials and core–shell microstructures [25–27].

Shlyakhtina et al. [28] and Savvin et al. [29,31] obtained $Ln_{6-x}Zr_xMoO_{12+\delta}$ (Ln = La, Nd, Sm, Dy) Zr-doped molybdates with mixed electronic–ionic (protonic) conductivity. A La_6MoO_{12} - based solid solution of composition $La_{5.8}Zr_{0.2}MoO_{12.1}$ showed high stability during thermal cycling under oxidizing and reducing conditions. Only the highest – frequency semicircle was observed in impedance spectroscopy data for $La_{5.8}Zr_{0.2}MoO_{12.1}$ in dry and wet atmospheres. Interestingly enough, $La_{5.8}Zr_{0.2}MoO_{12.1}$ was found to have an unusual, core–shell microstructure [28], in combination with stable conductivity during thermal cycling under oxidizing and reducing conditions. The formation of such microstructure seems to be related to the rich polymorphism of the Ln_6MoO_{12} (Ln = La-Lu) molybdates [32], which has not yet been fully investigated. Zirconium doping improves the stability of these materials to reduction, but it also decreases their ionic (protonic) conductivity by about one order of magnitude [33].

This led us to focus on the synthesis of various polymorphs of Zr-free molybdates of intermediate and heavy lanthanides: Ln_6MoO_{12} (Ln = Sm, Ho, Er, Tm, Yb). Our results may open up the possibility of producing oxygen-ion- and proton-conducting materials having an unusual, core–shell microstructure, which can only be formed if a few polymorphs are involved.

The synthesis of the Ln_6MoO_{12} (Ln = Sm, Ho, Yb) molybdates at room temperature was followed using X-ray diffraction (XRD) and electron spin resonance spectroscopy (ESR). Mechanical activation of MoO_3 is known to cause the formation of Mo^{5+} paramagnetic centers, whose concentration can be determined by ESR [34–38]. In this work, we analyze the dynamics of the Mo^{5+} paramagnetic response during the room-temperature mechanochemical synthesis of the Ln_6MoO_{12} (Ln = Sm, Ho, Yb) molybdates and discuss the formation kinetics of the rare-earth molybdates at relatively low temperatures (1200 °C). In the case of the $Ho_{6-x}MoO_{12-\delta}$ (x = 0.5) molybdate (on the boundary between two types of phase relations in the rare-earth molybdate systems [37]), a core–shell material can also be obtained. In this work we examine the conductivity of the $Ho_{6-x}MoO_{12-\delta}$ (x = 0.5) low-temperature polymorphs prepared at 1200 °C and different firing times. In this study, we have found conditions for the synthesis of the phase-pure tetragonal polymorph, which is difficult to obtain single-phase because of its low stability.

2. Experimental

All of the rare-earth oxides and molybdenum oxide used in our preparations were 99.9% pure. The $Ln_6MoO_{12-\delta}$ (Ln = Sm, Ho - Yb)