

Phase equilibria in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system, Crystal structures and properties of new triple molybdates $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$

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ARTICLE INFO

Article history:

Received 28 August 2014

Received in revised form

27 January 2015

Accepted 30 January 2015

Available online 31 January 2015

Keywords:

Cesium

Zinc

Zirconium

Triple molybdates

Crystal structure

X-ray diffraction

IR and Raman spectra

Conductivity

ABSTRACT

Subsolidus phase relations in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system were determined and two new compounds, $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$, were obtained. The structure of $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ ($a=5.7919(1)$ Å, $c=8.0490(3)$ Å; space group $P3m1$; $Z=0.5$; $R=0.0149$) belongs to the layered glaserite-like $\text{KAl}(\text{MoO}_4)_2$ structure type where the octahedral Al^{3+} positions are statistically occupied by $0.5 \text{Zn}^{2+} + 0.5 \text{Zr}^{4+}$. The second triple molybdate, $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ ($a=13.366(1)$ Å, $c=12.253(3)$ Å, space group $R\bar{3}$, $Z=3$, $R=0.0324$), is isostructural to $\text{Cs}_2\text{MnZr}_2(\text{MoO}_4)_6$ and $\text{Cs}_2\text{M}_2\text{Zr}(\text{MoO}_4)_6$ ($M=\text{Al}, \text{Fe}$) and contains a mixed 3D framework built of MoO_4 tetrahedra and $(\text{Zn}, \text{Zr})\text{O}_6$ octahedra sharing common vertices. Cesium cations are located in large channels of the framework. The latter compound undergoes a first-order phase transition at 723 K with considerable increasing its ionic conductivity.

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1. Introduction

Complex oxides, phosphates, molybdates, tungstates of Zr and Hf, for example, $(\text{Zr}, \text{Y})\text{O}_{2-x}$, NASICON-type compounds [1,2], AM_2O_8 , $\text{Zr}_2(\text{MO}_4)(\text{PO}_4)_2$ ($A=\text{Zr}, \text{Hf}$; $M=\text{Mo}, \text{W}$) [3,4], $\text{Ag}_4\text{Me}_2\text{Zr}(\text{MoO}_4)_6$ ($\text{Me}=\text{Mg}, \text{Mn}, \text{Co}, \text{Zn}$) [5], etc. are of a great practical interest due to their ionic conductivity, negative thermal expansion, immobilization of radionuclides and other properties. Typical crystal structures of these compounds are open frameworks or layers built of AO_6 octahedra ($A=\text{Zr}, \text{Hf}$) sharing corners with $\text{Mo}(\text{P})\text{O}_4$ tetrahedra where cavities are occupied by monovalent cations. Most frequent partners of Zr^{4+} and Hf^{4+} in the structures are medium-sized cations of divalent and trivalent metals (Cd, Mn, Zn, Cu, Co, Ni, Mg, Fe, Ga, Sc, In); the largest monovalent cation in this case is Rb^+ . Of these series of the

partner cations, original crystal-chemical features are characteristic of Zn^{2+} manifesting tetrahedral coordination along with octahedral one. These peculiarities of Zn^{2+} influence physical properties of double molybdates $\text{Cs}_2\text{Zn}(\text{MoO}_4)_2$, $\text{Rb}_4\text{Zn}(\text{MoO}_4)_3$, and $\text{K}_4\text{Zn}(\text{MoO}_4)_3$ undergoing distortive phase transitions and have ferroelastic and luminescent properties [6–8]. The above-mentioned interesting features of Zr, Hf and Zn-containing compounds can be combined and expected for triple molybdates with these metals. In addition, cesium containing ternary molybdate systems with zirconium and compounds formed in them remain poorly studied yet. The present work reports a study of phase formation in the system $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$, preparation of two new Zn-containing triple molybdates $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ and their structure determinations.

2. Experimental

The starting reagents for preparing simple molybdates of Cs^+ , Zn^{2+} , and Zr^{4+} were Cs_2CO_3 , ZnO , ZrO_2 and MoO_3 (all of reagent grade).

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ent grade). Synthesis of Cs_2MoO_4 was carried out by the reaction $\text{Cs}_2\text{CO}_3 + \text{MoO}_3 = \text{Cs}_2\text{MoO}_4 + \text{CO}_2\uparrow$ at gradually increasing temperatures in the range 473–923 K for 100 h. The high-temperature modification of $\text{Zr}(\text{MoO}_4)_2$ was prepared by annealing the stoichiometric mixture of constituent oxides at 673–1023 K for 80 h; the low-temperature modification of zirconium molybdate was obtained using the technique described in [9]. ZnMoO_4 was prepared from a mixture of ZnO and MoO_3 by annealing at 773–1023 K for 100 h. The X-ray diffraction (XRD) characteristics of the prepared cesium, zirconium, and zinc molybdates are in accordance with those in the ICDD PDF-2 Data Base (cards # 00-024-0276, # 00-038-1466, # 01-072-0289, # 01-073-1331, # 00-035-0765, # 01-072-2153).

Subsolidus phase relations in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system at 773 K were established by the intersecting joins method [10,11]. Compounds from the boundary systems were preliminarily synthesized, tested for monophasity and used as starting substances for the preparation of samples. The subsolidus triangulation was found on the phase compositions of the samples corresponding to the interception points of all joins originating from the composition points of simple and double molybdates.

Polycrystalline $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ were obtained by annealing stoichiometric mixtures of simple molybdates up to 873 K (for the former) and 903 K (for the latter) for 40–80 h. Individuality and compositions of the phases was confirmed by XRD and, for $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$, by spectroscopic analysis.

Transparent layered crystals of new triple molybdates $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ (\mathbf{S}_1) and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ (\mathbf{S}_2) were grown by spontaneous flux crystallization using $\text{Cs}_2\text{Mo}_2\text{O}_7$ as a solvent. The heating of ground mixtures, their isothermal holding and slow cooling of the melts were controlled and kept automatically with an accuracy of ± 0.5 K. The cooling rate was 4 K h^{-1} from 973 K to 573 K; subsequent cooling to room temperature was conducted in a switched-off furnace. Crystals of $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ were grown from a mixture of 12.5 mol% $\text{Cs}_2\text{MoO}_4 + 25 \text{ mol% ZnMoO}_4 + 37.5 \text{ mol% Zr}(\text{MoO}_4)_2 + 25 \text{ mol% Cs}_2\text{Mo}_2\text{O}_7$. Crystals of $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ were prepared from a mixture of 30.77 mol% $\text{Cs}_2\text{MoO}_4 + 30.77 \text{ mol% ZnMoO}_4 + 30.76 \text{ mol% Zr}(\text{MoO}_4)_2 + 7.7 \text{ mol% Cs}_2\text{Mo}_2\text{O}_7$.

X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer (Bragg–Brentano geometry, $\text{Cu K}\alpha$ radiation, secondary monochromator, 2θ range 10–70°, scan step 0.02°, exposition 0.5 s per point). XRD patterns at 673 K and 823 K were registered using a Bruker D8 Advance diffractometer with an Anton Paar HTK-16 high temperature chamber ($\text{Cu K}\alpha$ radiation, secondary monochromator, maximal angle $2\theta = 50^\circ$, scan step 0.02°, MgO as an external standard).

Single crystal X-ray data for structure determination of $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ were collected with a Bruker–Nonius X8 Apex CCD area-detector diffractometer at room temperature using a standart procedure ($\text{Mo K}\alpha$ radiation, graphite monochromator, φ scans with scan step of 0.5°). The structure was solved and refined using SHELX97 program package [12].

The differential scanning calorimetric (DSC) analysis of the samples was carried out on a NETZCH STA 449C thermoanalyzer in the temperature range 298–873 K with the heating rate of 5 K min^{-1} .

Infrared absorption spectra of polycrystalline samples were recorded in the frequency region of 4000–250 cm^{-1} with a resolution of 4 cm^{-1} on a Bomem MB-102 IR Fourier spectrometer (Canada). The samples were prepared with potassium bromide (2 mg sample in 500 mg KBr) and pressed into discs. Raman spectra were measured in a field of 3600–100 cm^{-1} at a resolution of 4 cm^{-1} on a Bruker RFS 100/S Fourier Raman spectrometer. An Nd:YAG laser at a wavelength of 1064 nm was used as the source of spectrum excitation.

The electrical conduction, σ were measured under an argon atmosphere on a Novocontrol Beta-N impedance-analyzer in a ProboStat measuring cell using the double-contact method [13] in a frequency range of 0.3 Hz to 1 MHz on heating at 353–873 K with 2 K min^{-1} ; ceramic pellets were 10.15 mm in diameter and 2.43 mm in height.

3. Results and discussion

3.1. Subsolidus phase relations in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system

The boundary systems $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4$ and $\text{Cs}_2\text{MoO}_4\text{--Zr}(\text{MoO}_4)_2$ are characterized by the formation of double molybdates $\text{Cs}_2\text{Zn}(\text{MoO}_4)_2$, $\text{Cs}_6\text{Zn}_5(\text{MoO}_4)_8$ and $\text{Cs}_8\text{Zr}(\text{MoO}_4)_6$, $\text{Cs}_2\text{Zr}(\text{MoO}_4)_3$, respectively. The results obtained for these systems match those previously published [14–16]. Phase formation in the third boundary system $\text{ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ was tested for compositions 1:1 and 2:5. Low-temperature $\text{Zr}(\text{MoO}_4)_2$ was used for the synthesis. XRD of the samples annealed in the temperature range 723–873 K shows no intermediate phases in this system.

In order to find new triple molybdates, the subsolidus phase equilibria of the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system was studied and its triangulated phase diagram constructed (Fig. 1). Solid-state interactions between Cs_2MoO_4 , ZnMoO_4 , and $\text{Zr}(\text{MoO}_4)_2$ over wide ranges of temperature and concentration led to the formation of two new triple molybdates $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ (\mathbf{S}_1) and $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ (\mathbf{S}_2). Compound \mathbf{S}_1 was found at the intersection point of the $\text{Cs}_2\text{Zn}(\text{MoO}_4)_2\text{--Zr}(\text{MoO}_4)_2$ and $\text{ZnMoO}_4\text{--Cs}_2\text{Zr}(\text{MoO}_4)_3$ joins. The second triple molybdate (\mathbf{S}_2) locates at the $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4\text{--Zr}(\text{MoO}_4)_2$ join.

The phase relations in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system are shown in Fig. 1. Quasi-binary joins $\text{ZnMoO}_4\text{--}\mathbf{S}_1$, $\mathbf{S}_1\text{--Cs}_2\text{Zr}(\text{MoO}_4)_3$, $\mathbf{S}_1\text{--Cs}_6\text{Zn}_5(\text{MoO}_4)_8$, $\text{Cs}_2\text{Zr}(\text{MoO}_4)_3\text{--Cs}_6\text{Zn}_5(\text{MoO}_4)_8$, $\text{Cs}_6\text{Zn}_5(\text{MoO}_4)_8\text{--Cs}_8\text{Zr}(\text{MoO}_4)_6$, $\text{Cs}_2\text{Zn}(\text{MoO}_4)_2\text{--Cs}_8\text{Zr}(\text{MoO}_4)_6$, $\text{ZnMoO}_4\text{--}\mathbf{S}_2$, $\mathbf{S}_2\text{--Cs}_2\text{Zr}(\text{MoO}_4)_3$, $\mathbf{S}_1\text{--}\mathbf{S}_2$, and $\mathbf{S}_2\text{--Zr}(\text{MoO}_4)_2$ divide the system into nine secondary triangles.

It was found that $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ (\mathbf{S}_1) crystallized in the glaserite-like $\text{KAl}(\text{MoO}_4)_2$ structure type [17]. The results of indexing X-ray diffraction pattern of this phase are shown in Table 1.

The analysis of vibration spectra of $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and

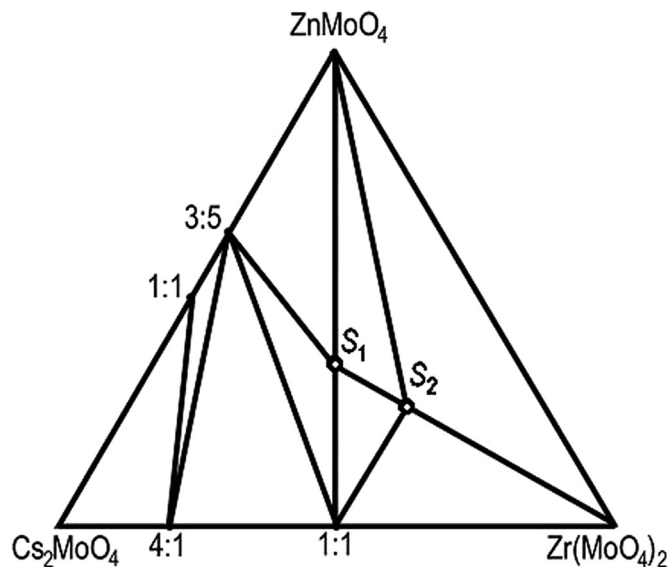


Fig. 1. Subsolidus phase relations in the $\text{Cs}_2\text{MoO}_4\text{--ZnMoO}_4\text{--Zr}(\text{MoO}_4)_2$ system at 773 K: $\mathbf{S}_1\text{--Cs}_2\text{ZnZr}(\text{MoO}_4)_4$ and $\mathbf{S}_2\text{--Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$.

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