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Preparation and properties of sodium iron orthooxomolybdates, $Na_xFe_y(MoO_4)_z$

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This work is dedicated to Prof. Dr.-Ing. Dr. h. c. Hartmut Fuess on the occasion of his 65th birthday

Abstract

Five different crystalline phases are established in the quaternary system Na–Fe–Mo–O with isolated MoO_4 tetrahedra: $NaFe(MoO_4)_2$, $Na_3Fe_2(MoO_4)_3$, α- and β-$NaFe_2(MoO_4)_3$ and $NaFe_4(MoO_4)_5$. The optimized conditions for sample preparation are described together with structural analyses by X-ray and neutron powder diffraction. The observed crystal structures are compared with known structure types. The high-temperature behaviour, thermal expansion, decomposition or congruent melting, is reported together with some preliminary characterisation of oxygen release as requested for catalytic activity in partial oxidation of hydrocarbons. Magnetic properties and antiferromagnetic ordering have been studied by magnetisation measurements and neutron diffraction.

Keywords: Sodium–iron molybdates; Anisotropic thermal expansion; Thermal stability; Antiferromagnetic ordering

1. Introduction

In the ternary system Fe–Mo–O exist three different orthomolybdates with the general formula $Fe_y(MoO_4)_z$, i.e., they crystallize in structures with isolated MoO_4 tetrahedra. These compositions are characterized by their $y : z$ ratios: (1) $y : z = 2$, Fe_2MoO_4 [1], (2) $y : z = 1$, β-$FeMoO_4$ [2], and (3) $y : z = 2 : 3$, $Fe_2Mo_3O_{12}$ [3]. This variety of stoichiometries for orthomolybdates with only the $y : z$ ratio as one degree of freedom is based on the stability of Fe- and Mo-ions in different oxidation states: Fe^{2+}/Mo^{4+} in Fe_2MoO_4, Fe^{3+}/Mo^{6+} in $Fe_2Mo_3O_{12}$, and a partial change from Fe^{2+}/Mo^{6+} into Fe^{3+}/Mo^{5+} is suggested for the temperature-induced transition from α- into β-$FeMoO_4$, based on X-ray photoelectron spectroscopy [4]. The variety in oxidation states results not only in a phase-rich system, but is also responsible for some properties like magnetism or catalytic activity: for example $Fe_2Mo_3O_{12}$ is a suitable model system for the geometry dependence of magnetic supersuperexchange coupling strengths, which allows to predict the ferrimagnetic structure correctly [5,6]. 3d-transitional metal molybdates are promising candidates for catalysts with high activity and selectivity in the partial oxidation of hydrocarbons [7]; for example, $Fe_2Mo_3O_{12}$ is used to promote the reaction of methanol to formaldehyde [8,9]. Losely packed network structures with sufficiently large channels and transitional metals in higher oxidation states are potential host materials for reversible alkaline ion insertion and extraction, accompanied by the reduction and oxidation of a metal ion, respectively, as required for application in rechargeable batteries. The investigation of valence-determined properties of iron orthooxomolybdates has now been extended to the quaternary system including additional sodium, $Na_xFe_y(MoO_4)_z$, which offers the $x : y$ ratio as a second degree of freedom. A systematic study of crystalline phases has revealed four different compositions, one existing in two polymorphs [10]: $NaFe(MoO_4)_2$, $Na_3Fe_2(MoO_4)_3$, $NaFe_4(MoO_4)_5$, α- and β-$NaFe_2(MoO_4)_3$. Lattice parameters and space groups are summarized in Ta-

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Table 1
Lattice parameters and space groups of all structures under consideration

Phase	Colour	Space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Ref.
$NaFe(MoO_4)_2$	green	C2/c	9.87	5.31	13.57	90	90.4	90	[11]
$NaFe(MoO_4)_2$	green	C2/c	9.870(3)	5.311(2)	13.546(4)	90	90.42(2)	90	[12]
α-$NaFe_2(MoO_4)_3$	black	$P\bar{1}$	6.9253(4)	6.9513(4)	11.0600(9)	80.205(6)	83.679(6)	80.818(5)	[10]
β-$NaFe_2(MoO_4)_3$	black	$P\bar{1}$	6.8340(10)	6.8930(10)	11.667(3)	76.23(2)	75.78(2)	87.76(2)	[10]
$NaFe_4(MoO_4)_5$	black	$P\bar{1}$	6.9337(3)	7.0196(4)	17.8033(8)	87.468(4)	87.615(4)	79.090(4)	[10]
$Na_3Fe_2(MoO_4)_3$	red-brown	C2/c	12.646(3)	13.685(3)	7.206(2)	90	112.56(3)	90	[10]

Table 2
Optimized conditions of synthesis and composition of the products

Educt composition	Temperature/K	Annealing time/days	Reaction product
$NaFe(MoO_4)_2$	883	10	97% (w/w) $NaFe(MoO_4)_2$, 3% (w/w) α-$NaFe_2(MoO_4)_3$
$NaFe_2(MoO_4)_3$	868	3[a]	98% (w/w) α-$NaFe_2(MoO_4)_3$, 2% (w/w) $NaFe_4(MoO_4)_5$
$NaFe_2(MoO_4)_3$	873	0.5[b]	pure β-$NaFe_2(MoO_4)_3$
$NaFe_4(MoO_4)_5$	978	6	94% (w/w) $NaFe_4(MoO_4)_5$, 6% (w/w) α-$FeMoO_4$
$Na_4Fe(MoO_4)_3$	853 or 863	4[c]	pure $Na_3Fe_2(MoO_4)_3$

[a] Followed by cooling to room temperature in 4 days.
[b] After 12 h at 600 °C the sample was slowly cooled down to 570 °C. The intermediate composition was 70% (w/w) β-$NaFe_2(MoO_4)_3$, 29% (w/w) α-$NaFe_2(MoO_4)_3$ and traces of $NaFe_4(MoO_4)_5$. After 2 additional days at 600 °C and successive quenching of the quartz tube in water the pure material was obtained.
[c] Note that a different composition of educts was used. The reaction product was inhomogeneous, and a white rim of α-Na_2MoO_4 could easily be separated from red-brown $Na_3Fe_2(MoO_4)_3$.

ble 1. The conditions of synthesis for samples with the highest obtained purity are reported in the following section, together with phase analyses by X-ray and neutron powder diffraction. All crystal structures are described as networks of [FeO_6]-octahedra and [MoO_4]-tetrahedra and will be compared with known structure types in the next section. Samples of high purity allow the determination of properties, and the high-temperature behaviour and the magnetic properties are described in the following two sections. A broader presentation including more details can be found in [12].

2. Sample preparation and phase analyses

All five Na–Fe-orthooxomolybdate phases were found in multi-phase samples and characterised by structure determination using single-crystal X-ray diffraction [10]. The crystal structure models are further supported by X-ray powder diffraction (STOE STADI P in transmission mode, Mo K_{α_1} radiation, curved Ge 111 monochromator, linear position sensitive detector), neutron powder diffraction (for experimental details see Section 5) and data analyses by the Rietveld method using WinPlotr [13]. All observed and calculated diffraction patterns are shown in [12] together with their difference curves.

The conditions of synthesis have been optimized to obtain single-phase material of highest possible purity. The following educts have been used: Na_2MoO_4 (Aldrich, 99%), Fe_2O_3 (Aldrich, 99.98%), FeO (Aldrich, 99.9%), MoO_3 (Johnson Matthey, Grade A1), and MoO_2 (STREM Chemicals, 99%). Appropriate ratios of the educts were intimately mixed in an agate mortar under acetone, pressed into pellets and placed either directly or within an additional open corundum crucible into a quartz tube with 8–10 cm^3 volume, which was sealed after evacuation to a pressure below 10^{-3} mbar. Table 2 summarizes the optimized temperature programs and the resulting compositions, based on X-ray powder diffraction and following analyses by the Rietveld method; the structure models were taken from our previous work [10], from [11] for $NaFe(MoO_4)_2$ and from [14] for α-$FeMoO_4$. Note that the ICSD data base entry 43012 for α-$FeMoO_4$ includes coordinates as for α-$CoMoO_4$ instead of those for the Fe-compound [15]. The effect of slightly different conditions of synthesis on the resulting reaction products is reported in [12].

3. Relationships with known structure types

The search for compounds with similar structures was focused on oxides including [XO_4] tetrahedrally coordinated elements with X = Mo, S, Se, Cr, P, or As.

The $NaFe(MoO_4)_2$ structure is closely related to the yavapaiite type, named after the mineral $KFe(SO_4)_2$ [16], see Fig. 1. However, the orientation of octahedra is alternating in $NaFe(MoO_4)_2$ in contrast to yavapaiite as emphasized by the arrows, resulting in a larger unit cell. The yavapaiite-type sheet structure of $NaFe(MoO_4)_2$ is compared with the characteristic chains in kröhnkite [17], $Na_2Cu(SO_4)_2{\cdot}2H_2O$, see Fig. 2. In the latter isolated chains exist in contrast to the marked additional corner-sharing of [MoO_4]-tetrahedra and [FeO_6]-octahedra in $NaFe(MoO_4)_2$. $NaFe(MoO_4)_2$ is the prototype of a pseudo-orthorhombic variation of the yavapaiite-motif in compounds with kröhnkite-type chains [18] and isotypic with $NaAl(MoO_4)_2$ [19], probably also with $NaCr(MoO_4)_2$ [20].

No isotypic structures could be found for the two $NaFe_2(MoO_4)_3$ polymorphs, see Table 1. Nonetheless, similar motifs exist in other molybdate compounds: The constituting layer A, as defined by [10], for α-$NaFe_2(MoO_4)_3$ differs from a similar layer in $K_2Ni(MoO_4)_2$ [21] only by the orientations of the