



## Phase formation in the $\text{Li}_2\text{MoO}_4\text{-K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$ system and crystal structures of new compounds $\text{K}_3\text{InMo}_4\text{O}_{15}$ and $\text{LiK}_2\text{In}(\text{MoO}_4)_3$

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### ABSTRACT

XRD study of solid-phase interaction in the  $\text{Li}_2\text{MoO}_4\text{-K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$  system was performed. The boundary  $\text{K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$  system is a non-quasibinary join of the  $\text{K}_2\text{O-In}_2\text{O}_3\text{-MoO}_3$  system where a new polymolybdate  $\text{K}_3\text{InMo}_4\text{O}_{15}$  isotypic to  $\text{K}_3\text{FeMo}_4\text{O}_{15}$  was found. In the structure ( $a=33.2905(8)$ ,  $b=5.8610(1)$ ,  $c=15.8967(4)$  Å,  $\beta=90.725(1)^\circ$ , sp. gr.  $C2/c$ ,  $Z=8$ ,  $R(F)=0.0407$ ),  $\text{InO}_6$  octahedra,  $\text{Mo}_2\text{O}_7$  diortho groups and  $\text{MoO}_4$  tetrahedra form infinite ribbons  $\{[\text{In}(\text{MoO}_4)_2(\text{Mo}_2\text{O}_7)]^{3-}\}_\infty$  along the  $b$ -axis. Between the chains, 8- to 10-coordinate potassium cations are located. A subsolidus phase diagram of the  $\text{Li}_2\text{MoO}_4\text{-K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$  system was constructed and a novel triple molybdate  $\text{LiK}_2\text{In}(\text{MoO}_4)_3$  was revealed. Its crystal structure ( $a=7.0087(2)$ ,  $b=9.2269(3)$ ,  $c=10.1289(3)$  Å,  $\beta=107.401(1)^\circ$ , sp. gr.  $P2_1$ ,  $Z=2$ ,  $R(F)=0.0280$ ) contains an open framework of vertex-shared  $\text{MoO}_4$  tetrahedra,  $\text{InO}_6$  octahedra and  $\text{LiO}_5$  tetragonal pyramids with nine- and seven-coordinate potassium ions in the framework channels.

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### 1. Introduction

Double molybdates  $\text{M}_x\text{M}'_y(\text{MoO}_4)_z$  ( $M$  – univalent cation,  $M'$  – uni-, di-, tri- or tetravalent cations) are well-known and promising as ferroelectrics, solid electrolytes, laser, acousto-optical, luminescent and other inorganic materials [1–5]. The range of complex Mo(VI) oxide phases has been expanding over the past two decades, mainly, for account of triple molybdates revealed in the course of exploring ternary salt systems [6–14].

We have already reported in [10–17] about a detection, synthesis and structural characterization of two isostructural series of triple molybdates of lithium, univalent and trivalent cations. The structures of tetragonal triple molybdates  $\text{Li}_2\text{M}_3\text{R}(\text{MoO}_4)_4$  ( $\text{MR}=\text{TlAl}$ ,  $\text{RbAl}$ ,  $\text{RbGa}$ ,  $\text{CsAl}$ ,  $\text{CsGa}$ ,  $\text{CsFe}$ ) [10] closely related to the cubic  $\text{Cs}_6\text{Zn}_5(\text{MoO}_4)_8$  type [18,19], contain open frameworks formed by  $\text{MoO}_4$ -,  $\text{LiO}_4$ - and  $\text{RO}_4$ -tetrahedra with 12-coordinate  $M^+$  ions located in their large cavities. A more extensive isostructural series of triple molybdates  $\text{LiMR}_2(\text{MoO}_4)_4$  ( $M=\text{K}$ ,  $\text{Rb}$ ,  $\text{Tl}$ ;  $\text{R}=\text{Ln}$ ,  $\text{Bi}$ ) comprising 26 members has a structure being a stuffed derivative of the monoclinic  $\text{BaNd}_2(\text{MoO}_4)_4$  structure type (space group  $C2/c$ ,  $Z=4$ ) [16,17,20]. In  $\text{LiMR}_2(\text{MoO}_4)_4$  structures,  $\text{RO}_8$

polyhedra sharing vertices with  $\text{MoO}_4$  tetrahedra form open layers linked via  $\text{MO}_{10}$  polyhedra and  $\text{LiO}_6$  octahedra. Since eight-fold coordination is not characteristic of trivalent cations smaller than  $\text{Lu}^{3+}$ ,  $\text{LiKLu}_2(\text{MoO}_4)_4$  is the last member of this family.

Occurrence of two aforementioned distinct families of triple molybdates in  $\text{Li}_2\text{MoO}_4\text{-M}_2\text{MoO}_4\text{-R}_2(\text{MoO}_4)_3$  systems (Fig. 1) raises the question about existence of triple molybdates containing (apart from lithium and a large monovalent cation) a medium-size trivalent cation such as  $\text{In}^{3+}$  or  $\text{Sc}^{3+}$ . The systems  $\text{Li}_2\text{MoO}_4\text{-M}_2\text{MoO}_4\text{-R}_2(\text{MoO}_4)_3$  ( $\text{R}=\text{In}$ ,  $\text{Sc}$ ) have never been studied in detail before. The only reported  $\text{LiIn}(\text{MoO}_4)_2\text{-MIn}(\text{MoO}_4)_2$  ( $M=\text{K}$ ,  $\text{Rb}$ ) joins [21,22] are eutectic with liquation.

This work deals with the study of phase formation in the  $\text{Li}_2\text{MoO}_4\text{-K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$  system, constructing a subsolidus phase diagram of such system and determination of the composition and structure of a new triple molybdate  $\text{LiK}_2\text{In}(\text{MoO}_4)_3$  formed in the system. In the course of this study, literature data on phase equilibrium in the  $\text{K}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$  boundary system were checked and corrected, and the structure of a newly revealed polymolybdate  $\text{K}_3\text{InMo}_4\text{O}_{15}$  was determined.

### 2. Experimental

Commercially available chemically pure  $\text{MoO}_3$ ,  $\text{LiNO}_3$ ,  $\text{KNO}_3$  and high-purity  $\text{In}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  were used as starting materials

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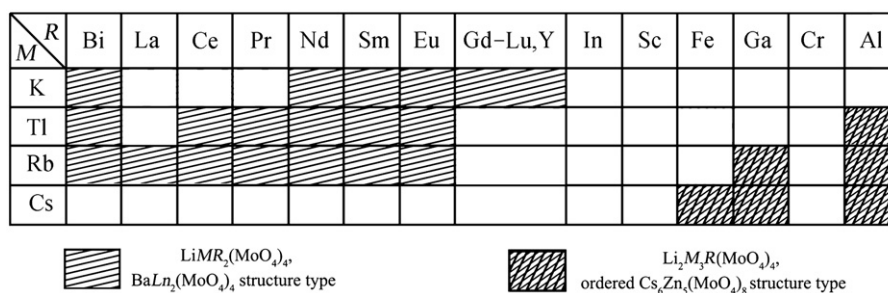


Fig. 1. The existence regions of isostructural series of triple molybdates of lithium, univalent and trivalent cations.

for the synthesis of simple, double and triple molybdates. Simple molybdates  $M_2MoO_4$  ( $M=Li, K$ ) and  $K_2Mo_2O_7$  used as a flux for crystallization experiments were synthesized by annealing stoichiometric mixtures of alkali carbonates or nitrates with molybdenum trioxide for 80–100 h. The initial calcination temperature was 400 °C when  $M_2CO_3$  was used or 350 °C when  $MNO_3$  was taken, while the final temperature depended on the thermal stability of the final product. Indium molybdate was synthesized from oxides of indium(III) and molybdenum(VI) at 500–700 °C. Monophasity of the prepared substances was confirmed by powder X-ray diffraction (XRD) and thermal analysis. Thermal and X-ray characteristics of the obtained substances were in accord with the data of [23–25].

Small single crystals of the compounds were grown by spontaneous crystallization of molten ceramic samples or mixtures of constituent molybdates. Heating of ground mixtures, their isothermal holding and slow cooling of the melts were controlled automatically with an accuracy of  $\pm 0.5^\circ$ .

Monitoring of solid-state synthesis and phase equilibration were carried out by X-ray powder diffraction by using an automated D8 ADVANCE Bruker diffractometer ( $CuK_\alpha$  radiation, secondary monochromator, maximal  $2\theta=100^\circ$ , scan step 0.01–0.02°, exposition 1–10 s). The unit cell parameters were refined by the least-squares method using ICDD program package for preparing experimental standards.

Single crystal X-ray diffraction data for structure determination were collected at room temperature by using a Bruker–Nonius X8 Apex CCD area-detector diffractometer ( $MoK_\alpha$  radiation, graphite monochromator,  $\varphi$ -scans with scan step of  $0.5^\circ$ ). Data processing was accomplished using SAINT program; an absorption correction was applied with SADABS program [26]. The structure was solved and refined by using SHELX-97 package [27].

Differential thermal analysis was performed with an MOM OD-103 derivatograph.

### 3. Results and discussion

#### 3.1. Phase formation in $Li_2MoO_4$ – $K_2MoO_4$ – $In_2(MoO_4)_3$ system

Information about the boundary elements of the  $Li_2MoO_4$ – $K_2MoO_4$ – $In_2(MoO_4)_3$  system required for correct triangulation of the system was taken from literature or obtained by us.

The  $T$ – $x$  diagram of the  $Li_2MoO_4$ – $K_2MoO_4$  system was reported in [28,29]. The single intermediate phase  $LiKMoO_4$  was found to melt congruently and to undergo some polymorphic transformations, according to [30–33]. Lattice parameters of the form of  $LiKMoO_4$ , which was obtained us, were close to those reported in [33].

Phase formation in the  $Li_2MoO_4$ – $In_2(MoO_4)_3$  system and the double molybdates  $LiIn(MoO_4)_2$  and  $Li_3In(MoO_4)_3$  formed in the system were described in literature in reasonable detail [34–38]. According to [37],  $LiIn(MoO_4)_2$  is dimorphic: the low-temperature modification has wolframite-like structure undergoing at 700 °C

a phase transition with changing octahedral coordination of molybdenum to tetrahedral one. The second compound,  $Li_3In(MoO_4)_3$ , belongs to the family of isostructural phases  $Li_3R(MoO_4)_3$  ( $R=In, Sc, Fe, Cr, Ga, Al$ ) [38–41] crystallizing in the orthorhombic structure type of lyonsite  $\alpha$ - $Cu_3Fe_4(VO_4)_6$  [42].

We have performed a repeated X-ray diffraction study of the  $Li_2MoO_4$ – $In_2(MoO_4)_3$  system using samples containing 90, 77.5, 75, 72.5, 70, 67.5, 65, 60, 50 and 25 mol% of  $Li_2MoO_4$ . A detailed examination of samples having composition close to 75 mol%  $Li_2MoO_4$  is explained with our attempt to find a homogeneity range in  $Li_3In(MoO_4)_3$  having the lyonsite structure that does not preclude the presence of such range [42].

It has been confirmed that the studied system is quasi-binary and forms two intermediate phases having composition of 1:1 and 3:1 in the subsolidus region. Crystallographic characteristics of the obtained compounds agree with the data of [43]. It has been shown for the first time that  $Li_3In(MoO_4)_3$  has a marked homogeneity range extending toward  $In_2(MoO_4)_3$  and reaching 5 mol% at 600–650 °C.

According to data [34,35], three double molybdates of 1:1, 3:1, and 5:1 composition occur in the  $K_2MoO_4$ – $In_2(MoO_4)_3$  system. Orthorhombic  $KIn(MoO_4)_2$  has its own structure type with a framework of  $InO_6$  octahedra and  $MoO_4$  tetrahedra [44].  $K_5In(MoO_4)_4$  is dimorphic, the structures of both modifications related to the palmierite  $K_2Pb(SO_4)_2$  type [45–47].  $K_3In(MoO_4)_3$  also has two forms [34], but their structures are unknown yet.

By annealing stoichiometric mixtures of  $K_2MoO_4$  and  $In_2(MoO_4)_3$ , we have synthesized  $K_5In(MoO_4)_4$  and  $KIn(MoO_4)_2$  having unit cell parameters close to those found in [34,35]. However, our numerous attempts to prepare  $K_3In(MoO_4)_3$  described in [34] have failed. Because of this reason we have repeatedly studied the full concentration range of the  $K_2MoO_4$ – $In_2(MoO_4)_3$  system at subsolidus temperatures. Reaction mixtures containing 90, 83.3, 78, 75, 70, 65, 64.3, 60, 50 and 25 mol% of  $K_2MoO_4$  were annealed and then studied by using X-ray diffraction phase analysis. Temperature (from 300 °C up to an appearance of a liquid phase) was increased with a step of 30–50 °C, and samples were annealed at each step for 50–100 h with daily intermittent grindings.

We found that the phase equilibrium pattern in the studied system substantially more complex than that shown in [34]. The quasi-binary character of the  $KIn(MoO_4)_2$ – $In_2(MoO_4)_3$  range is beyond doubt since XRD patterns of annealed samples in the range show only lines of the boundary compounds with intensities corresponding to their relative content in the reaction mixtures. However, X-ray powder patterns of samples in the  $K_5In(MoO_4)_4$ – $KIn(MoO_4)_2$  range annealed at 450 °C and above, revealed reflections of a new phase, resembling in their locations and intensities the diffraction pattern of  $K_3FeMo_4O_{15}$  described in [48–50]. These findings suggest the occurrence of a similar compound in the  $K_2O$ – $In_2O_3$ – $MoO_3$  system and the resulting partial violation of quasibinary of the join  $K_2MoO_4$ – $In_2(MoO_4)_3$ .

Such suggestion was supported by our data on a partial non-quasibinary of the  $M_2MoO_4-Fe_2(MoO_4)_3$  joins of the  $M_2O-Fe_2O_3-MoO_3$  ( $M=Rb, Cs$ ) systems apparently caused by a high thermodynamic stability of  $M_3FeMo_4O_{15}-Fe_2O_3$  pair [51]. Such hypothesis was experimentally proved when a single-phase  $K_3InMo_4O_{15}$  was synthesized by annealing a stoichiometric mixture of  $K_2MoO_4$ ,  $In_2(MoO_4)_3$ , and  $MoO_3$  at 450–600 °C for 100 h. The X-ray pattern of the compound was satisfactory indexed assuming the isostructurality to  $K_3FeMo_4O_{15}$ . The compound composition is confirmed by X-ray structure analysis of single crystals obtained when we tried to grow crystals of  $K_3In(MoO_4)_3$  described in [34]. Notice that the calculated powder pattern of  $K_3InMo_4O_{15}$  corresponds to a diffractogram of the sample with the same composition obtained using solid state synthesis.

Revealing, synthesis and determination of the structure of a new double polymolybdate  $K_3InMo_4O_{15}$  (see Section 3.2) allowed us to interpret correctly the experimental data on the  $K_2MoO_4-In_2(MoO_4)_3$  system. The diagram of phase fields of the system samples annealed at 450 °C (Fig. 2) shows that  $K_2MoO_4:In_2(MoO_4)_3=83.3:16.7$  and 50:50 samples corresponding to  $K_5In(MoO_4)_4$  and  $KIn(MoO_4)_2$  compounds are single-phase; samples of the  $K_2MoO_4-K_5In(MoO_4)_4$  and  $KIn(MoO_4)_2-In_2(MoO_4)_3$  ranges are two-phase, and samples of the  $K_5In(MoO_4)_4-KIn(MoO_4)_2$  range are three-phase. Furthermore, at 300–400 °C, i.e., beyond the temperature range of  $K_3InMo_4O_{15}$  formation, the quasibinary of the  $K_2MoO_4-In_2(MoO_4)_3$  join is broken by metathesis processes resulting in  $K_2Mo_2O_7$  and  $In_2O_3$  formation. Thus, the obtained results testify that  $K_2MoO_4-In_2(MoO_4)_3$  is an unstable (non-quasibinary) join of the  $K_2O-MoO_3-In_2O_3$  ternary oxide system. The quasibinary of the  $K_2MoO_4-In_2O_3$  join intersecting the  $K_2MoO_4-In_2(MoO_4)_3$  join in this ternary oxide system was confirmed by XRD analysis.

Previously, a partial non-quasibinary in the subsolidus region of the  $M_2MoO_4-R_2(MoO_4)_3$  systems was found only for  $M=Na, R=Fe, Cr$  [52]. Revealing by us a non-quasibinary in the  $M_2MoO_4-Fe_2(MoO_4)_3$  ( $M=Rb, Cs$ ) systems [51] and  $K_2MoO_4-In_2(MoO_4)_3$  (this work) allows to say that the non-quasibinary is characteristic of similar systems. The same features have the systems  $M_2XO_4-AXO_4$  ( $X=Mo, W$ ) [53] and  $M_2WO_4-R_2(WO_4)_3$  [54,55] that confirms abundance of a such phenomenon connected with metathesis processes in the systems containing molybdates and tungstates of uni- and bivalent (trivalent) metals. Practically, these observations are very important for developing solid state reaction conditions and correct studies of multicomponent systems.

Taking into account the literature and our data on the boundary systems, phase formation in the  $Li_2MoO_4-K_2MoO_4-In_2(MoO_4)_3$  system has been studied by using the “intersection joins” method [56,57]. For such purpose, we carried out XRD phase analysis of the samples corresponding to the intersection points of the joins connecting points of the components and boundary compounds. It makes possible to reveal quasibinary joins and to perform triangulation of the system. Since the range of the  $K_2MoO_4-In_2(MoO_4)_3$  system rich in potassium molybdate was found to be non-quasibinary, the study of the  $Li_2MoO_4-K_2MoO_4-In_2(MoO_4)_3$  system was limited to the  $Li_2MoO_4-KLiMoO_4-KIn(MoO_4)_2-In_2(MoO_4)_3$  region. Nevertheless,

we also examined samples corresponding to the compositions of the intersection points of the joins originating from  $K_2MoO_4, K_5In(MoO_4)_4$  and “ $K_3In(MoO_4)_3$ ” compositions and falling into the studied region. The obtained results are presented in Fig. 3. A new compound  $LiK_2In(MoO_4)_3$  is detected at the intersection point of the  $LiIn(MoO_4)_2-K_2MoO_4$  and  $LiKMoO_4-KIn(MoO_4)_2$  joins. The joins  $LiIn(MoO_4)_2-KIn(MoO_4)_2, Li_3In(MoO_4)_3-KIn(MoO_4)_2, Li_2MoO_4-KIn(MoO_4)_2$  and  $Li_2MoO_4-LiK_2In(MoO_4)_3$  divide the region  $Li_2MoO_4-LiKMoO_4-KIn(MoO_4)_2-In_2(MoO_4)_3$  into five subsystems.

The join  $LiKMoO_4-KIn(MoO_4)_2$ , where the intermediate phase is formed, was studied with a step of ~5–10 mol%, and in the vicinity of a new compound – with a step of 1.5–2.5 mol%. XRD pattern of the sample with composition corresponding to  $LiK_2In(MoO_4)_3$  is characterized with a specific set of reflections. It is noteworthy that the lack of triple molybdates in the  $LiIn(MoO_4)_2-KIn(MoO_4)_2$  join is in accord with the data of [21,22].

Single-phase sample of  $LiK_2In(MoO_4)_3$  was prepared by annealing of stoichiometric mixtures of  $LiKMoO_4$  and  $KIn(MoO_4)_2$  or simple molybdates at 450 °C for 80–100 h. When using  $Li_2MoO_4, K_2MoO_4$  and indium nitrate are as starting materials, annealing is better to start from 350 °C in order to avoid reagent spillage as a result of strong effervescing.

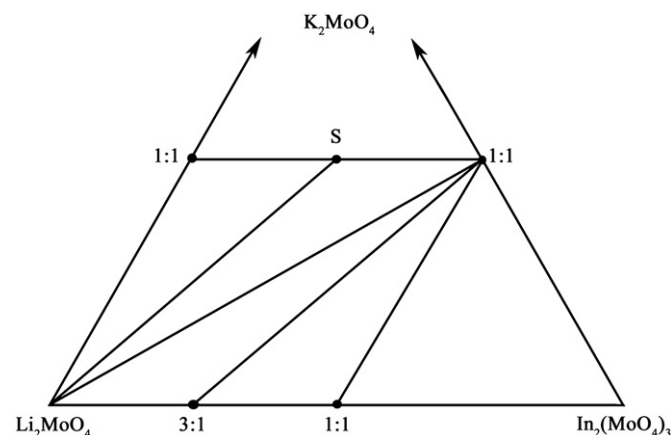


Fig. 3. Subsolidus phase diagram of the  $Li_2MoO_4-K_2MoO_4-In_2(MoO_4)_3$  system ( $t=450$  °C) S –  $LiK_2In(MoO_4)_3$ .

Table 1

Crystal data and structure refinement details for  $K_3InMo_4O_{15}$ .

Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions:	
a, Å	33.2905(8)
b, Å	5.8610(1)
c, Å	15.8967(4)
$\beta$ , °	90.725(1)
$V$ (Å <sup>3</sup> )/Z	3101.5(1)/8
Calculated density, g cm <sup>-3</sup>	3.666
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	5.486
Crystal size, mm	0.15 × 0.08 × 0.005
$\theta$ range (°) for data collection	1.22–30.79
Reflections collected/unique	7919/2877 [R(int)=0.0290]
No. of variables	210
Goodness-of-fit on $F^2$ (GOF)	1.013
Final R indices [ $I > 2\sigma(I)$ ]	R(F)=0.0407, wR(F <sup>2</sup> )=0.1120
R indices (all data)	R(F)=0.0486, wR(F <sup>2</sup> )=0.1248
Largest difference peak/hole (e Å <sup>-3</sup> )	1.873/–1.863

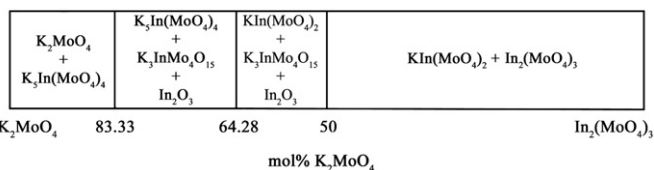


Fig. 2. Phase fields diagram of the  $K_2MoO_4-In_2(MoO_4)_3$  system at 450 °C.

Triple molybdate  $\text{LiK}_2\text{In}(\text{MoO}_4)_3$  melts at 590 °C; it is insoluble in water and usual organic solvents and soluble in HCl aqueous solution.

**Table 2**  
Atomic coordinates and equivalent isotropic displacement parameters for  $\text{K}_3\text{InMo}_4\text{O}_{15}$ .

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Mo(1)	0.0659(1)	−0.5044(1)	0.2326(1)	0.016(1)
Mo(2)	0.3518(1)	0.5119(1)	−0.1136(1)	0.016(1)
Mo(3)	0.2174(1)	−0.0125(1)	−0.1516(1)	0.014(1)
Mo(4)	0.0569(1)	0.4659(1)	−0.0014(1)	0.020(1)
In	0.3200(1)	0.0008(1)	0.2596(1)	0.014(1)
K(1)	0.3142(1)	0.0340(3)	0.0106(1)	0.026(1)
K(2)	0.0136(1)	−0.0125(2)	0.1289(1)	0.026(1)
K(3)	0.1037(1)	−0.0230(3)	−0.1363(2)	0.034(1)
O(1)	0.0437(2)	−0.2730(10)	0.2801(4)	0.030(1)
O(2)	0.1167(2)	−0.5138(8)	0.2617(5)	0.027(1)
O(3)	0.0431(2)	−0.7464(10)	0.2709(4)	0.030(1)
O(4)	0.0562(3)	−0.4851(8)	0.1173(4)	0.034(2)
O(5)	0.1833(1)	0.2201(8)	−0.1724(3)	0.023(1)
O(6)	0.1890(1)	−0.2742(7)	−0.1552(3)	0.022(1)
O(7)	0.3539(2)	0.4703(9)	−0.0057(5)	0.032(1)
O(8)	0.2560(2)	−0.0174(7)	−0.2254(5)	0.023(1)
O(9)	0.2368(2)	0.0220(8)	−0.0524(5)	0.032(1)
O(10)	0.3285(2)	0.7822(8)	−0.1358(3)	0.029(1)
O(11)	0.0481(2)	0.1834(9)	−0.0288(3)	0.035(1)
O(12)	0.3232(2)	0.2856(8)	−0.1586(4)	0.031(1)
O(13)	0.1037(2)	0.5390(11)	−0.0377(7)	0.051(2)
O(14)	0.3995(2)	0.5056(10)	−0.1547(7)	0.046(2)
O(15)	0.0231(2)	0.6445(11)	−0.0516(4)	0.045(1)

**Table 3**  
Selected interatomic distances (Å) for  $\text{K}_3\text{InMo}_4\text{O}_{15}$ .

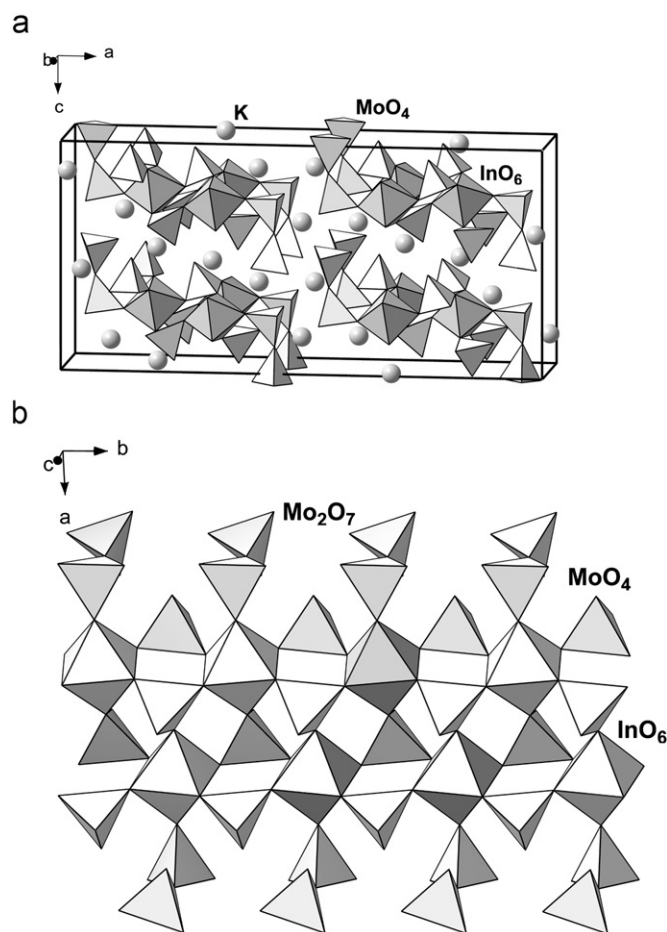
Mo(1)-tetrahedron		Mo(2)-tetrahedron	
Mo(1)–O(1)	1.723(5)	Mo(2)–O(14)	1.725(8)
Mo(1)–O(3)	1.723(5)	Mo(2)–O(7)	1.732(7)
Mo(1)–O(2)	1.749(6)	Mo(2)–O(12)	1.778(5)
Mo(1)–O(4)	1.860(7)	Mo(2)–O(10)	1.798(5)
⟨Mo(1)–O⟩	1.764	⟨Mo(2)–O⟩	1.758
Mo(3)-tetrahedron		Mo(4)-tetrahedron	
Mo(3)–O(9)	1.708(7)	Mo(4)–O(13)	1.723(8)
Mo(3)–O(8)	1.753(7)	Mo(4)–O(15)	1.724(6)
Mo(3)–O(6)	1.802(4)	Mo(4)–O(11)	1.736(5)
Mo(3)–O(5)	1.802(5)	Mo(4)–O(4)	1.908(7)
⟨Mo(3)–O⟩	1.766	⟨Mo(4)–O⟩	1.773
K(1)-polyhedron		K(2)-polyhedron	
K(1)–O(9)	2.754(7)	K(2)–O(15)	2.761(6)
K(1)–O(6)	2.759(5)	K(2)–O(11)	2.769(6)
K(1)–O(13)	2.796(9)	K(2)–O(1)	2.852(6)
K(1)–O(10)	2.803(5)	K(2)–O(3)	2.905(6)
K(1)–O(7)	2.893(6)	K(2)–O(14)	2.916(8)
K(1)–O(5)	2.948(5)	K(2)–O(3)	2.934(6)
K(1)–O(12)	3.085(6)	K(2)–O(11')	2.999(6)
K(1)–O(9)	3.182(6)	K(2)–O(1')	3.009(6)
⟨K(1)–O⟩	2.903	K(2)–O(4)	3.118(6)
		K(2)–O(4')	3.407(6)
		⟨K(2)–O⟩	2.967
K(3)-polyhedron		In-octahedron	
K(3)–O(7)	2.664(7)	In–O(10)	2.110(5)
K(3)–O(11)	2.809(6)	In–O(12)	2.125(5)
K(3)–O(3)	2.828(6)	In–O(2)	2.141(6)
K(3)–O(1)	2.949(6)	In–O(6)	2.144(5)
K(3)–O(13)	3.007(8)	In–O(5)	2.147(4)
K(3)–O(5)	3.067(5)	In–O(8)	2.149(6)
K(3)–O(2)	3.194(6)	⟨In–O⟩	2.136
K(3)–O(6)	3.216(5)		
K(3)–O(14)	3.327(11)		
⟨K(3)–O⟩	3.007		

Single crystals of this compound are obtained by spontaneous flux crystallization. Mixture of  $\text{Li}_2\text{MoO}_4$ ,  $\text{K}_2\text{MoO}_4$ ,  $\text{K}_2\text{Mo}_2\text{O}_7$  and  $\text{In}_2(\text{MoO}_4)_3$  with molar ratio 3:3:2:1 annealed at 450 °C was taken as a starting charge. The mixture was melted and held at 520 °C for 30 min and cooled down to 400 °C at a rate of 4 °C h<sup>−1</sup> and then in a switched-off furnace. The composition of the triple molybdate, preliminary established with XRD analysis, was confirmed in the course of crystal structure determination.

### 3.2. Crystal structure of $\text{K}_3\text{InMo}_4\text{O}_{15}$

Determination of the character of phase equilibria in the  $\text{K}_2\text{MoO}_4$ – $\text{In}_2(\text{MoO}_4)_3$  system became possible due to detection and structural characterization of  $\text{K}_3\text{InMo}_4\text{O}_{15}$ , which, as we expected, is proved to be isostructural with  $\text{K}_3\text{FeMo}_4\text{O}_{15} = \text{K}_3\text{Fe}(\text{MoO}_4)_2(\text{Mo}_2\text{O}_7)$  [48–50]. Crystal and structure refinement data for  $\text{K}_3\text{InMo}_4\text{O}_{15}$  are summarized in Table 1; the atomic coordinates, equivalent isotropic atomic displacement parameters and selected interatomic distances are listed in Tables 2 and 3. The crystal structure data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: mcrysdta@fiz.karlsruhe.de) on quoting the depository number CSD 423175. The general view of the structure is shown in Fig. 4(a).

In  $\text{K}_3\text{InMo}_4\text{O}_{15}$  structure, all atoms are in general positions. Four kinds of the molybdenum atoms have tetrahedral coordination with distances Mo–O 1.708(7)–1.908(7) Å. The longest bonds Mo(1)–O(4) 1.860(7) Å and Mo(4)–O(4) 1.908(7) Å correspond to bridge oxygen distances in separate tetrahedral dimer



**Fig. 4.** The structure of  $\text{K}_3\text{InMo}_4\text{O}_{15}$ : (a) a general view; (b) the infinite ribbon  $\{[\text{In}(\text{MoO}_4)_2(\text{Mo}_2\text{O}_7)]^{3-}\}_\infty$ .

Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup>. The Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> pyroanion has nearly eclipsed conformation with Mo(1)–O(4)–Mo(4) angle of 163.9(4)°. A close configuration of dimolybdate pyroanion was found in MgMo<sub>2</sub>O<sub>7</sub> [58]. All indium atoms are crystallographically equivalent and have a common distorted octahedral coordination; the In–O bond lengths are 2.110(5)–2.149(6) Å, the O–In–O angles change from 88.1(2) to 93.1(2)°. Three kinds of the potassium atoms have coordination numbers of 8 to 10 (Table 3). In the structure, we can see infinite complex-shaped ribbons {[In(MoO<sub>4</sub>)<sub>2</sub>(Mo<sub>2</sub>O<sub>7</sub>)]<sup>3-</sup>}<sub>∞</sub> running along the *b*-axis and containing the InO<sub>6</sub> octahedra, terminal Mo<sub>2</sub>O<sub>7</sub> groups and bridge MoO<sub>4</sub> tetrahedra connecting two or three InO<sub>6</sub> octahedra (Fig. 4(b)). Between the chains potassium cations are located (Fig. 4(a)). Other structure details were described early for isostructural K<sub>3</sub>FeMo<sub>4</sub>O<sub>15</sub> [50].

The interesting feature of the structure is a clearly pronounced pseudo-period *c'* = *c*/2 and a mirror pseudo-symmetry normal to the same axis. It suggests a considerable probability of existing a distortional high-temperature phase transition into a phase with a possible space group *C2/m* and the *c* parameter decreased in half. The same phenomenon may be also expected for K<sub>3</sub>FeMo<sub>4</sub>O<sub>15</sub>.

**Table 4**  
Crystal data and structure refinement details for LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>.

Crystal system	Monoclinic
Space group	<i>P2</i> <sub>1</sub>
Unit cell dimensions	<i>a</i> = 7.0087(2) Å, <i>b</i> = 9.2269(3) Å, <i>c</i> = 10.1289(3) Å, <i>β</i> = 107.401(1)°
<i>V</i> (Å <sup>3</sup> )/ <i>Z</i>	625.04(3)/2
Calculated density, g cm <sup>-3</sup>	3.612
<i>μ</i> (MoK <sub>α</sub> ), mm <sup>-1</sup>	5.479
Crystal size, mm	0.10 × 0.07 × 0.06
<i>θ</i> range (deg) for data collection	2.11–32.60
Reflections collected/unique	6630/4271 [R(int) = 0.0233]
No. of variables	173
Goodness-of-fit on <i>F</i> <sup>2</sup> (GOF)	1.033
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> ( <i>F</i> ) = 0.0280, <i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.0522
<i>R</i> indices (all data)	<i>R</i> ( <i>F</i> ) = 0.0306, <i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.0532
Largest difference peak/hole (e Å <sup>-3</sup> )	1.789/–1.734

**Table 5**  
Atomic coordinates and equivalent isotropic displacement parameters for LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Mo(1)	0.80454(5)	0.32843(4)	0.81174(4)	0.01172(8)
Mo(2)	0.57175(5)	0.71572(5)	–0.07909(4)	0.01290(8)
Mo(3)	0.95177(5)	0.21316(4)	0.45816(4)	0.01173(8)
In	0.72164(4)	0.90414(3)	0.26193(3)	0.00910(6)
K(1)	0.15969(17)	–0.00207(13)	0.79700(13)	0.0244(3)
K(2)	0.4538(3)	0.4940(3)	0.4206(2)	0.0945(10)
O(1)	0.8317(6)	0.1575(5)	0.7506(4)	0.0273(9)
O(2)	0.8228(5)	0.3080(4)	0.9867(4)	0.0202(8)
O(3)	0.0091(5)	0.4354(4)	0.7943(4)	0.0162(7)
O(4)	0.5641(4)	0.3937(4)	0.7083(3)	0.0146(6)
O(5)	0.5304(6)	0.8743(4)	–0.1727(4)	0.0296(10)
O(6)	0.7831(5)	0.6297(5)	–0.0966(4)	0.0243(9)
O(7)	0.6223(5)	0.7496(4)	0.0062(4)	0.0186(8)
O(8)	0.3596(5)	0.5974(4)	–0.1407(4)	0.0178(8)
O(9)	0.7859(5)	0.3468(4)	0.4697(4)	0.0254(9)
O(10)	0.0257(6)	0.2500(4)	0.3123(4)	0.0222(8)
O(11)	0.8313(5)	0.0395(4)	0.4432(4)	0.0177(7)
O(12)	0.1707(5)	0.2193(4)	0.6067(3)	0.0167(7)
Li	0.9488(13)	0.1493(10)	0.1279(10)	0.0213(19)

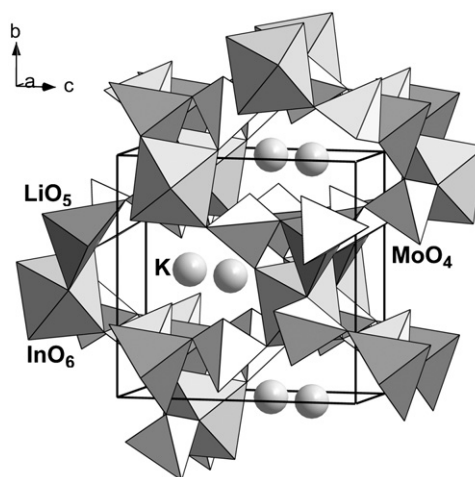
### 3.3. Crystal structure of LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>

Crystallographic data and results of LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub> structure refinement are presented in Table 4; the atomic coordinates, equivalent isotropic atomic displacement parameters and selected interatomic distances are given in Tables 5 and 6. The crystal structure data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 423176. The general view of the structure is shown in Fig. 5.

In the acentric structure of LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>, all atoms are located in general positions. Three kinds of the molybdenum atoms have a common tetrahedral coordination and distances Mo–O 1.720(4)–1.801(3) Å. The cations In<sup>3+</sup> are located in oxygen octahedra with bond lengths In–O 2.114(3)–2.163(4) Å.

**Table 6**  
Selected interatomic distances (Å) for LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>.

Mo(1)-tetrahedron		Mo(2)-tetrahedron		Mo(3)-tetrahedron	
Mo(1)–O(1)	1.725(4)	Mo(2)–O(5)	1.720(4)	Mo(3)–O(9)	1.723(4)
Mo(1)–O(2)	1.748(4)	Mo(2)–O(6)	1.736(4)	Mo(3)–O(10)	1.739(4)
Mo(1)–O(3)	1.792(3)	Mo(2)–O(7)	1.775(4)	Mo(3)–O(11)	1.796(4)
Mo(1)–O(4)	1.801(3)	Mo(2)–O(8)	1.799(3)	Mo(3)–O(12)	1.800(3)
<Mo(1)–O>	1.767	<Mo(2)–O>	1.758	<Mo(3)–O>	1.765
In-octahedron		K(1)-polyhedron			
In–O(4)	2.114(3)	K(1)–O(1)	2.651(4)		
In–O(7)	2.123(3)	K(1)–O(10)	2.700(4)		
In–O(8)	2.144(3)	K(1)–O(5)	2.770(4)		
In–O(3)	2.147(3)	K(1)–O(2)	2.780(4)		
In–O(12)	2.156(4)	K(1)–O(7)	2.803(4)		
In–O(11)	2.163(3)	K(1)–O(12)	2.826(4)		
<In(1)–O>	2.142	K(1)–O(9)	3.163(4)		
		K(1)–O(6)	3.181(4)		
		K(1)–O(11)	3.654(4)		
		K(1)–O(11)	3.654(4)		
		<K(1)–O>	2.948		
K(2)-polyhedron		Li-polyhedron			
K(2)–O(9)	2.611(4)	Li–O(6)	2.005(10)		
K(2)–O(1)	2.686(4)	Li–O(10)	2.010(10)		
K(2)–O(5)	2.775(5)	Li–O(2)	2.053(10)		
K(2)–O(11)	2.778(4)	Li–O(3)	2.113(10)		
K(2)–O(4)	2.932(4)	Li–O(8)#12	2.255(10)		
K(2)–O(12)	3.429(5)	<Li–O>	2.087		
K(2)–O(10)	3.648(5)				
<K(2)–O>	2.980				



**Fig. 5.** A general view of the structure of LiK<sub>2</sub>In(MoO<sub>4</sub>)<sub>3</sub>.

The lithium cations possess a fairly distorted tetragonal pyramidal coordination with distances Li–O 2.01(1)–2.25(1) Å.

In the structure of  $\text{LiK}_2\text{In}(\text{MoO}_4)_3$ , the  $\text{MoO}_4$  tetrahedra,  $\text{InO}_6$  octahedra and  $\text{LiO}_5$  tetragonal pyramids are connected via their common vertices to form a 3D mixed open framework penetrated with channels along the *a* axis (Fig. 5). The channel cavities of the polyhedral framework contain two kinds of the potassium ions with coordination numbers 9 and 7 (Table 6).

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## Appendix A. Supplementary materials

Supplementary materials associated with this article can be found in the online version at doi:10.1016/j.jssc.2012.01.010.

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