K$_5$InHf(MoO$_4$)$_6$: A solid state conductor

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Abstract. Potassium indium hafnium molybdate of composition K$_5$InHf(MoO$_4$)$_6$ has been studied by powder X-ray diffraction, differential scanning calorimetric (DSC) analysis and impedance spectroscopy. The compound has high ion conductivity. The high conductivity of K$_5$InHf(MoO$_4$)$_6$ allows us to consider it as a promising solid electrolyte.

1. Introduction

So far, fossil fuels remain our primary power supply resource. However, extensive use of fossil fuels is the main cause of global warming because they emit large amounts of carbon dioxide. Developing low cost energy storage systems is required for the successful launch of electric vehicles and efficient utilization of renewable energy sources such as solar and wind [1, 2]. The average annual demand for lithium carbonate (Li$_2$CO$_3$) will grow by 16.76 % within the next six years; therefore, global lithium reserves without recycling can only last for 28 years. It should be noted that K and Na occupy 2.09 and 2.36 wt. % of the earth's crust, whereas Li occupies 0.0017 wt. %. Recently, much attention has been focused on room-temperature Na-ion and K-ion batteries due to the cost-effectiveness of sodium and potassium. Furthermore, in comparison to Na$^+$, K$^+$ ions exhibit closer negative redox potential to Li$^+$. In the last few decades, there has been a surge of interest in molybdates. They found application in different fields of science and engineering. Many molybdates containing tetrahedral anions MoO$_4$ and various cations are valuable and promising laser materials [3, 4], ferroelectrics and ferroelastics [5], phosphors [6, 7], ionic conductors [8, 9], materials for Li(Na, K)-ion batteries [10, 11], etc. Some molybdates of alkali metals have high ionic conductivity [12–14]. On the basis of these molybdates, energy saving devices can be created.

Materials on the base In$_2$(MoO$_4$)$_3$ have attention due to their extensive chemical flexibility and resulting immense promise for applications in microelectrical, micro-machine, optical and high temperature devices [15, 16]. This paper presents our findings on the phase relations, thermal and electrical properties of molybdate K$_5$InHf(MoO$_4$)$_6$ in the ternary system K$_2$MoO$_4$–In$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$. Neither phase relations in the system K$_2$MoO$_4$–In$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$, nor thermal and electrical properties of K$_5$InHf(MoO$_4$)$_6$ have been studied previously. The ternary molybdate K$_5$InHf(MoO$_4$)$_6$ and its crystal structure have been previously reported [17]. A three-dimensional mixed framework of the structure is formed by Mo tetrahedrons and two independent (In, Hf) octahedrons, which are connected through shared vertexes. Two types of potassium atoms occupy large voids of the framework (Figure 1). Thus, there are structural prerequisites for fast ion transport.
Figure 1. Mixed framework of MoO$_4$ tetrahedra and two types of octahedra (In,Hf)O$_6$ in the K$_5$InHf(MoO$_4$)$_6$ crystal structure. M(1) = 0.413(1) Hf + 0.587(1) In; M(2) = 0.587(1) Hf + 0.413(1) In.

2. Models and Methods

Starting simple molybdates were obtained by gradual annealing of stoichiometric mixtures of HfO$_2$ (chemically pure), In$_2$O$_3$ (chemically pure), and MoO$_3$ (chemically pure) at 673–973 K for Hf(MoO$_4$)$_2$ and 673–1073 K for In$_2$(MoO$_4$)$_3$, respectively. Commercially available K$_2$MoO$_4$ (analytical grade) was used as starting material. Powder XRD of all prepared compounds agree well with corresponding data reported in [18, 19].

Subsolidus phase relations in the K$_2$MoO$_4$‒In$_2$(MoO$_4$)$_3$‒Hf(MoO$_4$)$_2$ system at 773–823 K were established by the intersecting joins method [20, 21]. 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 K$_5$InHf(MoO$_4$)$_6$ was obtained by annealing stoichiometric mixtures of simple molybdates up to 823 K for 80–100 h.

The powder X-ray diffraction was recorded on a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Berlin, Germany) with Cu-Kα radiation (λ = 1.5418 Å) at room temperature. The scanning range is between 5 and 100° with a scanning width of 0.02 and a rate of 0.1 s$^{-1}$.

The thermal property was investigated by the differential scanning calorimetric (DSC) analysis and the thermogravimetric analysis (TGA) using a NETZSCH STA 449C TG/DSC/DTA thermal analyzer (NETZSCH, Berlin, Germany). A 17 mg sample of powder was placed in a Pt crucible and heated from room temperature at a rate of 10 °C min$^{-1}$ in an Ar atmosphere.

Electrical conductivity measurements were carried out on cylinder-shaped ceramic samples which were 10 mm in diameter and 2 mm thick, with platinum electrodes by the electrochemical impedance method on a Z-1500 J immitance meter in the temperature range 473–913 K. Impedance spectra were recorded in the frequency range from 1 Hz to 1 MHz. Electrical conductivity $\sigma$ for each temperature was calculated from

$$\sigma = \frac{4h}{\pi D^2 R}$$  \hspace{1cm} (1)

where $h$ is sample thickness in cm, $D$ is diameter in cm, and $R$ is ohmic resistance in Ω.

3. Results and Discussion

Data on the bounding sides of the K$_2$MoO$_4$‒In$_2$(MoO$_4$)$_3$‒Hf(MoO$_4$)$_2$ system were taken from the literature. It is known [22] that the double molybdates K$_8$Hf(MoO$_4$)$_6$ and K$_2$Hf(MoO$_4$)$_3$ are formed at
the lateral side $K_2MoO_4–Hf(MoO_4)\_2$. New compounds are not formed in the $In_2(MoO_4)\_3–Hf(MoO_4)\_2$ system [23]. According to data [24], three double molybdates of 1:1, 3:1 and 5:1 compositions occur in the $K_2MoO_4–In_2(MoO_4)\_3$ system. Orthorhombic $KIn(MoO_4)\_3$ has its own structure type with a framework of $InO_6$ octahedra and $MoO_4$ tetrahedra [25]. $K_3In(MoO_4)\_3$ also has two forms, but their structures are unknown yet. In the work [26] it was found that the quasibinarity of the $K_2MoO_4–In_2(MoO_4)\_3$ system is broken as a result of the formation of $KInMo_4O_{15}$ and $In_2O_3$. $K_5In(MoO_4)\_4$ is dimorphic, the structures of both modifications related to the palmierite $K_2Pb(SO_4)\_2$ type [27–29].

The results of the investigation of the system are presented in Figure 2. The following quasibinary cross-sections exist in the subsolidus region 773–823 K: $KIn(MoO_4)\_2–K_8Hf(MoO_4)\_6$; $KIn(MoO_4)\_2–K_2Hf(MoO_4)\_3$; $KIn(MoO_4)\_2–Hf(MoO_4)\_2$; $KIn(MoO_4)\_2–K_5InHf(MoO_4)\_6$; $K_8Hf(MoO_4)\_6–K_5InHf(MoO_4)\_6$; $K_2Hf(MoO_4)\_3–K_5InHf(MoO_4)\_6$; $K_5InHf(MoO_4)\_6–K_2InHf(MoO_4)\_6$.

Figure 3 represents DSC scans of $K_5InHf(MoO_4)\_6$ in the temperature range 300–1000 K. The temperature of the phase transition for $K_5InHf(MoO_4)\_6$ corresponds to 910 K, $\Delta H = −1.279$ J/g. $K_5InHf(MoO_4)\_6$ melts at $T = 1015$ K, $\Delta H = −44.48$ J/g.

In Figure 4 the variation of AC conductivity ($\sigma$) with $1000/T$ at various frequencies and with $\omega$ (at various temperatures) are presented for $K_5InHf(MoO_4)\_6$.

Below 800 K, the $K_5InHf(MoO_4)\_6$ conductivity is not high and has a low activation energy. Above this temperature, a kink appears on the curve, and the conductivity steadily increases to reach $1.3 \times 10^{-3}$ S/cm at 913 K.

The frequency dependences of conductivity can be divided into three regions: 1 (low frequencies), region of increasing specific conductivity because of less significant charge accumulation in the region of electrodes at higher frequencies; 2 (medium frequencies), frequencies-independent region; and 3 (high frequencies), region with the universal dynamic response (Figure 4(b)).

We have plotted impedance diagrams viz., $ReZ$ (pure resistive part of the impedance) versus $ImZ$ (capacitive reactance). A typical AC impedance Nyquist spectrum of a solid electrolyte material may include arcs corresponding to the grain bulk, grain boundary, electrode-related impedance. The impedance plots drawn at multiple temperatures shown in Figure 5 (a, b). The diagrams are found to be in semicircular shape with inclined spur at low frequency region Figure 5 (a). As the temperature of measurement is increased, the area under the curve exhibited a decreasing trend. The impedance spectra suggest that there are two types of charge carriers in the bulk material. The semicircular arc is connected with bulk conduction, whereas the spur represents the piling of conducting species at the platinum electrodes on surface of the samples. The higher the magnitude of the inclined spur, the larger is the concentration of charge carriers that accumulate at the electrodes. At a temperature of about 800 K,
we observe two distorted semicircles. With increasing temperature, the left semicircle becomes more pronounced (Figure 5 (b)).

The high conductivity of $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ is made possible by sufficiently large sizes of voids in structure, which appreciably decrease the steric hindrances to transport. Potassium ions, with their large radii, form comparatively weak bonds with their oxygen surrounding, and these bonds are cleaved more easily than those of smaller cations. The high ion conductivity of $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ molybdate allows us to consider its as promising conductor.

![Figure 4](image1)

**Figure 4.** Variation in AC conductivity with 1000/T at different frequencies (a; triangles - heating, circles - cooling) and (b) with frequency at different temperatures for the sample $\text{K}_5\text{InHf(MoO}_4\text{)_6}$.

![Figure 5](image2)

**Figure 5.** Impedance plots for the $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ at specified temperatures.

4. Conclusion

Phase relations in the system $\text{K}_2\text{MoO}_4 - \text{In}_2(\text{MoO}_4)_3 - \text{Hf(}\text{MoO}_4\text)_2$ have been investigated. The $\text{K}_2\text{MoO}_4 - \text{In}_2(\text{MoO}_4)_3 - \text{Hf(}\text{MoO}_4\text)_2$ system consists of three binary compounds and one ternary compound $\text{K}_5\text{InHf(MoO}_4\text{)_6}$. The electrophysical and thermal properties of molybdate have been studied. The temperature of the phase transition for $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ corresponds to 910 K, $\Delta H = -1.279$ J/g. $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ molybdate melts at $T = 1015$ K, $\Delta H = -44.48$ J/g. The studied material are characterized with ionic conductivity of $10^{-9} - 10^{-3}$ S·cm$^{-1}$ at 496–913 K. The high conductivity of $\text{K}_5\text{InHf(MoO}_4\text{)_6}$ molybdate allows us to consider it as promising solid electrolyte.
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References
[1] Bonaccorso F, Colombo L, Yu G, Stoller M, Tozzi T, Ferrari A C, Ruoff R S and Pellegrini V 2015 Science \textbf{347} 1246507
[2] Choi J W and Aurbach D, 2016 \textit{Nat. Rev. Mater.} \textbf{1} 16013
[3] Kaminskii A A 2007 \textit{Laser Photon. Rev.} \textbf{1} 93-177
[4] Macalik L 2002 \textit{J. Alloy. Compd.} \textbf{341} 226-32
[5] Dudnik E F and Kiosse G A 1983 \textit{Ferroelectrics} \textbf{48} 33-48
[6] Benoit G, Véronique J, Arnaud A and Alain G 2011 \textit{Solid State Sci.} \textbf{13} 460-7
[7] Wang Zh, Liang H, Wang Q, Luo L and Gong Menglian 2009 \textit{Mater. Sci. Eng. B.} \textbf{164} 120-3
[8] Savina A A, Solodovnikov S F and Belov D A 2014 \textit{J. Solid State Chem.} \textbf{220} 217-20
[9] Bazarova J G, Logvinova A V, Bazarov B G, Tushinova Y L, Dorzhieva S G and Temuujin J 2018 \textit{J. Alloy. Compd.} \textbf{741} 834-9
[10] Mikhailova D, Sarapulova A, Voss A, Thomas A, Oswald S, Gruner W, Trots D M, Bramnik N N and Ehrenberg H 2010 \textit{Chem. Mater.} \textbf{22} 3165-73
[11] Gao J, Zhao P and Feng K 2017 \textit{Chem. Mater.} \textbf{29} 940-4
[12] Solodovnikov O S, Klevtsova R F and Klevtsov P V 1994 \textit{J. Struct. Chem.} \textbf{35} (6) 879-9
[13] Kruglyashov A L and Skou E M 1988 \textit{Solid State Ion.} \textbf{28–30} 233-6
[14] Solodovnikov S F, Solodovnikova Z A, Zolotova E S, Yudin V N, Gulyaeva O A and Tushinova 2017 \textit{J. Solid State Chem.} \textbf{253} 121-8
[15] Evans J S O, Mary T A and Sleight A W 1997 \textit{Phys.B: Condens. Matter.} \textbf{241} 311-6
[16] Evans J S O 1999 \textit{J. Chem. Soc.} \textbf{19} 3317-26
[17] Bazarov B G, Bazarova Ts T, Fedorov K N, Bazarova Zh G, Klevtsova R F and Glinskaya L A 2005 \textit{Russ. J. Inorg. Chem.} \textbf{50} (8) 1146-9
[18] Plyasova L M, Klevtsova R F, Borisov S V and Kefeli L M 1968 \textit{Kristallogr.} \textbf{13} 38-42
[19] Thoret J 1974 \textit{Rev. Chim. Miner.} \textbf{11} 237-61
[20] Guertler W Z 1926 \textit{Anorg. Allg. Chem. Bd} \textbf{154} (1–4) 439–55
[21] Niepel L and Malinovsky M 1978 \textit{Chem. Zvesti} \textbf{32} (6) 810-20
[22] Zolotova E S, Glinskaya L A and Klevtsov P V 1977 \textit{Zhurn. Neorg. Khimii} \textbf{22} (3) 704-7
[23] Tushinova Yu L, Bazarova J G and Arhincheeva S I 2002 Phase equilibria in R2(MoO4)3–Zr(MoO4)2 systems \textit{All-Russian Scientific Conf. with Int. Partic.} (Ulan-Ude: BSC SB RAS Press) pp 90-1
[24] Velikodny Yu A, Trunov V K and Markelova N I 1970 \textit{Russ. J. Inorg. Chem.} \textbf{15} 1587-90
[25] Klevtsova R F and Klevtsov P V 1971 \textit{Kristallografiya} \textbf{16} 292-8
[26] Khal’baeva K M, Solodovnikov S F, Khaikina E G, Kadyrova Yu M, Solodovnikova Z A and Basovich O M 2012 \textit{J. Solid State Chem.} \textbf{187} 276-81
[27] Lazoryak B I and Efremov V A 1987 \textit{Kristallografiya} \textbf{32} 378-84
[28] Lazoryak B I 1996 \textit{Russ. Chem. Rev.} \textbf{65} 287
[29] Kudin O V, Efremov V A, Trunov V K and Velikodny Yu A 1981 \textit{Zh. Neorg. Khim.} \textbf{26} 2734