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**Evidences of the non-stoichiometry and control of the composition of the
cluster-based solid solution $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ ($x=2.75-3.63$)**

Tatiana I. Lappi^{1,2}, Yakov M. Gaifulin¹, Vadim V. Yanshole^{3,4}, Stephane Cordier², Nikolay G. Naumov^{1*}

¹ Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Acad. Lavrentiev ave., 630090 Novosibirsk, Russia;

² Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000

³ International Tomography Center, Siberian Branch of the Russian Academy of Sciences (SB RAS), Novosibirsk 630090, Russia;

⁴ Novosibirsk State University, Novosibirsk 630090, Russia

*Email: naumov@niic.nsc.ru

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Abstract. In this work, we investigated a high-temperature reaction between ReS_2 , MoS_2 and KCN resulting in the formation of the cluster-based $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ solid solution. The crystal structure is based on chains of $[Re_{6-x}Mo_xS_8(CN)_6]$ cluster units. It was found that both the sintering temperature of starting sulfides and the reaction temperature with KCN have an influence on the composition of the product allowing x to be varied within the range $x = 2.75-3.63$. The molar ration of $ReS_2:MoS_2:KCN$ loaded composition is fixed to 3:3:14 in all experiments. Energy dispersive spectroscopy (EDS), powder X-ray diffraction (PXRD) and high-resolution electrospray (ESI) mass spectrometry were used to characterize the solid solution $K_6[Re_{6-x}Mo_xS_8(CN)_5]$. It was shown by mass spectrometry that the solid solution with fractional x contains anions based on the $\{Re_4Mo_2S_8\}$, $\{Re_3Mo_3S_8\}$ and $\{Re_2Mo_4S_8\}$ cluster cores in different proportions depending on the above-mentioned factors. Particularly, the rise of the temperature of the synthesis or temperature of sintering of metal sulfides led to increase of the rhenium content in the solid solution.

Introduction

Octahedral chalcogenide and halide clusters built on face-capped $\{M_6X_8\}$ cluster core represent a large and practically important class of inorganic compounds ^[1-6]. They are widely studied and demonstrate promising catalytic, magnetic and photophysical properties (selected references are: ^[7-12]). The eight faces of the M_6 cluster are coordinated by inner ligands forming the cluster cores $\{M_6(\mu_3-X)_8\}^{m+}$ ($M = Mo, W, X = Cl, Br, I, S, Se, \text{ or } Te; M = Tc, Re, X = S, Se, \text{ or } Te$). With a few exceptions, cluster compounds generally consist of similar $[M_6X_8L_6]$ building blocks and crystallize as phases of stoichiometric composition. Formation of non-stoichiometric phases is quite rare in the chemistry of clusters. Heterometallic clusters represent a special type of cluster compounds containing different metal atoms within the core ^[13-23]. The introduction of another metal atom makes it possible to change the properties of cluster compounds in a controlled manner, and can also lead to interesting optical properties due to a decrease of the symmetry of the cluster core. A few detailed studies of heterometallic clusters have shown that they may crystallize as non-stoichiometric compounds containing cluster cores with different metal-to-metal ratio and their properties are closely related to the composition of the cluster core ^[18, 21-23]. Such co-crystallization occurs as a result of high-temperature synthesis. The presence of cluster cores with different metal-to-metal ratio in the lattice of the resulting compounds was confirmed by their dissolution and investigation by spectroscopic methods (UV-Vis, NMR), mass spectrometry, chemical separation and crystallization of different species. For example, compound $K_2[Re_3Os_3Se_8Cl_6][Re_4Os_2Se_7Cl_7]$, which was obtained by reaction between Re, Os, Se, $ReCl_5$ and KCl, is a solid solution ^[22]. Cluster anions with $\{Re_3Os_3Se_8\}$ and $\{Re_4Os_2Se_7Cl\}$ cores were detected using electrospray mass spectrometry of the aqueous solution of this compound.

Heterometallic clusters with $\{Re_3Mo_3S_8\}$ cores were synthesized using high-temperature reaction between ReS_2 , MoS_2 and KCN. It was shown that the resulting polymeric phase $K_6[Re_3Mo_3S_8(CN)_5]$ comprises $\{Re_3Mo_3S_8\}$ based cluster ^[18]. A closer examination of this reaction and in particular the Re/Mo ratio in the final product revealed that despite the loaded composition was “ $K_6[Re_3Mo_3Se_8(CN)_5]$ ” in all experiments, the true final composition corresponds to the non-stoichiometric $K_6[Re_{6-x}Mo_xS_8(CN)_5]$. The x value depends on the experimental conditions. In order to clarify the nature of non-stoichiometry of the $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ phase, we investigated the dependence of the composition as a function of two parameters: 1) the synthesis temperature of the ReS_2 and MoS_2 used as reagents and 2) the temperature of interaction of sulfides with KCN. The molar ratio of $ReS_2:MoS_2:KCN$ loaded composition was fixed to 3:3:14 in all experiments. We found that both parameters affect the composition and consequently, the resulting phase is composed of cluster anions of different core

composition, namely, $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$, $\{\text{Re}_3\text{Mo}_3\text{S}_8\}$ and $\{\text{Re}_2\text{Mo}_4\text{S}_8\}$ co-existing in the crystal lattice in different ratio.

Experimental

Materials and methods

Elementary rhenium and molybdenum were annealed under H_2 flow to reduce the traces of oxides. Water and other solvents were purged with Ar before use. Metal disulfides MS_2 were obtained in silica ampoules from corresponding metals and sulfur taken in stoichiometric amounts at temperatures (T_1) specified in Table 1. The syntheses were carried out for 48 h; ampoules have been recovered after the oven has cooled to room temperature. The particle size of the obtained metal sulfides was estimated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with a Libra 120 (Zeiss, Germany) at an acceleration voltage of 60 kV, as well as by the Scherer formula from powder X-ray diffraction data (PXRD). Other reagents were purchased from commercial sources and used without further purification.

The crystals were analyzed using a JXA-8100 (JEOL, Japan) Electron Probe Micro-analyzer equipped with a wavelength-dispersive spectrometer. Elemental intensities for K, Re, Mo and S were determined relative to single crystal standards using metallic Re for Re, metallic Mo for Mo and MoS_2 for S. About 20 points of quantitative data were collected for the major phase of each crystal and converted to crystal-chemical formulas by assuming 26 atoms per formula unit. Averages and standard deviations were calculated to be ± 0.04 , which were consistent with the 3 σ criteria.

Electrospray ionization mass spectrometric (ESI–MS) analysis was performed on a Bruker maXis 4G high-resolution ESI-q-TOF spectrometer. The mass spectra were recorded under the following conditions: registration mode of negative ions from $m/z = 600$ Da to 4000 Da, voltage +2500 V, pressure on the nebulizer 0.8 bar, drying gas flow 4 l/min, drying gas temperature 180 °C.

Preparation of $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$

For the preparation of $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$, ReS_2 (1.02 g, 4.0 mmol) and MoS_2 (0.65 g, 4.0 mmol) were thoroughly grounded and placed in a silica ampoule with KCN (1.68 g, 25.0 mmol). Ampoule was evacuated and sealed. The reaction was carried out at the temperatures T_2 (given in Table 2) for 8 days and ampoule was slowly cooled to the room temperature. Resulting product was washed with EtOH/ H_2O mixture to remove soluble by-products. The sample contained octahedral black crystals with an admixture of unreacted metal sulfides, which were

separated by sonication in EtOH with subsequent decantation. Black crystals of $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ were filtered and dried in argon atmosphere. The analysis of the PXRD pattern of $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ revealed that it is isostructural with the reported compound $K_6[Re_3Mo_3S_8(CN)_5]$ [18]. The yields and mean chemical compositions of $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ $x = 2.75-3.63$ are given in Table 2. The x values were taken from the EDS. Several crystals were selected from each synthesis, where points were measured the content of each metal, ranging from 10 to 15 points.

Preparation of $(Ph_4P)_5[Re_{6-x}Mo_xS_8(CN)_6]$

Samples for the ESI-MS analyses were prepared by quantitative precipitation of $(Ph_4P)_5[Re_{6-x}Mo_xS_8(CN)_6]$. To dissolve $K_6[Re_{6-x}Mo_xS_8(CN)_5]$, the technique reported in [18] was used: KCN (10 mg, 0.16 mmol) and H₂O (5 ml) were added to $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ (250 mg, 0.16 mmol). The solution of Ph₄PCl (300 mg, 0.8 mmol) in H₂O (5 ml) was added to the solution of cluster complex, causing immediate precipitation of $(Ph_4P)_5[Re_{6-x}Mo_xS_8(CN)_6]$. After centrifugation and washing, the obtained salt was dissolved in CH₃CN (3 ml) and the resulting solution was investigated by ESI-MS.

Results and discussion

According to [18], the reaction of ReS₂ and MoS₂ with KCN at elevated temperature resulted in formation of cluster-based phase $K_6[Re_3Mo_3S_8(CN)_5]$ by reaction:



During investigation of the “ $K_6[Re_3Mo_3S_8(CN)_5]$ ” phase we have discovered that its precise composition and in particular the Re/Mo ratio, depends on the synthesis temperature of both cluster phase and MS₂ precursors. This results in a phase stoichiometry deviation from the ideal $K_6[Re_3Mo_3S_8(CN)_5]$. To understand the non-stoichiometry of the $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ phase, we investigated the dependence of the composition on i) sulfide sintering temperature (T_1) and ii) the synthesis temperature of $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ phase (T_2). The comparison of XRD patterns (Figure 1) of binary sulfides sintered at different temperatures expectedly showed that the increase of sintering temperature leads to the increase of the average particle size (Table 1) and narrowing the XRD reflections. Estimation by the Scherrer equation showed a trend in the average size of crystals, and the broadening of the diffraction peaks confirms the change. The increasing of particles size was confirmed by SEM and TEM studies (Fig S2 – S3). Determination of the average size has been challenging due to the ability of metal sulfides to form agglomerates and

due to high aspect ration of crystallites. The effect of sintering temperature on the peak broadening and average particle size is well known for metal sulfides.

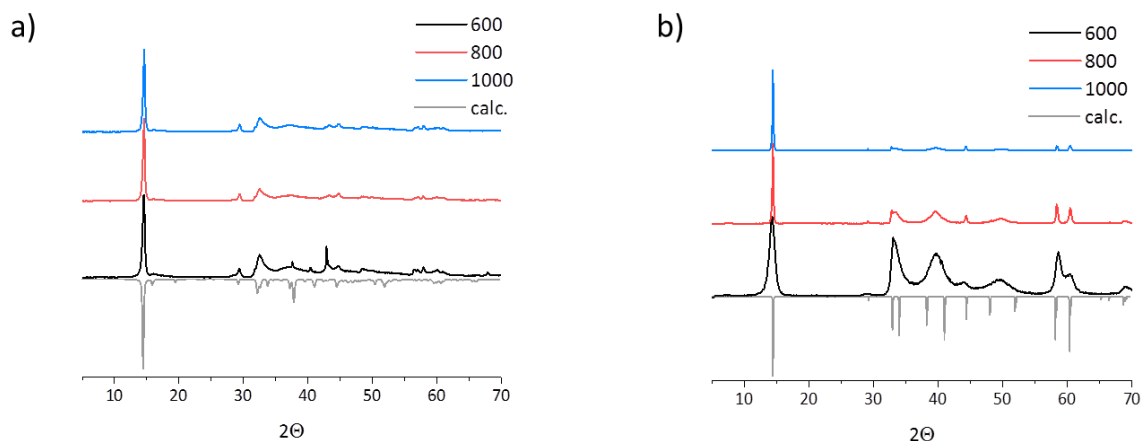


Fig. 1. Dependence of XRD for the ReS₂ (a) and MoS₂ (b) from the temperature T₁.

T ₁ (°C)	d ReS ₂ (nm)	d MoS ₂ (nm)
600	18.9	7.8
800	22.7	35.6
1000	23.3	38.4

Table 1. The mean particle size of the obtained metal sulfides estimated by PXRD by the Scherer formula

In order to reduce the number of parameters to be changed, we fixed the ratio of rhenium and molybdenum sulfides, the amount of KCN in the ampoule, the synthesis time (8 days) and the isolation procedure described in the Experimental part. Table 2 summarizes the product yield and ratio of heavy atoms according to EDS analysis. It should be noted that in some cases, a temperature higher than 850 °C leads to the degradation of ampoules, and lower temperatures resulted in by-products.

T ₁ (MS ₂ , °C)	600	800	1000

T_2 (°C)			
700	Yield 67%	Yield 74%	Yield 66%
	<i>EDS</i> $K : Mo : Re : S =$ 6.12:3.63:2.37:8.06	<i>EDS</i> $K : Mo : Re : S =$ 5.77:2.85:3.15:8.05	<i>EDS</i> $K : Mo : Re : S =$ 5.87:2.84:3.16:8.11
750	Yield 78%	Yield 89%	Yield 85%
	<i>EDS</i> $K : Mo : Re : S =$ 6.07:2.87:3.13:8.17	<i>EDS</i> $K : Mo : Re : S =$ 5.88:2.89:3.11:8.10	<i>EDS</i> $K : Mo : Re : S =$ 5.88:2.76:3.23:8.16
850	Yield 61%	*	Yield 72%
	<i>EDS</i> $K : Mo : Re : S =$ 6.04:2.75:3.25:8.20		<i>EDS</i> $K : Mo : Re : S =$ 6.07:2.76:3.24:8.12

* Numerous attempts to obtain the compound have been unsuccessful due to degradation of silica ampoule

Table 2. Yield of products and EDS results for $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ obtained at different temperatures.

The comparison of the ratio of rhenium to molybdenum in the samples obtained from different series and synthesized at different temperatures showed that both factors affect the composition of the $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ phase. According to the Table 2, the highest molybdenum content was observed in the sample prepared from rhenium and molybdenum sulfides obtained at low temperature (600°C). This phase has a average ratio of Re/Mo equal to 2.37/3.63. The increase of the sulfide sintering temperature and/or synthesis temperature leads to

the formation of rhenium richer phases. According to data given in Table 2, for the reaction with KCN carried out at a temperature of 700°C, the total amount of rhenium in the reaction product increases from 2.37 to 3.16 with rising temperature preparation of metal sulfides. In the case of syntheses carried out at higher temperatures, the content of rhenium in the product changes insignificantly with changing of the precursors. There is a slight increase in the Re content from 3.13 to 3.23 for reaction carried out at 750 °C, and at 850 °C the Re/Mo ratio in the samples is practically insensitive to the MS₂ synthesis temperature.

Analysis of the EDS results showed that the metal ratio can vary even within one crystal of the K₆[Re_{6-x}Mo_xS₈(CN)₅] phase (Fig. 2). It has been observed that the edges of the crystal have different Re/Mo ratio in comparison with the area closer to the crystal center. Each crystal was investigated in several measuring points, including its edges and center. For example, for a sintering temperature T₁ equal to 600°C and a synthesis temperature T₂ equal to 750°C, the Re/Mo ratio in the center of the crystal and at the edge was 2.74:3.26 and 3.69:2.31, respectively. Similar gradient of composition was observed for many crystals in all syntheses.

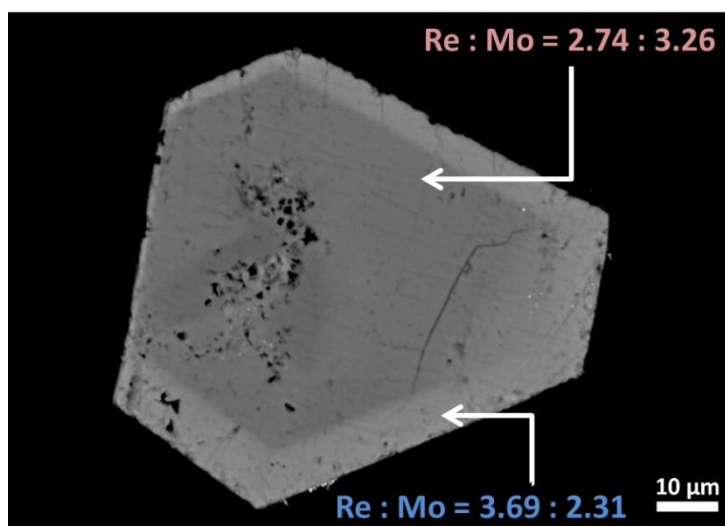


Fig. 2. Image of a crystal of compound **1** obtained at sintering temperature T₁ equal to 600°C and synthesis temperature T₂ equal to 750°C.

To confirm the complex nature of solid solutions, we used high-resolution electrospray mass spectrometry. As it was shown in ^[18], the K₆[Re₃Mo₃S₈(CN)₅] phase can be dissolved in aerated KCN solution giving [Re₃Mo₃S₈(CN)₆]⁵⁻ anion. To clarify the nature of non-stoichiometry of K₆[Re_{6-x}Mo_xS₈(CN)₅] solid solutions, we have dissolved them in a similar way and analyzed all prepared samples by ESI-MS analysis. The dissolution of K₆[Re_{6-x}Mo_xS₈(CN)₅] resulted in formation of [Re_{6-x}Mo_xS₈(CN)₆]⁵⁻ anions which were precipitated as tetraphenylphosphonium

salts. Acetonitrile solution of $(\text{Ph}_4\text{P})_5[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_6]$ was used for registration of ESI-MS spectra.

Regardless the composition of $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ samples, all mass spectra reveal the presence of $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$, $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$ and $[\text{Re}_2\text{Mo}_4\text{S}_8(\text{CN})_6]$ cluster anions with a 6-charge (Figure 3). The ratio of these anions in different samples varies strongly depending on the sintering temperature T_1 and the synthesis temperature T_2 . Table 3 graphically represents the mole ratios between the anions $[\text{Re}_{6-n}\text{Mo}_n\text{S}_8(\text{CN})_6]$, $n = 2, 3$ and 4 based on the mass-spectrometry data.

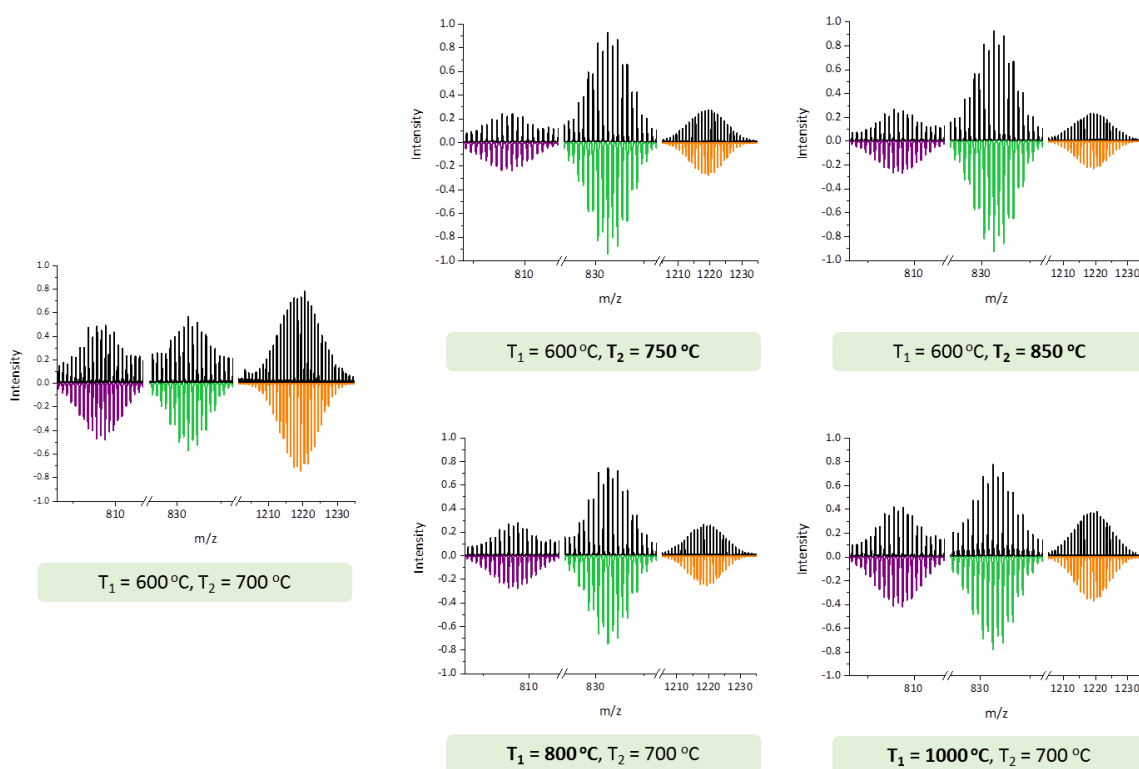


Fig. 3. Isotopic distributions of cluster adducts presented in CH_3CN solution of $(\text{Ph}_4\text{P})_5[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_6]$ salt prepared at different T_1 (600, 800, 1000 °C) and T_2 (700, 750, 850 °C) (top). Bottom: calculated isotopic distributions for corresponding adduct. Signals corresponds to the adducts $\{(\text{Ph}_4\text{P})[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot \text{H}_2\text{O}\}^{2-}$ ($m/z_{\text{calcd}} = 808.758$ Da), $\{(\text{Ph}_4\text{P})[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_5]\}^{2-}$ ($m/z_{\text{calcd}} = 831.276$ Da), $\{\text{H}_2[\text{Re}_2\text{Mo}_4\text{S}_8(\text{CN})_4] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}\}^{2-}$ ($m/z_{\text{calcd}} = 1220.399$ Da) left to right, correspondingly).

Reaction temperature	Temperature of sintering of sulfides (T_1)		
	600	800	1000

re (T ₂)				
700	<p>T₁ = 600, T₂ = 700</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 2.37: 3.63</p> <p>a</p>	<p>T₁ = 800, T₂ = 700</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.15: 2.85</p> <p>b</p>	<p>T₁ = 1000, T₂ = 700</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.16: 2.84</p> <p>c</p>	
	750	<p>T₁ = 600, T₂ = 750</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.13: 2.87</p> <p>d</p>	<p>T₁ = 800, T₂ = 750</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.11: 2.89</p> <p>e</p>	<p>T₁ = 1000, T₂ = 750</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.23: 2.77</p> <p>f</p>
		800	<p>T₁ = 600, T₂ = 850</p> <p>■ {Re₃Mo₃S₈} ■ {Re₄Mo₂S₈} ■ {Re₂Mo₄S₈}</p> <p>EDS: Re: Mo = 3.25: 2.75</p> <p>g</p>	<p>*</p>

* Numerous attempts to obtain the compound have been unsuccessful due to degradation of silica ampoules

Table 3. Graphical representation of the mole ratio between the anions [Re_{6-n}Mo_nS₈(CN)₆] (n= 2–4) based on the mass-spectrometry depending on the sintering temperature T₁ and synthesis temperature T₂.

It is clearly seen that the sample obtained from sulfides sintered at T₁ = 600°C at T₂ = 700°C contains a significant amount of [Re₂Mo₄S₈(CN)₄]⁵⁻ anion. That correlates with the high molybdenum content in the initial K₆[Re_{2.37}Mo_{3.63}S₈(CN)₅] phase. The rise of the synthesis

temperature resulted in the increase of the $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$ form, while the amount of the $\{\text{Re}_3\text{Mo}_3\text{S}_8\}$ and $\{\text{Re}_2\text{Mo}_4\text{S}_8\}$ forms decreases (Figure 6a->b->c). Similar trend is observed with increase of sintering temperature of sulfides (Figure 6a->d->g). Therefore, the $\text{K}_6[\text{Re}_{3.24}\text{Mo}_{2.76}\text{S}_8(\text{CN})_5]$ phase synthesized at higher T_1 and T_2 is rhenium-rich and contains significant amount of $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$ anion. These data are in agreement with the EDS data (Table 2). Thus, mass-spectrometry reveals that $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ phase is built up from 3 different cluster-based units with $\{\text{Re}_2\text{Mo}_4\text{S}_8\}$, $\{\text{Re}_3\text{Mo}_3\text{S}_8\}$, $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$ cluster cores in different amounts which leads to x values ranging from 2.75 to 3.63. The presence of different anions with integer metal content was also observed earlier in the selenide phase $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{Se}_8(\text{CN})_5]$ [19, 21]. Apparently, the formation of solid solution substitution at non-isovalent substitution is a common feature of heterometallic clusters.

Conclusion

In this work, we described the effect of the synthesis temperature, as well as the sintering temperature of starting metal sulfides precursors MoS_2 and ReS_2 on the content of rhenium and molybdenum in the solid solution $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ ($x = 2.75-3.63$). It was found that the temperature of the sintering of the starting metal sulfides affects the size of the resulting particles and subsequently the composition of $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ phase. It was determined that starting from sulfides sintered at $600\text{ }^\circ\text{C}$ leads to molybdenum rich phase $\text{K}_6[\text{Re}_{2.37}\text{Mo}_{3.63}\text{S}_8(\text{CN})_5]$ when the reaction temperature is low ($700\text{ }^\circ\text{C}$). With the rise in the reaction temperature, the rhenium content in the reaction product increases. ESI-MS spectrometry reveals that the solutions prepared from these compounds contain 3 different anions cores based on the three following cluster cores: $\{\text{Re}_2\text{Mo}_4\text{S}_8\}$, $\{\text{Re}_3\text{Mo}_3\text{S}_8\}$ and $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$. The sintering temperature of sulfides and temperature of the synthesis of $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ phase influence on the proportions of these forms. With a rise in the synthesis temperature, the amount of the $\{\text{Re}_4\text{Mo}_2\text{S}_8\}$ form increases, and the amount of the $\{\text{Re}_3\text{Mo}_3\text{S}_8\}$ and $\{\text{Re}_2\text{Mo}_4\text{S}_8\}$ forms decrease. Thus, EDS analysis and mass-spectrometry reveal that $\text{K}_6[\text{Re}_{6-x}\text{Mo}_x\text{S}_8(\text{CN})_5]$ phase is the substitution solid solution with the fractional indexes ($x = 2.75-3.63$) composed of discrete cluster cores with an integer indexes n in $\text{Re}_{6-n}\text{Mo}_n\text{S}_8$, $n = 2, 3$ or 4 .

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