Reactions in Molten Alkalimetal Polychalcogenides: What Happens in the Melt? A Study of the Reactions in the System K-Nb-S Using Differential Scanning Calorimetry, Infrared Spectroscopy, and X-Ray Powder Diffraction

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Alkalimetal Niobium Polychalcogenides, Infrared Spectroscopy, Differential Scanning Calorimetry

The reactions of potassium polysulfides with elemental Nb were investigated with different analytical techniques. The amount of the polysulfide applied has no influence onto product formation, *i. e.* the ratio K_2S_x: Nb is not important. The length of the polsysulfide chain, *i. e.* the value of x in K_2S_x determines what product is formed. In sulfur-poor melts, K_3NbS_4 is observed. Increasing x to 5 - 6, $K_4Nb_2S_{11}$ is formed with a structure containing S_2^{2-} anions. Finally, applying a melt with $x > 6$, $K_6Nb_4S_{25}$ is found as the product with a crystal structure containing the S_5^{2-} polysulfide anion. When K_2S_x ($x < 5$) is heated with sulfur in the first step the pentasulfide K_2S_5 is formed. Immediately after melting of K_2S_5 a reaction with elemental Nb occurs. The results of FT-IR and X-ray investigations have demonstrated that after oxidation the anion $[Nb_2S_{11}]^{4-}$ is formed relatively fast, and after a short time crystalline $K_4Nb_2S_{11}$ can be detected. After 24 h the reaction is complete.

Introduction

During the last decade many new multinary chalcogen compounds were prepared applying the low melting alkali metal polychalcogenides. Comprehensive collections of the compounds are reported in several review articles [1 - 8].

We focussed our syntheses on group 4 and 5 metals with the aim to prepare low-dimensional compounds exhibiting interesting physical properties. In the K-Nb-S system we synthesised several new compounds with compositions $K_4Nb_2S_{11}$ [9], $K_4Nb_2S_{14}$ [10], $K_6Nb_4S_{22}$ [11], and $K_6Nb_4S_{25}$ [12].

Until now the synthetic work can still be described as a 'trial and error' endeavour and only very few rules of thumb are at hand allowing the prediction of the composition of the final product.

To the best of our knowledge there is only one contribution in which the synthesis of compounds was systematically investigated using different educts and synthesis conditions [13]. The formation of β-$CsBiS_2$ and γ-$CsBiS_2$ was investigated with differential scanning calorimetry (DSC) and X-ray powder diffractometry. The reaction of elemental Bi with Cs_2S_x melts (ratio: 1:4.5; $x = 2.5$ - 3.0) in the temperature range of 250 °C to 300 °C was found to yield exclusively the β modification. Changing the Bi to Cs_2S_x ratio to 1:4, increasing x to 3.0 - 3.7 and using a temperature of 350 °C lead to the formation of γ-$CsBiS_2$. The results have demonstrated that for each modification a distinct temperature and composition range is required. The knowledge of the influence of the different synthesis parameters onto product formation is a prerequisite for a more rational synthesis strategy. Reactions between Bi and Li_2S_x resp. Na_2S_x ($x = 2.2$ - 5) in the temperature range from 290 to 345 °C always yield $LiBiS_2$ and $NaBiS_2$. Of special interest is also the observation made by the authors that reactions performed with commercially available Cs_2S result in the formation of Bi_2S_3 whereas $CsBiS_2$ is formed if freshly prepared Cs_2S is used. It was argued that the variations in reactivity are due to the different particle sizes of Cs_2S.

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Table 1. Reactions of Nb with K_2S_3 and different amounts of S.

No.	Mixture	Ratio	Product	Temperature
1	K_2S_3 : S : Nb	2 : 0 : 1	K_3NbS_4	350 °C
2	K_2S_3 : S : Nb	2 : 2 : 1	K_3NbS_4	350 °C
3	K_2S_3 : S : Nb	2 : 4 : 1	$K_4Nb_2S_{11}$	350 °C
4	K_2S_3 : S : Nb	2 : 6 : 1	$K_4Nb_2S_{11}$	350 °C

Here we report the results of a systematic study of the processes occurring in the melts of the K-Nb-S system. The system was chosen because the five well characterised compounds K_3NbS_4, $K_4Nb_2S_{11}$, $K_4Nb_2S_{14}$, $K_6Nb_4S_{22}$, and $K_6Nb_4S_{25}$ are formed depending on the actual preparation conditions.

Experimental Section

The potassium polysulfides were prepared by the reaction of stoichiometric amounts of the elements (K 99.95%, Strem) in liquid ammonia under argon atmosphere. Elemental Nb (99.97 %, Fluka) was used as supplied. Differential scanning calorimetry (DSC) was conducted on a Netzsch device. All measurements were performed in evacuated and sealed glass ampoules using heating and cooling rates of 3 K min^{-1}. The compositions of all reaction products were determined by elemental analysis and X-ray powder diffractometry. The FT-IR spectra were recorded on an ISF-66 device (Bruker) in the range from 80 to 550 cm^{-1} with a resolution of 2 cm^{-1}. The samples were prepared as polyethylene pellets. X-ray powder diffractometry experiments were performed with a D5000 diffractometer (Siemens AG) in reflection geometry and with the STADI P diffractometer (STOE) operating in transmission geometry (CuK_α radiation, λ = 1.54056 Å).

Results and Discussion

For reactions between polychalcogenides and certain very reactive metals it was assumed that the metal reacts with the original starting material A_2Q_x (A = alkali metal, Q = S, Se, Te) before a polychalcogenide flux containing different polychalcogenides has formed [4]. Therefore, it cannot be excluded that different products are formed when a mixture of K_2S and sulfur or the already synthesised polysulfide *e. g.* K_2S_5 is supplied. Hence, in the first part of the experiments the influence of different polychalcogenides (K_2S_x) onto the product formation was investigated. The experiments were performed with a fixed amount of K_2S_3 and Nb and a variable amount of S (Table 1). The composition of the products was investigated with X-ray powder diffractometry.

Table 2. Reactions of Nb with K_2S_x, x = 1, 3, 5 and S.

No.	Mixture	Ratio	⇒ K_2S_x	Product	Temperature
5	K_2S:S:Nb	2:8:1	K_2S_5	$K_4Nb_2S_{11}$	300 - 400 °C
6	K_2S_3:S:Nb	2:4:1	K_2S_5	$K_4Nb_2S_{11}$	300 - 400 °C
7	K_2S_5:S:Nb	2:0:1	K_2S_5	$K_4Nb_2S_{11}$	300 - 400 °C

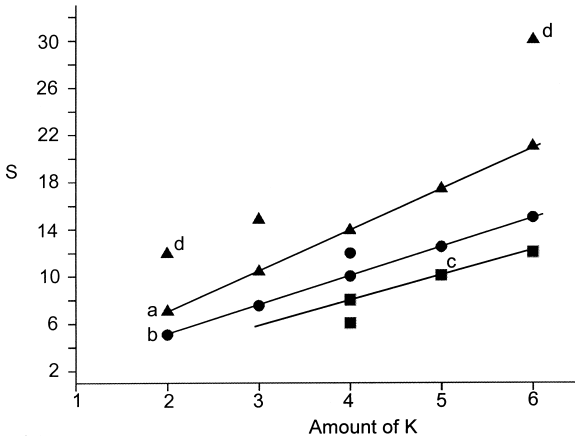


Fig. 1. Reaction products in the system K/Nb/S for varying compositions of the melt (T = 350 °C). a: $K_6Nb_4S_{25}$ is the main phase; by-product: $K_4Nb_2S_{14}$. b: $K_4Nb_2S_{11}$ and K_3NbS_4 c: K_3NbS_4. d in the melt solidified sulfur is present. Symbols: squares: K_3NbS_4; circles: $K_4Nb_2S_{11}$; triangles: $K_6Nb_4S_{25}$. The lines join melts with identical composition.

Obviously, less S rich melts like K_2S_3 or K_2S_4 lead to the formation of K_3NbS_4 which contains no polysulfide anions in the structure, and the most S rich reaction mixtures favour the formation of $K_4Nb_2S_{11}$ which contains several S_2^{2-} anions in the structure. The same results were obtained at 300 °C and 400 °C. Therefore, the composition of the melt determines the final product within a temperature range of 300 °C to 400 °C.

The next set of experiments was performed with different K_2S_x (x = 1, 3, 5) chalcogenides (Table 2).

Within the temperature range 300 - 400 °C no influence of the chalcogenide K_2S_x supplied onto product formation could be observed. In all syntheses only $K_4Nb_2S_{11}$ was formed. Based on the amount of Nb used in the syntheses the yields were identical. In the next series of experiments two pa-

rameters were varied: x in K_2S_x as well as the ratio K_2S_x : Nb. For syntheses with a polysulfide with $x \geq 5$ we used K_2S_5 plus additional sulfur when necessary and syntheses with $x < 5$ were done with K_2S and the appropriate amount of S. All experiments were conducted at 350 °C. The results of the experiments are displayed in Fig. 1. In the graph the amount of S is plotted *vs.* the amount of K with the concentration of Nb set to one. The different symbols mark the products formed with the different mixtures. The lines are guides for the eyes and connect the K_2S_x samples with different x values.

We note that as major phases only 3 different compounds with composition K_3NbS_4, $K_4Nb_2S_{11}$ and $K_6Nb_4S_{25}$ were formed. As a by-product $K_4Nb_2S_{14}$ was obtained using a polysulfide melt with formal composition "K_2S_7". In the X-ray powder pattern of the products marked with **d** elemental sulfur could be identified. Hence, there is an upper limit where additional sulfur plays no role for the syntheses.

One important point should be mentioned here: Using a K:Nb ratio of 2:1 and low amounts of S (symbols marked with **a** and **b**) no "true" meltcake is formed but rather a dense and crumbly product is obtained. Treating the product with DMF and diethylether nearly no excess polysulfide is dissolved and the crystals are small and of poor quality. This observation may indicate that the product consists of a phase mixture. Obviously, when no true melt is formed the diffusion is low at the low temperatures leading to local inhomogeneities. On the other hand it cannot be excluded that inhomogeneities within the mixture of the educts are present that are not removed during the reaction.

The most important result is that the amount of the polysulfide applied has no influence onto product formation, *i. e.* the ratio K_2S_x: Nb is not important. The length of the polysulfide chain, *i. e.* the value of x in K_2S_x determines what product is formed. For x = 3 - 4 only K_3NbS_4 is observed which only contains S^{2-} anions. Increasing x to 5 - 6 $K_4Nb_2S_{11}$ is formed with a structure containing S_2^{2-} anions. Finally, applying a melt with $x >$ 6 $K_6Nb_4S_{25}$ is found as the product with a crystal structure containing S_5^{2-} polysulfide anion. It must be noted that the polysulfide $K_6Nb_4S_{22}$ was synthesised using NbS_2 instead of Nb [11] and all attempts to prepare this compound in the usual way failed. Hence, we are not surprised that this polysulfide was not formed during our experiments.

Ex-situ Investigations

The reactions occurring in the melt were also investigated with DSC, FT-IR spectroscopy and X-ray diffractometry (XRD). The DSC experiments were conducted in sealed and evacuated glass ampoules with about 20 mg of K_2S_x. The material was heated to 400 °C with a heating rate of 3 °C/min., held at this temperature for 2 h and cooled to room temperature with 3 °C/min. This heating cycle was performed two times. At the end of the treatment the products were characterised with XRD.

For a better understanding of the DSC curves of the reactions between Nb and K_2S_x the pure polysulfides K_2S_3 und K_2S_5 were characterised with DSC in advance. In addition, mixtures of S with K_2S were also investigated with DSC (K_2S:S = 1:4 and K_2S_3:S = 1:2).

For K_2S_3 and K_2S_5 the melting points (T_{onset} values) were 294 °C and 206 °C respectively. Both values are in good agreement with data published in the literature (K_2S_3: 292 °C; K_2S_5: 211 °C [14, 15]. Upon heating a mixture of K_2S/S with a ratio of 1:4 several thermal events were observed during the first heating cycle. But on heating the product a second time only one melting point at 206 °C was observed. The X-ray powder pattern of the product contained only reflections of K_2S_5. For the reaction between K_2S_3 and S (ratio 1:2) again several thermal events were observed in the first heating curve. But only one endothermic signal at 206 °C in the second heating cycle indicated the melting of K_2S_5 formed during the first treatment. In the X-ray powder pattern of the product only the reflections of K_2S_5 were seen.

The results of our DSC as well as XRD investigations of reactions between K_2S_x and sulfur suggest that in all cases the pentasulfide is formed *in-situ*. Hence, the reaction of K_2S_5 with Nb in the 2:1 ratio was studied with DSC, XRD, and FT-IR. According to the results presented above the only product of the reaction is $K_4Nb_2S_{11}$.

The DSC curve for the reaction of Nb with pure K_2S_5 leading to $K_4Nb_2S_{11}$ is displayed in Fig. 2. A weak endothermic event occurs at 190 °C followed by the melting of K_2S_5 at 206 °C. The melting is followed by two exothermic processes (216

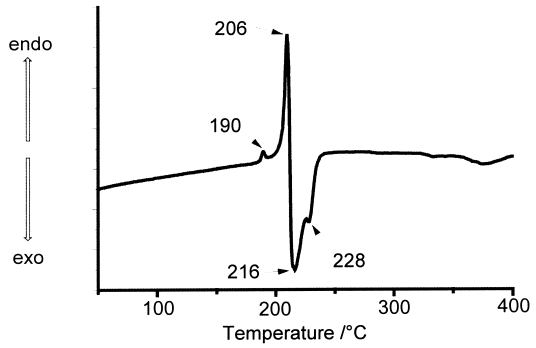
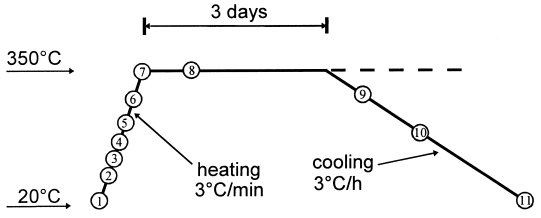


Fig. 2. DSC curve for a mixture of K_2S_5 with Nb.



Scheme 1. Temperature program for the quenching experiments. The numbers are the steps where ampoules are removed and immediately quenched. 1: 20 °C, 2: 210 °C, 3: 213 °C, 4: 217 °C, 5: 230 °C, 6: 290 °C, 7: 350 °C, 8: 350 °C after 24 h, 9: 300 °C, 10: 230 °C, 11: final product after cool to room temperature.

and 228 °C) that are due to the oxidation of Nb. No further thermal events occur up to 400 °C and in the cooling curve.

For the XRD and FT-IR investigations a reaction mixture K_2S_5 + Nb was prepared and distributed over 9 ampoules. The heat treatment of the ampoules was identical with the heat procedure used for the syntheses of $K_4Nb_2S_{11}$.

During the heating procedure ampoules were removed from the furnace at distinct temperatures (see numbers in Scheme 1). These ampoules were immediately quenched in liquid nitrogen, opened in a glove-box and characterised with XRD and FT-IR in the as received state. The spectra are displayed in Fig. 3. In the figure the spectra of pure K_2S_5 measured at 20 °C and of pure $K_4Nb_2S_{11}$ are also shown.

At 210 °C which is the melting temperature of K_2S_5 the absorption modes of the pentasulfide are seen. Upon increasing the temperature to about 213 °C the intensities of the bands strongly decrease. According to the DSC experiments at this temperature the reaction between Nb and the molten poly-

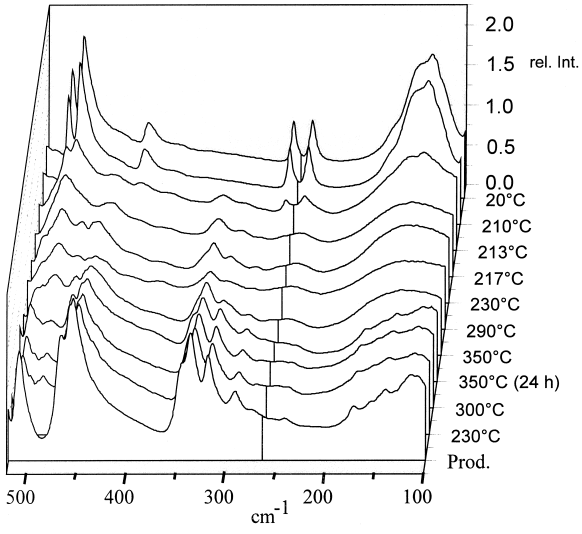


Fig. 3. FT-IR spectra of the products formed at the different temperatures indicated in Scheme 1.

sulfide starts. In the spectrum a weak absorption at 335 cm^{-1} starts to grow. This band is characteristic for $K_4Nb_2S_{11}$. At 217 °C the bands of K_2S_5 have nearly disappeared and the mode at 335 cm^{-1} becomes more intense. In the spectra of the samples quenched from even higher temperatures K_2S_5 cannot be identified and the intensities of the typical absorptions of the product are more pronounced. At the end of the heating cycle (350 °C) the characteristic pattern of $K_4Nb_2S_{11}$ located between 260 and 360 cm^{-1} is found. After annealing for 24 h the IR spectrum is very similar to that of the pure product $K_4Nb_2S_{11}$. Differences of the intensities are due to the fact that the spectrum was recorded with the as-prepared mixture whereas the spectrum of $K_4Nb_2S_{11}$ was measured after purification, *i. e.* removal of unreacted educts.

The last two spectra obtained with samples quenched during the cooling cycle show no significant changes. A similar picture was obtained with X-ray diffraction experiments [8]. The metal is not consumed within the first exothermic reaction and reflections of elemental Nb could be detected up to 350 °C. After 24 h the Nb had completely reacted with the sulfide melt. Interestingly, reflections of the crystalline product $K_4Nb_2S_{11}$ develop immediately after the reaction of Nb with the K_2S_5 melt. It is highly likely that the species formed at the surface of the Nb crystallites diffuse away to crystallise as

$K_4Nb_2S_{11}$. We have no hints for the formation of a crystalline intermediate compound.

The results of the present experiments yield the following picture for the reaction of Nb in potassium polysulfide melts: The amount of the polysulfide applied has no influence onto product formation. That means the ratio K_2S_x : Nb is not important. As discussed above the length of the polysulfide chain determines which product is formed. Exclusive crystallisation of K_3NbS_4 is observed in K_2S_x melts with x = 3 - 4. When x is increased to 5 - 6, the polysulfide $K_4Nb_2S_{11}$ is formed with a structure containing S_2^{2-} anions. The compound $K_6Nb_4S_{25}$ with a structure containing the S_5^{2-} polysulfide anion is the only product upon applying melts with $x > 6$.

When K_2S_x ($x < 5$) is heated with sulfur, in the first step the pentasulfide K_2S_5 is formed which melts at about 206 °C. Immediately after melting the polysulfide reacts with elemental Nb. The FT-IR and X-ray investigations demonstrate that after oxidation the anion $[Nb_2S_{11}]^{4-}$ is formed relatively fast and after a short time crystalline $K_4Nb_2S_{11}$ appears. After 24 h the reaction is complete as is evidenced by the very small changes of the intensities of the absorptions in the FT-IR spectra and of the reflection intensities in the X-ray powder patterns [8].

Acknowledgements

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