Technical University of Denmark

DTU

Raman Spectroscopy Evidence of 1:1:1 Complex Formation during Dissolution of WO3 in a Melt of K2S2O7: K2SO4

Berg, Rolf W.; Ferré, Irene Maijó; Schäffer, Susan Jeanne Cline

Link to publication

Raman spectroscopy evidence of 1:1:1 complex formation during dissolution of WO₃ in a melt of K₂S₂O₇:K₂SO₄

Rolf W. Berg [a,*], Irene Maijó Ferré [a,b], Susan J. Cline Schäffer [a]

[a] Department of Chemistry, The Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Lyngby, Denmark
[b] Facultat de Química, University of Rovira i Virgili, Tarragona 43007, Spain

Abstract

Highly inert yellow solid WO₃ was found to be soluble in considerable amounts in molten $K_2S_2O_7$ at elevated temperatures ($\sim$650 °C), if only similar molar amounts of sulfates were also present. The dissolution reaction of WO₃ into a melt consisting of a 1:1 molar mixture of $K_2S_2O_7$ and K_2SO_4 was studied in detail, and Raman spectroscopy was used to characterize the products. In combination with single crystal X-ray crystal structure determination, it was shown that a new dimeric compound, $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$, was formed and its assigned Raman spectrum at room temperature is given. The WO_2^{2+} cores of the dimeric complex have their symmetrical and antisymmetrical stretching modes $\nu_1(WO_2^{2+})$ and $\nu_3(WO_2^{2+})$ at around 1054 (strong) and 1042 (weak), and the bending mode $\nu_2(WO_2^{2+})$ at around 292 (medium intensity), respectively (positions given in cm^{-1}).

© 2006 Elsevier B.V. All rights reserved.

Keywords: Assignment; Dissolution; K_2SO_4; $K_2S_2O_7$; $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$; Melt; Raman; Solid; Spectroscopy; Tungsten oxide; WO₃

1. Introduction

Previously we have studied the dissolution properties of a number of oxide salts in disulfate (pyrosulfate) salt melts. In one case, Nb_2O_5 was found to dissolve in considerable amounts into molten $K_2S_2O_7$ at about 450 °C [1,2]. The stoichiometric properties of this and similar reactions were studied by Raman spectroscopy [3] and X-ray single crystal diffraction [4]. Other oxide salts, e.g. ZnO [5] and MoO₃ [6], were recently found to dissolve into $Na_2S_2O_7$ and $K_2S_2O_7$, and references to more systems are described there.

In this communication, we report results on tungsten oxide, WO₃. This oxide is known as a highly inert yellow solid compound that is practically insoluble in acids. This insolubility, combined with other properties, makes tungsten oxide itself and mixtures with other metal oxides commonly used catalysts or supported catalyst surfaces, see e.g. [7].

Recently we confirmed that WO₃ is sparingly soluble in acidic melts of $K_2S_2O_7$, but, surprisingly, we also discovered [8] that considerable amounts of WO₃ did dissolve in into melts of $K_2S_2O_7$ at elevated temperatures ($\sim$650 °C) if similar amounts of sulfates (or possibly potassium oxide and SO₃) were also present. The purpose of the present project, therefore, was to use Raman spectroscopy to characterize the products formed by mixing WO₃, K_2SO_4 and $K_2S_2O_7$ in varying molar amounts in sealed ampoules, and then to study the range of stability of the products.

In the following, we will interpret the Raman spectra of the molten solutions to show that a 1:1:1 reaction:

$$WO_3 + K_2SO_4 + K_2S_2O_7 \rightarrow products$$
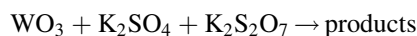
took place, and that $[WO_2]^{2+}$ ions solvated by SO_4^{2-} ions are formed. The stoichiometry of the reaction was determined by isolating crystals and examining them by single crystal X-ray diffraction; the results were confirmed by Raman spectroscopy.

2. Experimental

2.1. Samples

The hygroscopic $K_2S_2O_7$ [7790-62-7] was synthesized from dried $K_2S_2O_8$ salt [7727-21-1] (Merck, pro analysi > 99%) by thermal decomposition at 250 °C for 1 h under a dry nitrogen

---

Table 1
Relative molar compositions studied by Raman spectroscopy

WO_3 (mol%)	K_2SO_4 (mol%)	$K_2S_2O_7$ (mol%)
0.0	0.0	100.0
3.0	3.0	94.0
7.0	7.0	86.0
10.0	10.0	80.0
13.0	13.0	74.0
17.0	17.0	66.0
18.0	18.0	64.0
19.0	19.0	62.0
21.0	21.0	58.0
27.0	27.0	46.0
29.0	29.0	42.0
33.0	33.0	34.0

Fig. 2. Three samples (frozen melts) in ampoules at 25 °C are shown; at the top: 3% WO_3 + 3% K_2SO_4; in the middle: 17% + 17%; at the bottom: 29% WO_3 + 29% K_2SO_4 (in $K_2S_2O_7$ on mole basis).

atmosphere [9]. The anhydrous product was immediately transferred to an air-filled dry box (the hygroscopic $K_2S_2O_7$ requires handling in a dry box to avoid that it picks up water) [9]. In the box weighed amounts of WO_3 (tungsten (VI) oxide [1314-35-8], Merck, reinst > 99%) and K_2SO_4 ([7778-80-5], Merck, suprapur > 99.999%), were mixed with $K_2S_2O_7$ in varying molar amounts. The mixtures were introduced into cylindrical quartz ampoules that were subsequently removed from the dry box and immediately sealed under vacuum. The relative molar compositions are given in Table 1. A composition triangle diagram is shown in Fig. 1. The ampoules were heated for a few hours in a rocking furnace at ~650 °C, a temperature high enough for liquids to form (the m.p. of $K_2S_2O_7$ is 419 °C [10]). The appearance of three samples after reaction is shown in Fig. 2.

2.2. Raman equipment

Raman spectra were obtained by use of a DILOR-XY 800 mm focal-length multi-channel spectrometer with macro- and micro-entrances (see Fig. 3). Excitation was done with filtered Ar$^+$-ion laser light (wavelength 514.5 nm, power
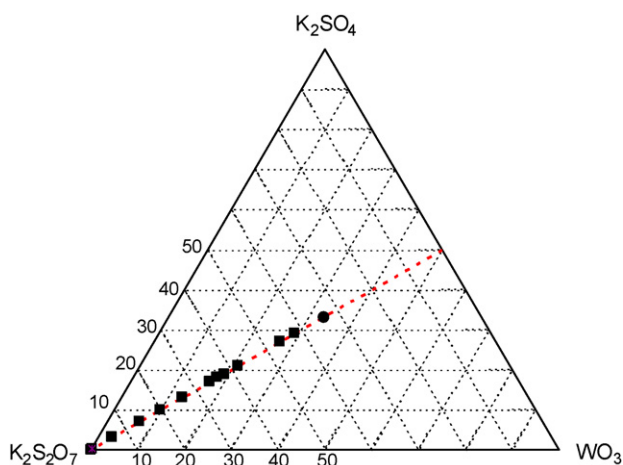
~400 mW continuously, vertical polarization obtained by suitable rotation of the half-wave plate). The horizontal macro-entrance was used for the melts, and crystals were measured under the microscope. Filtration of Rayleigh scattering was done with a Kaiser holographic SuperNotch-Plus® filter or near the laser line with the double pre-monochromator. Depending on the selected grating, the Raman spectral resolution was within 2–8 cm^{-1}. The light was detected with a liquid N$_2$-cooled CCD detector (140 K) connected to a MS Windows-98 computer with the Horiba-JobinYvon LAB-SPEC® software. A sheet polarization analyzer, permitting vertically (V) or horizontally (H) polarized light to pass, was used to obtain VV- and VH-polarized spectra of liquids. Calibration was done with cyclohexane and sulfur lines to a precision of 1 cm^{-1} [11].

2.3. Heating

Sample temperature control was achieved by means of a homemade four-window electric furnace with PID regulation, based on C/A thermocouple control, or for the case of crystals under the microscope, by a LINKAM HFS91/TP93 cryostat/furnace stage. The temperature was determined with a Pt 100 Ω resistor (±5 °C).

3. Results and discussion

By inspection through the furnace windows, it was found that WO_3 dissolved (reacted) in considerable amounts in molten $K_2S_2O_7$ + K_2SO_4 mixtures to form viscous yellowish melts, especially at high temperatures. When samples were cooled slowly, the melts froze to microcrystalline lumps (for low WO_3 contents) and clear glasses (for higher WO_3 contents) (see Fig. 2, bottom).

Equimolar amounts of $K_2S_2O_7$, K_2SO_4 and WO_3 gave clear homogeneous glass masses of gross formulae $K_4(WO_2)(SO_4)_3$. No chemical analysis was made, since the compositions were already known and the melts were homogeneous. No attack on the quartz wall was seen even after prolonged heating.

Crystals were grown by quenching the melts, partly remelting them and then cooling at a rate of 6 °C per hour, allowing for better crystallization. The ampoules were studied directly or, for crystallographic examination, broken and the

Fig. 1. Ternary composition diagram. Molar percentages of the two reactants (WO_3 and K_2SO_4) are given along the axes as denoted. The solid circle in the middle corresponds to the dimeric compound $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$.

Fig. 3. Schematics of the Raman DILOR-XY spectrometer. M, mirror; λ/2, half-wave plate; IF, interference filter; L, lens; NF, notch filter; P, polarizer; G, grating. The furnace was mounted on a XYZ-table (not shown), allowing the melts to be placed at the sample position to the right.
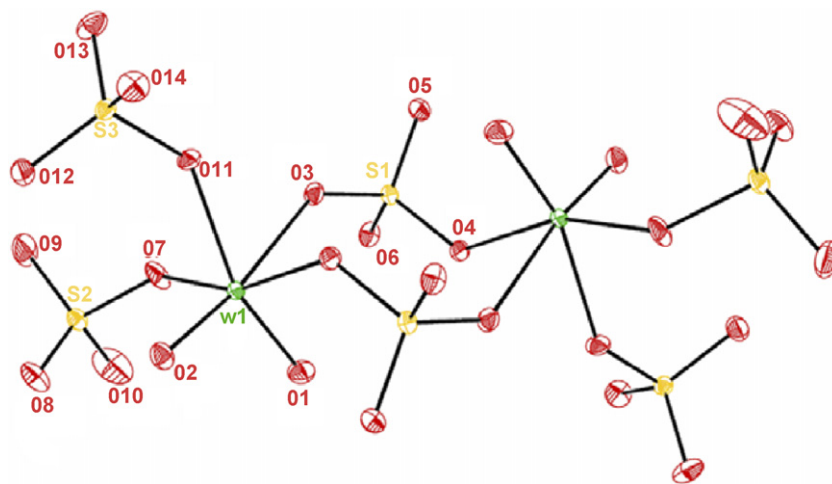
Fig. 4. Plot of the $[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]^{8-}$ anion, showing 50% probability ellipsoids. The eight K^+ ions have been omitted for clarity.

colorless crystals taken out at ambient temperature. They proved to be quite stable in ordinary air. Single crystals of a compound, made from $1WO_3:1K_2S_2O_7:1K_2SO_4$, have recently been obtained, and the X-ray structures of a couple of crystals solved [8] to show that the dimeric compound, $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$, is formed. The structure is shown in Fig. 4. The compound crystallizes in the monoclinic space group $P2_1/n$ with two dimeric units in the unit cell of dimensions $a = 9.4362$ Å, $b = 13.9625$ Å, $c = 10.1948$ Å, and $\beta = 90.780°$ [8].

The $(\mu\text{-}SO_4)_2$ way of linking of two MO_2^{2+} centers (see Fig. 4, M = metal) has previously been found for molybdenum, where polymeric strands occurred by repetition of the linking in the $K_2MoO_2(SO_4)_2$ structure [6]. Here in the Mo-containing melts, bands assignable to $\nu_1(C_{2v})$ in bridging sulfato groups were seen at 958 cm^{-1} [6]. The W(VI) coordination sphere [8] shown in Fig. 4 is generated by inversion symmetry from the independent $[W(VI)O_2(SO_4)_3]^{4+}$ moiety, resulting in two bridging sulfato ligands.

During this work, by varying the composition of the melt (Table 1) and isolating crystals, it was shown that the dimeric compound $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$ exists from at least 5 to 29 mol% (see Fig. 1). Melting of the $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$ crystals started at about 600 °C (visual observation).

3.1. Vibrational spectra

Raman spectra of melts at ~650 °C and frozen solutions at ~25 °C are shown in Figs. 5–8 (X = formal mole fraction of WO_3 and K_2SO_4 in the WO_3–K_2SO_4–$K_2S_2O_7$ system, see Table 1).

The spectra of melts of different compositions (see Fig. 5) showed that the characteristic bands of $K_2S_2O_7$ gradually disappeared when the tungsten oxide content was increased. At the same time, new bands appeared monotonically, indicating that a reaction has occurred. More precisely, it was seen that the most characteristic 1086 cm^{-1} band of $K_2S_2O_7$ disappeared and the new 1045 cm^{-1} band of the mixture (the new compound)
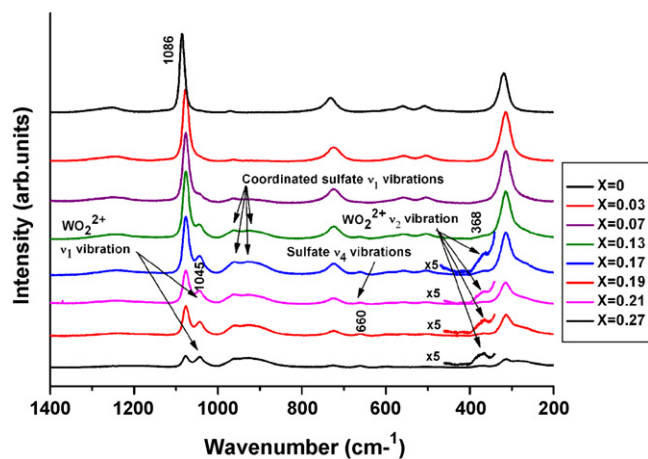
Fig. 5. Raman spectra of melts of different compositions (X = formal mole fraction of WO_3 and K_2SO_4 in the WO_3–K_2SO_4–$K_2S_2O_7$ system) at ~650 °C (spectra shifted in y-axis for clarity).

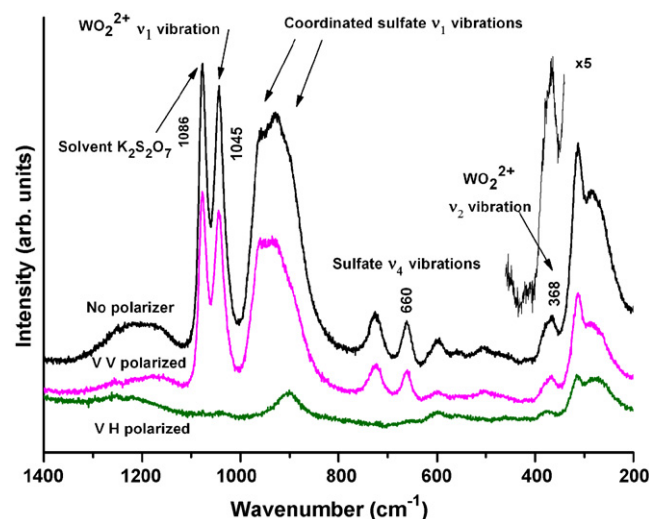Fig. 6. Polarized Raman spectra of the melt of composition X = 0.27 (X = formal mole fraction of WO_3 and K_2SO_4 in the WO_3–K_2SO_4–$K_2S_2O_7$ system) at ~650 °C. WO_2^{2+} and SO_4^{2-} stretches and WO_2^{2+} bending can be assigned to bands at ~1100, ~900 and ~390 cm^{-1}. Other assignments are presented in Table 2. Spectra have been shifted in y-axis for clarity.

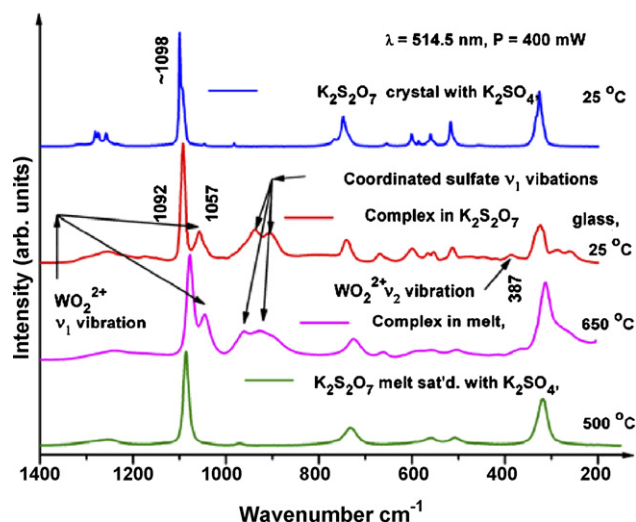Fig. 7. Raman spectra at temperatures indicated (from below): $K_2S_2O_7$ melt saturated with K_2SO_4, complex in melt, complex in frozen glass, and frozen $K_2S_2O_7$ "solvent". WO_2^{2+} and SO_4^{2-} stretches and WO_2^{2+} bending can be assigned to bands at ~1100, ~900 and ~390 cm^{-1}, depending on the temperature. Assignments are presented in Table 2. Spectra have been shifted in y-axis for clarity.

increased with the WO_3 percentage. Even at the highest contents of tungsten oxide and sulfate (Fig. 6), we only saw indication of one kind of complex. In Fig. 6 the polarized Raman spectra of the melt of composition $X = 0.27$ is shown as an example. In Fig. 7, Raman spectra are presented of a $K_2S_2O_7$ melt, saturated with K_2SO_4, of the complex in the hot melt, of the complex in a frozen glassy $K_2S_2O_7$ "solvent", and of the microcrystalline frozen $K_2S_2O_7$ "solvent".
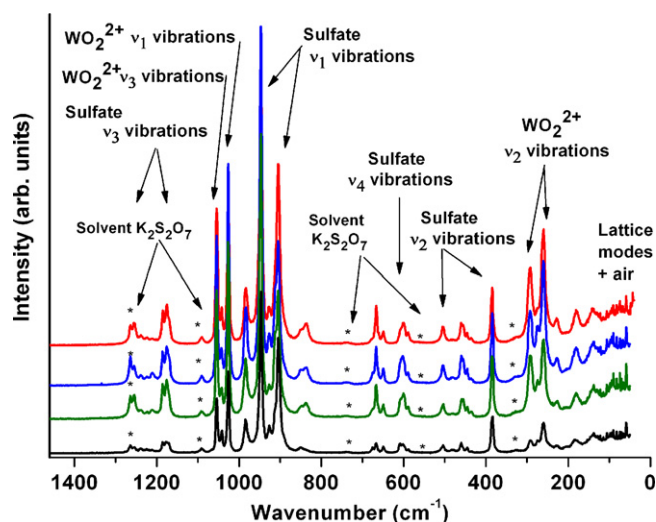

Fig. 8. Raman spectra of four $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$ crystals, measured under the microscope while still inside the ampoule. The crystals were grown at $\sim600\,^\circ$C and decanted from a WO_3–K_2SO_4–$K_2S_2O_7$ melt with a formal WO_3 mole fraction of 0.27. Assignments of bands at ~1100, ~900 and ~390 cm^{-1} to modes in WO_2^{2+} and SO_4^{2-} ions are shown (see also Table 2). Narrow lines below ~150 cm^{-1} from surrounding air and bands likely to come from traces of $K_2S_2O_7$ (indicated with asterisks) are also seen. Spectra have been shifted in y-axis for clarity.
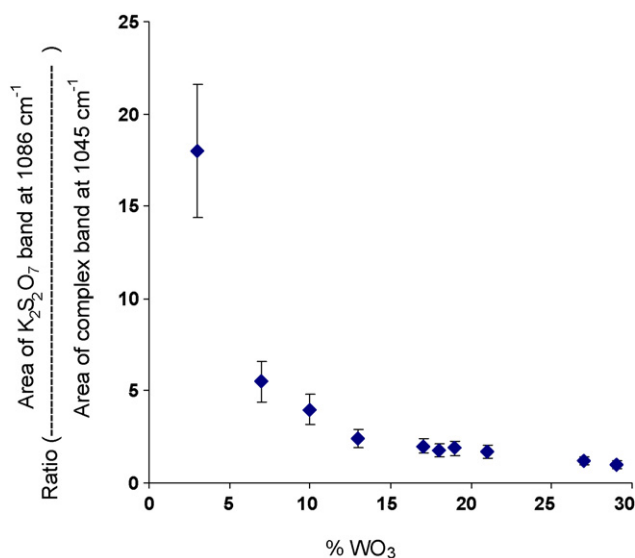

Fig. 9. Plot of the area ratios of the two bands ($\nu_{\text{disulfate}} = 1086$ cm^{-1}, $\nu_{\text{compound}} = \sim1045$ cm^{-1}) vs. composition.

The reaction is accordingly interpreted as a formation of $[WO_2]^{2+}$ ions solvated by bridging SO_4^{2-} ions. In the light of the X-ray results and the similarity of the spectra in the solid and dissolved state, the stoichiometry of the reaction is represented as 1:1:1, i.e. the reaction:

$$2WO_3 + 2K_2SO_4 + 2K_2S_2O_7 \rightarrow 8K^+$$
$$+ \left[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2\right]^{8-}$$
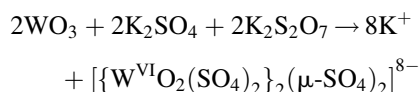
Previously we have described [1,3] a method to determine the stoichiometry of such reactions. When trying to use the method here, by plotting the area ratios between these two bands ($\nu_{\text{compound}} = \sim1045$ cm^{-1}, $\nu_{\text{disulfate}} = 1086$ cm^{-1} above the background) versus composition (in Fig. 9) we see a decrease of the area ratio with the increase of the WO_3 concentration. The curve obtained is not straight; however, it extrapolates smoothly towards the 1:1:1 reaction product, as expected from the X-ray results.

3.2. Assignments

The positions of the fundamental bands of a regular free SO_4^{2-} ion of T_d symmetry are well known: $\nu_1 = 983$, $\nu_2 = 450$, $\nu_3 = 1105$ and $\nu_4 = 611$ cm^{-1} [12]. When the symmetry of the SO_4^{2-} ion is lowered by complex formation (Fig. 4), two different approximate symmetries for the sulfate ion have been found previously; C_{3v} (bound unidentately) and C_{2v} (bound bridged bidentately) with shifted vibrational frequencies [12]. The vibrational spectrum for the disulfate (pyrosulfate) ion is well known and well understood, based on recent ab initio calculations [13]. Therefore, the bands due to the SO_4^{2-} and $S_2O_7^{2-}$ ions can be quite definitely identified.

The free bent $[WO_2]^{2+}$ ion has three vibrational degrees of freedom. Under the C_{2v} point group symmetry, the fundamentals are expected at around: $\nu_1 = 972$, $\nu_2 = 300$ and $\nu_3 = 928$ cm^{-1}.

Table 2
Observed Raman bands at ~600 °C (in cm^{-1}) and tentative assignments to fundamental group vibrations[a]

K$_2$S$_2$O$_7$ melt saturated with K$_2$SO$_4$ at 500 °C (Fig. 7)	Complex in melt at 650 °C (Figs. 6 and 7)	K$_2$S$_2$O$_7$ crystal at 25 °C (Fig. 7)	Complex in frozen glass at 25 °C (Fig. 7)	K$_8$W$_2$S$_6$O$_{28}$ crystal at 25 °C (Fig. 8)	Tentative assignment
~1304 w, br, dp		1281 m		1264 s	Asymmetric S–O stretches in SO$_4^{2-}$ and S$_2$O$_7^{2-}$ like ν_3(SO$_4^{2-}$) stretches
~1253 w, br, dp		1274 m	1256 w, br	1255 s, m	
	~1240 w, br	1257 m		1239 w	
		1231 w		1224 w	
				1211 w	
				1185 s	
~1137 vw				1175 s	
			1170 w, br	1170 sh	
~1085 vs, p	~1086 s, p	1098 vs	1092 vs	1090 w, p	ν(S$_2$O$_7^{2-}$) symmetric stretching
		1092 w, sh			
~1045 s, p		1046 vw			
		983 vw			
	~1045 s, p		1057 s	1054 s	ν_1(WO$_2^{2+}$) symmetric stretching
				1042 w	ν_3(WO$_2^{2+}$) asymmetric stretching
				1025 s	ν_1(WO$_2^{2+}$) symmetric stretching
			980 vw, br	983 m	Coordinated SO$_4^{2-}$: bridging ν_1(C$_{2v}$) at ~950 °C and terminal ν_1(C$_{3v}$) at ~925 °C
	~958 s, br, p		940 s, br	947 s	
	~928 s, br, p			927 w	
			905 m, br	911 w, sh	
	~900 m, br, dp			904 s	
				849 w	
				838 w	
~775 w, br, dp		765 w			K$_2$S$_2$O$_7$–SO$_4^{2-}$ bending
~730 m, p	~727 m, p	746 s	740 m	740 vw	
	~660 m, p			675 w, sh	ν_4(SO$_4^{2-}$) bending in complex
	~590 w, dp		669 w	667 m	
				607 m, sh	
		653 w	655 vw	649 w	K$_2$S$_2$O$_7$ and complex SO$_4^{2-}$ and S$_2$O$_7^{2-}$ bending
~599 w, dp		600 m	600 m	600 m	
		585 w	565 w	590 w	
~560 w, dp	~558 w, br, p	561 w	554 w		
~508 w, p	~506 w, dp	517 m	512 m	504 w	
				481 vw	Complex
~450 vw		455 vw		460 w	K$_2$S$_2$O$_7$
				455 w	
				446 w	
				435 w	
	~368 w, dp		387 w	385 m	Complex
~320 m, dp	~313 s, p	326 m	324 m	325 vw, br	ν(S$_2$O$_7^{2-}$) bending
	~278 m, br, dp		287 w, br	292 m	ν_2(WO$_2^{2+}$) bending
			261 w, br	274 w	
				260 m	
				227 w	Lattice
				207 vw, br	
191 w, p				180 w, br	
				139 w, br	
				92 w, br	

[a] Intensity codes: w, weak; m, medium; s, strong; sh, shoulder; v, very; br, broad; p, polarized; dp, depolarized.

These values refer to matrix isolated WO$_2$ molecules at low temperatures (in neon and argon gas matrix 4 and 20 K) and have been obtained from analysis of electronic transition spectra with long vibrational progressions [14]. Vibrations in different WO$_3$ polymorphous phases occur in the same range [15].

Hence, WO$_2^{2+}$ stretches and bendings should occur at about ~1100, ~900 and ~390 cm^{-1}. For the melts, we observed (Table 2) the appearance of two of these bands, $\nu_1 = 1045$ and $\nu_2 = 368$ cm^{-1}, ν_3 being probably weak and broad. The higher values observed here relative to the WO$_2$ at low temperature are due to the hexavalent state of W in the [WO$_2$]$^{2+}$ ion and to the high temperature.

This means, taking into consideration the low symmetry and the bonding between the WO$_2^{2+}$ and SO$_4^{2-}$ units in the dimeric

$[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]^{8-}$, that excessive mixing of group vibrations must occur. The assignments presented in Table 2 are therefore only tentative approximations.

In Fig. 8 we present Raman spectra of four $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$ crystals, recorded while still inside the ampoule. The crystals were grown and decanted from a melt at $\sim600\,^{\circ}C$ of composition $X = 0.27$ (X = formal mole fraction of WO_3 in the WO_3–K_2SO_4–$K_2S_2O_7$ system).

Again stretching vibrations from WO_2^{2+} and SO_4^{2-} are assigned to bands between ~1100 and $\sim900\,cm^{-1}$. We clearly see increasing bands that we assign to coordinated sulfate: bridging $\nu_1(C_{2\nu})$ at $\sim950\,cm^{-1}$ and terminal $\nu_1(C_{3\nu})$ at $\sim925\,cm^{-1}$. WO_2^{2+} bendings can be assigned to the bands in the range from ~200 to $\sim400\,cm^{-1}$, as presented in Table 2.

The narrow lines seen below $150\,cm^{-1}$ are rotational bands from the air surrounding the ampoule. Bands likely to be (at least partly) due to traces of the frozen $K_2S_2O_7$ solvent are indicated with asterisks in Fig. 8.

4. Conclusion

By means of Raman spectroscopy and X-rays work [8], it has been possible to determine and confirm the stoichiometry of the reaction as 1:1:1. We have only indication of formation of one kind of complex, the dimeric $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$ with two bridging sulfate ligands and four terminally bound sulfato groups. The complex seems to be very stable and exists as the only compound formed in the molten and solid state. It seems reasonable to describe the system in terms of the formation of rather free bent $[WO_2]^{2+}$ ions of $C_{2\nu}$ point group symmetry with fundamentals at around: $\nu_1 = 1045$, $\nu_2 = 278\,cm^{-1}$, and with ν_3 being weak and broad at the high temperature. In the dimeric $[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]^{8-}$ complexes, excessive mixing of these $[WO_2]^{2+}$-group vibrations with modes in coordinated bridging and terminal sulfate $\{\nu_1(C_{2\nu})$ at $\sim950\,cm^{-1}$ and $\nu_1(C_{3\nu})$ at $\sim925\,cm^{-1}\}$ must occur so the assignments presented are only tentative approximations.

References

[1] S. Boghosian, F. Borup, R.W. Berg, Stoichiometry, vibrational modes and structure of molten Nb_2O_5–$K_2S_2O_7$ mixtures, in: Proceedings of the 11th International Symposium on Molten Salts, The Electrochemical Society, Pennington, NJ, November, (1998), pp. 536–543.

[2] A. Paulsen, F. Borup, R.W. Berg, S. Boghosian, Spectroscopic study of niobium oxosulfato complexes in the Nb_2O_5–$K_2S_2O_7$–K_2SO_4 system at 450–700 $^{\circ}C$. Determination of complex stoichiometry by Raman spectroscopy, in: R.W. Berg, H.A. Hjuler (Eds.), Progress in Molten Salts Chemistry, vol. 1, Elsevier, 2000, pp. 393–397.

[3] S. Boghosian, R.W. Berg, Determination of stoichiometry of solutes in molten salt solvents by correlations of relative Raman band intensities, Appl. Spectrosc. 53 (1999) 565–571.

[4] F. Borup, R.W. Berg, K. Nielsen, The crystal structure of $K_7Nb(SO_4)_6$ and $K_7Ta(SO_4)_6$, Acta Chem. Scand. 44 (1990) 328–331.

[5] R.W. Berg, N. Thorup, The reaction between ZnO and molten $Na_2S_2O_7$ or $K_2S_2O_7$ forming $Na_2Zn(SO_4)_2$ or $K_2Zn(SO_4)_2$, studied by Raman spectroscopy and X-ray diffraction, Inorg. Chem. 44 (2005) 3485–3493.

[6] T. Nørbygaard, R.W. Berg, K. Nielsen, Reaction between MoO_3 and molten $K_2S_2O_7$, forming $K_2MoO_2(SO_4)_2$, studied by Raman and IR spectroscopy and X-ray crystal structure determination, in: Proceedings of the 11th International Symposium on Molten Salts, The Electrochemical Society, Pennington, NJ, November, (1998), pp. 553–573.

[7] G. Mestl, In situ Raman spectroscopy for the characterization of MoVW mixed oxide catalysts, J. Raman Spectrosc. 33 (2002) 333–347.

[8] S.J.C. Schäffer, R.W. Berg, Potassium bis(μ-sulfato-1κO:2κO′)bis-[*cis*-dioxido-*cis*-bis(sulfato-κO)tungstate(VI)], Acta Crystallogr. E 61 (2005) i49–i51.

[9] N.H. Hansen, R. Fehrmann, N.J. Bjerrum, Complex formation in pyrosulfate melts. 1, Inorg. Chem. 21 (1982) 744–752.

[10] S.B. Rasmussen, K.M. Eriksen, G. Hatem, F. da Silva, K. Ståhl, R. Fehrmann, Conductivity, thermal measurements, X-ray investigations, and phase diagram of the $Na_2S_2O_7$–$K_2S_2O_7$ system, J. Phys. Chem. B 105 (2001) 2747–2752.

[11] R.L. McCreery, Calibration and validation. Raman Spectroscopy for Chemical Analysis, Chemical Analysis, vol. 157, Wiley-Interscience, 2000, pp. 251–291 (Chapter 10).

[12] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, John Wiley and Sons Inc., New York, 1997 .

[13] J.D. Dyekjaer, R.W. Berg, H. Johansen, Ab initio calculation of conformation and vibrational spectrum for the pyrosulfate ion, J. Phys. Chem. A 107 (2003) 5826–5830.

[14] W. Weltner Jr., D. McLeod Jr., Spectroscopy of tungsten oxide molecules in neon and argon matrices at 4 and 20 K, J. Mol. Spectrosc. 17 (1965) 276–299.

[15] J. Gabrusenoks, A. Veispals, A. von Czarnowski, K.-H. Meiwes-Broer, Infrared and Raman spectroscopy of WO_3 and $CdWO_4$, Electrochim. Acta 46 (2001) 2229–2231.