



# Molten and glassy tellurium(IV) oxosulfato complexes in the $\text{TeO}_2 - \text{K}_2\text{S}_2\text{O}_7$ system studied by Raman spectroscopy: Stoichiometry, vibrational properties and molecular structure

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## ABSTRACT

Tellurium(IV) oxide dissolves in molten potassium pyrosulfate following a reaction that leads to  $\text{Te}^{\text{IV}}$  oxosulfato complexes. High temperature Raman spectroscopy is used under static equilibrium conditions at temperatures of 550 – 740°C for inferring the structural properties of the complex(es) formed in  $\text{TeO}_2\text{-K}_2\text{S}_2\text{O}_7$  molten mixtures ( $X_{\text{TeO}_2}^0 = 0 - 0.70$ ) under  $\text{O}_2$  atmosphere. The composition effects on the Raman spectra together with the outcome of a quantitative exploitation of the relative Raman band intensities point to a 3:1  $\text{TeO}_2\text{:K}_2\text{S}_2\text{O}_7$  stoichiometry, which combined with the observed vibrational properties is suggestive of a  $(\text{Te}=\text{O})_3\text{O}_2(\text{SO}_4)_2^{2-}$  structural formula for the simplest building unit formed. A 3-fold coordination around Te becomes evident comprising an oxide ligand and two oxygen atoms bridging to adjacent Te or S atoms. A gradual association of building units takes place with increasing  $X_{\text{TeO}_2}^0$ . Cooling results in formation of stable glasses with a concomitant change in the coordination number of  $\text{Te}^{\text{IV}}$  from 3 to 4 by means of a structural mechanism suggestively involving a  $\text{TeO}_{2/2}(\text{=O}) \rightarrow \text{TeO}_{4/2}$  transformation. Totally ten bands are attributed to the  $\text{Te}^{\text{IV}}$  oxosulfato complex; the most characteristic ones pertain to the 1040  $\text{cm}^{-1}$  band assigned to symmetric stretching unidentate sulphate and to the 850  $\text{cm}^{-1}$  band assigned to  $\text{Te}=\text{O}$  terminal stretching, the latter band being attenuated on going from the molten to the glassy state due to the  $\text{TeO}_{2/2}(\text{=O}) \rightarrow \text{TeO}_{4/2}$  interconversion.

## 1. Introduction

The field of high temperature molten salt chemistry is replete with numerous paradigms of coordination complexes, the systematics of which were being the central subject of extensive reviews in previous decades when the pertinent interest towards (e.g. catalytic and electrochemical) applications was of topical character [1]. In this context, we have previously been concerned with the reactive dissolution of metal oxides in molten alkali pyrosulfates, resulting in formation of metal oxosulfato complexes wherein the initial attention was focused on the  $\text{V}_2\text{O}_5\text{-M}_2\text{S}_2\text{O}_7\text{-M}_2\text{SO}_4$  ( $M = \text{K}, \text{Cs}$ ) [2,3] and  $\text{V}_2\text{O}_5\text{-M}_2\text{SO}_4$  ( $M = \text{K}, \text{Cs}$ ) [4] systems due to the practical importance of the identified anionic V-oxosulfato and sulfato complexes as components of the active molten salt phase that catalyses the oxidation of  $\text{SO}_2$  [5–7]. Significantly, our endeavours for a valid structural characterisation of such and similar solutes in molten salts and ionic liquids were fructified with the derivation of a Raman band intensity correlation formalism for

determining the stoichiometry of the pertinent complex formation dissolution reactions [8].

Several reactions of dissolution of refractory transition metal oxides in  $\text{K}_2\text{S}_2\text{O}_7\text{-K}_2\text{SO}_4$  molten salts at moderate temperatures have been studied to date, namely  $\text{ZnO}$  [9],  $\text{Nb}_2\text{O}_5$  [10],  $\text{WO}_3$  [11] and  $\text{MoO}_3$  [12]. Remarkably high (reaction-induced) solubilities were inferred for the aforementioned oxides and high temperature Raman spectroscopy was adequate for establishing the stoichiometry, the vibrational properties and (wherever of relevance) the temperature dependent behavior of the metal oxosulfato complexes formed. Di-oxo cores were inferred for  $\text{W}^{\text{VI}}$  and  $\text{Mo}^{\text{VI}}$  oxosulfato complexes ( $\text{WO}_2(\text{SO}_4)_2^{2-}$ ,  $\text{WO}_2(\text{SO}_4)_3^{4-}$ ,  $\text{MoO}_2(\text{SO}_4)_2^{2-}$  and  $\text{MoO}_2(\text{SO}_4)_3^{4-}$ ) [11,12] whereas mono-oxo (primarily) as well as di-oxo configurations were evidenced for the  $\text{Nb}^{\text{V}}$  counterparts ( $\text{NbO}(\text{SO}_4)_3^{3-}$ ,  $\text{NbO}(\text{SO}_4)_4\text{S}_2\text{O}_7^{7-}$  and  $\text{NbO}_2(\text{SO}_4)_2^{3-}$ ) [10]. The occurrence of di-oxo and mono-oxo cores within an environment comprising exclusively oxygen ligands renders the above and similar metal oxosulfato complexes as reliable reference compounds for

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inferring the configurations of oxo-metallic ( $MO_x$ )<sub>n</sub> sites in supported transition metal oxide catalysts [13]. Single crystal XRD has been applied to structurally characterise V<sup>III</sup>, [14,15] V<sup>IV</sup>, [16–19] V<sup>V</sup>, [20–22] Nb<sup>V</sup>, [23] Ta<sup>V</sup>, [23] W<sup>VI</sup>, [24–26] and Mo<sup>VI</sup> [27,28] crystalline sulfato and oxosulfato complexes synthesised by precipitation from the respective metal oxide containing pyrosulfate/sulfate molten salts under different controlled gas atmospheres.

Tellurium oxide is a well-known glass former with potential applications for optical switching devices and laser hosts [29–31]. Spectroscopic and diffraction methods have extensively been used to shed light on the structural properties of TeO<sub>2</sub> as well as TeO<sub>2</sub> – based glasses [32–42]. Whereas pure TeO<sub>2</sub> glass is mainly consisted of TeO<sub>4</sub> trigonal bipyramid units, changes in the Te coordination take place upon inclusion of modifiers in the TeO<sub>2</sub> matrix (*i.e.* from TeO<sub>4</sub> trigonal bipyramid to TeO<sub>3</sub> trigonal pyramid units) [32–42].

The aim of the present work was to examine whether TeO<sub>2</sub> could undergo a dissolution reaction with molten K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and elucidate the structural properties of the complexes formed both in the molten and glassy state. Raman spectroscopy is used under static equilibrium conditions at temperatures up to 740 °C for exploring the structures of TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> molten mixtures and glasses thereof in the composition ranges  $X_{TeO_2}^0 = 0 - 0.7$  and  $X_{TeO_2}^0 = 0.2-1$ , respectively. The composition effects on the relative Raman band intensities due to the species present are exploited quantitatively for determining the stoichiometry of the complexes formed in the molten and glassy state and pertinent consistent band assignments are proposed.

## 2. Experimental

### 2.1. Materials and sample preparation

The samples were prepared by mixing appropriate amounts of TeO<sub>2</sub> (regent grade, 99.99%, Alfa Aesar) with K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> synthesised by thermal decomposition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Fluka, pro analysi), as earlier described [43,44]. Handling and weighing of the materials as well as filling of the Raman cells was undertaken under nitrogen inert atmosphere in a glove-box. The cells were made of quartz tubing (6 ± 0.1 mm o.d., 4 ± 0.1 mm i.d. and ~3 cm long) and each cell contained ~400 mg of mixture. In order to facilitate the melting procedure, thorough grinding and mixing of each mechanical mixture of the chemicals was performed in an agate mortar inside the glove-box before filling the optical cell. Each cell was then attached to a vacuum line, where oxygen gas (L'Air Liquide, 99.995%) was admitted in the cell at a pressure of 0.2 atm in order to prevent self-reduction of Te<sup>IV</sup> and subsequently the cells were sealed using an oxygen-propane torch. The compositions of the samples prepared and studied in this work are compiled in Table 1. The mole fractions  $X_{TeO_2}^0$  listed in Table 1 are based on the weighed-in amounts of the chemicals before heating up and letting TeO<sub>2</sub> react with (and

dissolve in) molten K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. The sealed cells were heated in vertical position at 550–750 °C for several days to enable the dissolution of TeO<sub>2</sub>. It was possible to dissolve up to 70 mol% TeO<sub>2</sub> at 750 °C. Transparent melts were thus obtained. After obtaining the Raman spectrum for each molten mixture with  $X_{TeO_2}^0 = 0 - 0.70$  at temperatures of 550–740 °C, the cells were placed back for short equilibration in a vertical tube furnace at 750 °C. Glass formation was achieved by moderate cooling, *i.e.* by removing each cell from the vertical tube furnace and immersing it in cold water. The so-obtained glasses were transparent and free of optical defects, thereby permitting accurate measurements of Raman spectra in two polarization configurations.

### 2.2. Raman spectra

Detailed descriptions of the Raman furnace for the optical cells and of the protocol followed for performing high temperature Raman spectroscopic measurements in molten salts and vapors have been reported elsewhere [2–4,45,46]. Raman spectra were excited with the 532.0 nm line (linearly polarized) of a Diode Pumped Solid State laser (Excelsior, Spectra-Physics). The laser was operated at a power of 50 mW. Two polarization configurations of the scattered light to the horizontal scattering plane were used: the vertical-vertical (VV) and the horizontal-vertical (HV). Polarization and possible drifts of the monochromator's gratings were checked by a calibration procedure with the aid of a CCl<sub>4</sub> sample. The Raman set up used was earlier described in detail [42].

## 3. Results and discussion

### 3.1. Complex formation in the molten TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> system

#### 3.1.1. High temperature Raman spectra of TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> molten mixtures

Fig. 1 shows the high temperature Raman spectra obtained under static equilibrium for the TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> molten mixtures with  $X_{TeO_2}^0 = 0.10 - 0.70$  at temperatures of 550–740 °C. The Raman spectra obtained for pure molten K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> at 620 °C are included for comparison. Representative spectra obtained with the HV polarisation configuration are also shown in order to reveal the polarisation characteristics of the observed Raman bands. The wavenumbers, intensity and polarisation characteristics as well as the tentative assignment for the observed bands are compiled in Table 2.

The well-known [3,10–12] spectral features due to S<sub>2</sub>O<sub>7</sub><sup>2-</sup>, comprising characteristic bands at 1085, 730 and 318 cm<sup>-1</sup> dominate the spectra of mixtures with low TeO<sub>2</sub> content (*i.e.*  $X_{TeO_2}^0 = 0.10 - 0.25$ , spectra Fig. 1b and c). However, the progressive reactive dissolution of TeO<sub>2</sub> in molten K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> results in the emergence of new bands, of which the intensities gradually increase with increasing TeO<sub>2</sub> content while at the same time the peak intensities due to S<sub>2</sub>O<sub>7</sub><sup>2-</sup> are decreased (see, *e.g.*, spectrum Fig. 1g for the molten mixture with initial composition  $X_{TeO_2}^0 = 0.60$  obtained at 650 °C). The observed behaviour is consistent with a dissolution reaction of TeO<sub>2</sub> resulting in the formation of a molten complex species C at the expense of S<sub>2</sub>O<sub>7</sub><sup>2-</sup> according to the general reaction scheme



The evolution of the Raman bands due to complex formation with increasing TeO<sub>2</sub> content follows *mutatis mutandis* the corresponding general behavior of metal oxosulfato complexes formed upon reactive dissolution of a metal oxide M<sub>x</sub>O<sub>y</sub> (M = V, Nb, W, Mo) in molten K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> [3,8–12]. Notably, all bands ascribed to the complex evolve monotonically, thereby suggesting the formation of *one* single complex structural unit, albeit possibly in different evolving extents of association in the composition range studied (*i.e.* with higher degree of polymerisation with increasing TeO<sub>2</sub> content). Interestingly, as shown in Table 2, three bands attributable to Te – O modes are found at 850, ~770 and 650 cm<sup>-1</sup> due to oxo-Te<sup>IV</sup> sites of different termination

**Table 1**  
Compositions (mole fractions),  $X_{TeO_2}^0$ <sup>a</sup>, of TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> samples.

Cell #	$X_{TeO_2}^0$ <sup>a</sup>
1	0
2	0.098
3	0.244
4	0.337
5	0.401
6	0.501
7	0.602
8	0.702
9	1.000

<sup>a</sup>  $X_{TeO_2}^0$  is the mole fraction of the of the TeO<sub>2</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> mixture based on the weighed-in amounts.

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