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Photo-electron Spectra of Germanium, Arsenic and Lead-containing Sulphide Glasses Favouring Lanthanide Luminescence *

Renata Reisfeld **, C. K. Jørgensen ***, A. Bornstein ** and H. Berthou
Département de Chimie minérale, analytique et appliquée, Université de Genève

Summary

Thio germanate and thio arsenite glasses containing bivalent calcium or lead have low phonon wave-numbers and enhance line-emission of trivalent lanthanides by less extensive multi-phonon de-excitation and by energy transfer. Photo-electron spectra of such glasses, elemental sulphur, and arsenic sulphides are studied. The Wagner parameter of the chemical shift of Auger signals is larger for thio germanate glasses than for germanium(IV) bound to oxide.

The germanate and tellurite glasses formed by oxygen-containing anions have particularly low phonon frequencies and show high fluorescence yields of trivalent lanthanides [1] because of the lower probability of multi-phonon relaxation. The detailed behaviour of the excited states of holmium(III) [2] and of erbium(III) and thulium(III) [3] can be described by the three Judd-Ofelt parameters of band intensities. The relative luminescent intensity of three transitions of samarium(III) and of four transitions of terbium(III) was recently studied [4] in mixed arsenite-borate glasses and Sm(III) compared [5] in borate and ternary germanate glasses. One conceivable way of decreasing the phonon frequencies further is to use sulphur-containing glasses. One can hope for laser action [6] in the infra-red (below 13000 cm^{-1}) only, because of strong, continuous absorption in the visible of the thio arsenite (though the energy gap may be up to 20000 cm^{-1} in germanium(IV) sulphide glass) but on the other hand, this may

present the advantage of energy transfer [7] to the rare earth, as has already been observed (in the blue region) in tellurite glasses. Sulphur-containing glasses are known with germanium [8,9] and arsenic [10,11] as constituents of the network-former.

We prepared the sulphide glasses by melting stoichiometric amounts (1g batches) of the elements p.a. (to which might be added CaS from Hopkins and Williams or PbS from Alfa Ventron) in evacuated sealed Vycor glass tubes at 550°C for 2 hours. During subsequent heating to 900°C during 18 hours, the ampoules were turned around several times in order to assure perfect mixing. It is recommended to cool the tubes at 200°C instead of room temperature, because the ampoules tend to explode in the latter case. After breaking the tubes, the samples can be polished for spectroscopic purposes.

In a previous note [12] we described the 1253.6 eV induced photo-electron spectra of oxidic glasses, measured on a Varian IEE-15 instrument. Besides the sulphur-containing samples mentioned above, elemental sulphur (which we had not previously measured on our photo-electron spectrometer) and two arsenic sulphides [10] were studied for comparison. Contrary to oxide-containing glasses [12] and most typical non-conducting salts [13,14] we did not generally observe two distinct C 1s signals from the hydrocarbon originating in the one-sided scotch tape (600 P from the 3M company) carrying the freshly pulverized samples. With exception of a shoulder indicating $C_{st}' = 3.5\text{ eV}$ in the calcium thio germanate glass containing holmium(III) the observed C_{st} given in Table 1 can be identified with C_{st}' corrected for charging effects. This is also the

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** Permanent address: Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

*** Prof. Dr. C. K. Jørgensen, 30, quai E. Ansermet, CH-1211 Genève 4

Table 1: Photo-electron spectra of sulphur-containing materials, the ionization energies I' relative to vacuo [13] being the sum of I^* recorded by the instrument and C'_{st} (the difference between 290 eV and the highest I^* (C1s) of the hydrocarbon). Values connected with «&» correspond to two j -values of the same nl -shell; values separated by a comma refer to non-equivalent atoms of a given element M.

Chemical composition Semi-quantitative ESCA analysis	C'_{st}	I' (Mnl) values in eV
S ₈ (sublimed) 0.09 O: 1S	5.3	S2s: 233.35; S2p: 170.1 & 168.95 (Gaussian analysis), maximum 169.1; O1s: 537.8
0.9 GeS ₂ : 0.1 CaS < 0.07 Ca: 1Ge: 2S	4.0	Ge3p: 133.6 & 129.7; Ge3d: 37.5; Ge Auger: 117.8 eff.; S2p: 168.4
0.86 GeS ₂ : 0.1 CaS: 0.04 Ho ₂ S ₃ 0.7 O: 1Ge: 2S	3.5	Ge3p: 133.7 & 129.5; Ge3d: 37.2; Ge Auger: 117.6 eff.; S2p: 168.3; O1s: 537.2
As ₂ S ₃ 0.7 O: 2As: 3S	4.5	As3p: 152.1 & 147.3; As3d: 48.2; S2p: 167.3; O1s: 537.8
As ₂ S ₄ 1 O: 1As: 2S	4.6	As3p: 152 & 147.6; As3d: 48.4; S2p: 168.1; O1s: 540.1
0.9 As ₂ S ₃ : 0.1 PbS 3 O: 2As: 3S: 0.16 Pb	4.2	As3p: 151.6 & 146.7; As3d: 47.9; S2p: (168), 167.0; O1s: 537.4, Pb4f: 148.3 & 143.35
0.7 As ₂ S ₃ : 0.3 PbS 4 O: 2As: 3S: 0.23 Pb	4.5	As3p: 152.5 & 147.7; As3d: 48.5; S2p: (169), 167.7; O1s: 537.8; Pb4f: 149 & 144.0

case for sulphur, which must become conducting under the influence of the X-rays, since this solid otherwise is one of the most pronounced isolators. The one-sided half-width $\delta(-)$ of the symmetric C1s signal has its minimum value 0.85 eV, and actually, the resolution is sufficiently good to show the spin-orbit splitting 1.2 eV of S2p known from gaseous compounds [15] to be compared with 1.256 eV in gaseous S⁺⁷. Hence, $\delta(-) = 1.15$ eV of our S2s signal contains an intrinsic contribution 0.65 eV if one assumes [13] the half-width to be the square-root of the sum of squared contributions. Most samples show oxygen 1s signal due to tenaciously adsorbed water, or hydroxo or oxo groups on the surface [16]. This contamination is almost absent on the sulphur.

The calcium content of the thiogermanate glass (measured several times) could not be detected, the Ca2p region shows three indistinct signals at $I' = 359, 356$ and 353 eV, of which the last may be due to the ($j = 3/2$) component [13]. It is not surprising that $I'(\text{Ge}3p_{3/2}) = 130.8$ and $I'(\text{Ge}3d) = 38.9$ eV of K₂GeF₆ [13] and 130.3 and 38.4 eV of GeO₂ [13] are larger than in Table 1, but it may be noted that the values for a germanate glass [12] 129 and 37.1 eV are even lower. The weak, broad and rather uncharacteristic holmium 4d and 4f signals [13] could not be detected beyond experimental uncertainty in the Ho-containing thiogermanate glass, showing a relatively high oxygen content on the surface. Using a magnesium anti-cathode, the strongest germanium signal is an Auger transition (initial 2p_{3/2} ionization, final state ¹G₄ belonging to 3d⁸) previously noted [17] in gaseous compounds. The Auger parameter introduced by Wagner [18] as the difference between the kinetic energy of the Auger electron and the kinetic energy of the photo-electron ejected by the initial ionization indicates to a good approximation chemical polarization effects [14] by being invariant with charging effects and independent of chemical shifts (if they are the same for all inner

shells). The Auger parameter is equivalent with the difference between I for initial ionization (unfortunately, in the special case of Ge2p_{3/2} it is necessary [13] to use 1486.6 eV photons from an aluminium anti-cathode) and I_{eff} measured for the Auger electron. We find this distance 870.55 eV for K₂GeF₆ (Wagner [18] finds 870.3 eV for Na₂GeF₆) and 872.3 eV for GeO₂ (871.7 eV [18]). If it is accepted that the I difference between Ge2p_{3/2} and Ge3d is 1187 eV (we found [13] previously 1187.4 and 1186.8 eV) the Auger parameter for the sulphide glass in Table 1 is 37.5 - 117.8 + 1187 + 1253.6 - 1486.6 = 873.7 eV showing a considerably larger inter-atomic relaxation effect and approaching 875.9 eV for crystalline germanium [18].

The almost identical $I(\text{As}3p)$ and $I(\text{As}3d)$ in As₂S₃ and As₂S₄ are similar to the values [13] for arsenic(III) diethyldithiocarbamate, but 3 to 5 eV lower than for typical arsenates. There is no direct evidence for non-equivalent arsenic atoms [10] in As₂S₄ though $\delta(-) = 1.25$ eV for the S2p signal is unusually large, and the superficial oxygen content rather high. Similar statements are true for the lead-containing thioarsenite glasses, where the shoulder at higher $I(\text{S}2p)$ may be due to elemental sulphur formed by air oxidation. The Pb4f signals (to some extent coinciding with As 3p) are quite typical [13] for other lead(II) compounds. Previously, photo-electron spectra of chalcogenide glasses having the general formula GeS_{3-x}Te_xAs₂ have been reported [19]. The I^* values relative to $I^*(\text{Au}4f_{7/2}) = 84.0$ eV of metallic gold are 161.6 eV (within a-tenth eV) of S2p (for $x = 0, 0.5, 1, 1.5, 2$ and 2.5 as well as for GeS₂) to be compared with 162.9 eV for elemental sulphur (6 to 7 eV below $I'(\text{S}2p)$ in Table 1), 122.2 eV for Ge 3p_{3/2} (with slightly larger variation) and 30.2 eV for Ge 3d, again 7 eV below our glasses, and 140.4 eV (140.7 eV for elemental arsenic) for As 3p_{3/2} also some 7 eV lower. Either these glasses [19] show larger inter-atomic relaxation effects [14] than our sulphide glasses, or the calibration of the I' values is intrinsically

different [19]. Anyhow, the variation of Wagner's Auger parameter shows a clear-cut difference between sulphur- and oxygen-containing glasses, and excludes the possibility that the sulphide glasses are superficially hydrolyzed or oxidized.

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2H-Pyrrole und Pyrrole aus 3-Phenyl-2H-azirinen*

48. Mitteilung über Photoreaktionen¹

Ulrich Widmer, Nikolas Gakis, Bruno Arnet, Heinz Heimgartner und Hans Schmid**

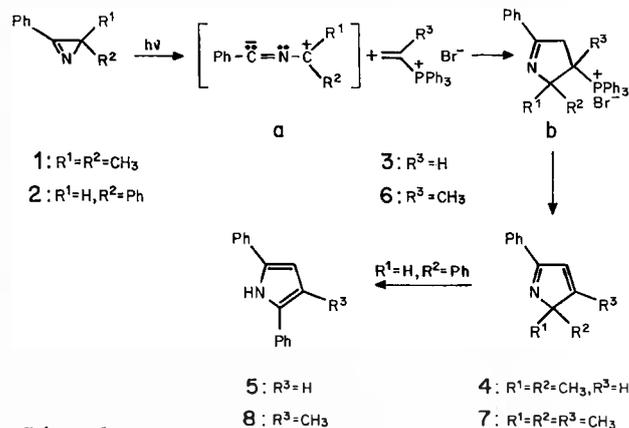
Organisch-chemisches Institut der Universität Zürich

Summary

Vinyl-phosphonium salts [2] and phenyl-vinyl-sulfone or divinyl-sulfone react with benzonitril-methylides **a** (which are photochemically generated from 3-phenyl-2H-azirines **1** and **2**) to give, via the nonisolated intermediates of type **b**, 2H-pyrrole **4** and the pyrrole **5**, respectively. In the reaction of sulfone **11** it was shown that the addition reaction occurs with the retention of configuration of the olefin and with the same regioselectivity as observed in the cycloadditions of acrylic ester or acrylic nitrile with **a** [5]. In the case of **11** the primary photoproduct **13** (scheme 2) could be isolated, which on photolysis was converted to **4** by the formal elimination of p-tosylchloride. Under mild base catalysis, for instance with the azirine **1** as a base, elimination of p-toluenesulfonic acid occurs easily at room temperature to give the 2H-pyrrole **12**.

Vinyl-phosphonium salts or vinyl-sulfones can be considered equivalents of non activated acetylenes which do not react with **a**.

Vor einiger Zeit berichteten wir über photochemische Cycloadditionen von 3-Phenyl-2H-azirinen wie **1** und **2** mit Triphenyl-vinyl-phosphoniumbromid (**3**) als neuem Zugang zum 2H-Pyrrol **4** bzw. dem Pyrrol **5** [2]. Die vermutlichen, via **a** gebildeten Primäraddukte **b** (Schema 1) konnten in keinem Fall isoliert werden, so dass eine Aussage über die Regioselektivität der Cycloaddition nicht möglich war.



Scheme 1

Bestrahlung (Hg-Hochdrucklampe, Pyrex) von 2,2-Dimethyl-3-phenyl-2H-azirin (**1**) in Gegenwart einer äquimolaren Menge Isopropenyl-triphenyl-phosphoniumbromid (**6**) [3] in Acetonitril (c stets $1-3 \cdot 10^{-2}$ M) während 3 Std. lieferte in 20% Ausbeute 2,2,3-Trimethyl-5-phenyl-2H-pyrrol (**7**, Schema 1). Die Struktur von **7** wurde mit Hilfe der spektralen Daten, insbesondere dem ¹³C-NMR-Spektrum (CDCl₃) bewiesen: Das Atom C(3) erscheint als Singulett bei 169,7 ppm², die transoide ³J(C,H)-Kopplung zwischen C(2) und H-C(4) beträgt 11 Hz (vgl. [4]). Im isomeren 2,2,4-Trimethyl-5-phenyl-2H-pyrrol müsste C(3) als Dublett absorbieren; zudem wäre eine ²J(C,H)-Kopplung zwischen C(2) und H-C(3) von 3-4 Hz zu erwarten ([4]); vgl. auch das ¹³C-Spektrum von **4**). Die Regioselektivität der Anlagerung von **6** an **a** entspricht

¹ 47. Mitteilung siehe [1].

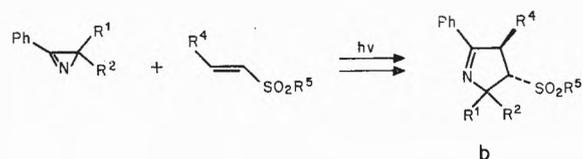
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** Korrespondenz an Prof. Dr. H. Schmid, Organisch-chemisches Institut der Universität, Rämistrasse 76, CH-8001 Zürich

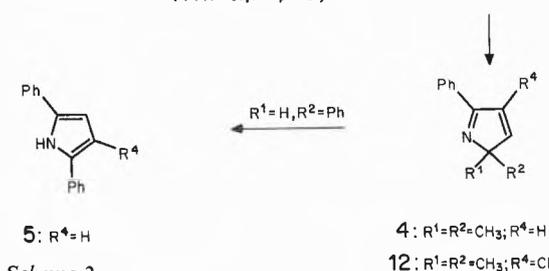
² Interner Standard: Tetramethylsilan.

derjenigen von Acrylsäuremethylester oder Acrylonitril ([5]; vgl. [6]). Photolyse von 2,3-Diphenyl-2H-azirin (**2**) in Gegenwart eines Moläqu. **6** in Acetonitril hinter Pyrex lieferte mit derselben Regioselektivität in 26% Ausbeute das bekannte Pyrrol **8** [7].

Bestrahlung von **1** in Gegenwart von 0,85 Moläqu. Phenyl-vinylsulfon (**9**) (3 Std.) bzw. 0,8 Moläqu. Divinylsulfon (**10**) (1 Std.) in Benzol hinter Quarz lieferte in Ausbeuten von 66% bzw. 49% das bereits erwähnte 2,2-Dimethyl-5-phenyl-2H-pyrrol (**4**, Schema 2). Pho-



- 1**: R¹ = R² = CH₃ **9**: R⁴ = H, R⁵ = Ph
2: R¹ = H, R² = Ph **10**: R⁴ = H, R⁵ = -CH=CH₂ **13**: R¹ = R² = CH₃; R⁴ = Cl, R⁵ = p-Tolyl
11: R⁴ = Cl; R⁵ = p-Tolyl



Schema 2

tolylse von **2** in Gegenwart von 0,6 Moläqu. Divinylsulfon (**10**) (6 Std.) hinter Quarz ergab in 23% Ausbeute das Pyrrol **5** [8]. Wenig einheitlich verlief die Bestrahlung (3 Std.) von **1** hinter Pyrex in Gegenwart eines Moläqu. (E)-p-Tolyl-β-chlorvinylsulfon (**11**) [9] in Benzol. Die (E)-Konfiguration des Sulfons folgt aus der grossen Kopplungskonstante der 2 Vinylprotonen ($J = 13,9$ Hz). Neben **4** (5%) entstand in 8% Ausbeute das 4-Chlor-2,2-dimethyl-5-phenyl-2H-pyrrol (**12**) sowie trans-3-Chlor-5,5-dimethyl-2-phenyl-4-(p-tolylsulfonyl)-1-pyrrolin (**13**) in 5% Ausbeute (Schema 2). **13** stellt das primäre Addukt von **11** an das aus **1** photochemisch erzeugte Benzonitril-isopropylid (vgl. [10]) dar. Die trans-Konfiguration von **13** ist aufgrund der Befunde, wonach elektronendefiziente Olefine mit Benzonitril-methyliden eine cis-Addition eingehen, zu erwarten gewesen. Diese Zuordnung wird ferner durch die NMR-Kopplungskonstante $J(3,4) = 6,8$ Hz gestützt (vgl. [5, 11]).

Die weitere Bestrahlung von **13** unter den oben aufgeführten Bedingungen gab gemäss Gaschromatographie in 3% Ausbeute **4**. Beim Stehenlassen der benzolischen Lösung von **13** mit 2 Moläqu. **1** im Dunkeln bei 25°, also unter milder Basenkatalyse, entstand in 2% Ausbeute das chlorhaltige 2H-Pyrrol **12**. Bei der photochemischen Umwandlung von **13** erfolgt somit formal die Abspaltung von p-Tosyl-chlorid. Zwischenprodukte vom Typ *b* sind isoelektronisch mit β-Sulfonylketonen, die leicht unter Abspaltung von Sulfinsäure in die α,β-ungesättigten Ketone übergehen [12].

Die Reaktionen von 3-Phenyl-2H-azirinen mit Vinylphosphoniumsalzen bzw. Vinyl-sulfonen unter Bildung der Produkte vom Typ **4** und **5** entsprechen formal der Addition von Acetylderivaten an photochemisch erzeugte Benzonitril-methylide. Nicht aktivierte Acetylene addieren sich nicht an Benzonitril-methylide. Hin-gegen reagieren die Dreifachbindung von Acetylen-carbonsäureestern; so gab die Bestrahlung von **2** mit Acetyldicarbonsäuredimethylester in 40% Ausbeute 2,5-Diphenyl-3,4-dimethoxycarbonylpyrrol [5, 13] (vgl. [14]).

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Experimenteller Teil

Alle Bestrahlungen wurden mit einer Quecksilberhochdrucklampe (TQ-150, Quarzlampengesellschaft mbH Hanau) durchgeführt ($c = 1-3 \cdot 10^{-2}$ M). Die Aufarbeitung erfolgte mittels präparativer Schichtchromatographie (Pentan/Äther- oder Hexan/Essigester-Gemische). Die Ausbeuten sind im Text angegeben. Die physikalischen Daten der bisher nicht beschriebenen Verbindungen sind nachstehend aufgeführt. Alle Verbindungen ergaben korrekte C,H,Cl,N,S-Analysen ($\pm 0,3\%$).

2,2,3-Trimethyl-5-phenyl-2H-pyrrol (**7**):

Farbloses Öl durch Kugelrohrdestillation bei 75–85°/0,01 Torr (Luftbad). UV (Äthanol): λ_{\max} 244 (4,14); Schultern bei 277 (3,5) und 285 (3,3). IR (CCl₄): 1629 (C=N). NMR (CCl₄): 8,0–7,7 (m, 2 arom. H); 7,6–7,15 (m, 3 arom. H); 6,40 (q, $J \approx 1,5$ Hz, H–C(4)); 2,03 (s, CH₃–C(3)); 1,26 (s, 2 CH₃–C(2)). ¹³C-NMR (CDCl₃): 173,0 (s, C(5)); 169,7 (s, C(3)); 134,7–127,7 (aromat. C); 119,9 (d, C(4)); 79,1 (s, C(2)); 23,3 (q, 2 CH₃–C(2)); 13,1 (q, CH₃–C(3)). MS: 185 (M⁺, 100), 184 (87), 170 (60), 145 (10), 129 (62), 128 (32), 105 (38), 104 (20), 77 (24).

2,2-Dimethyl-5-phenyl-2H-pyrrol (**4**) [2]:

¹³C-NMR (CDCl₃): 169,4 (s, C(5)); 162,4 (d, C(3)); 134,0 (s, arom. C quartär); 130,1, 128,5, 127,6 (3d, 3 arom. C); 123,0 (d, C(4)); 79,4 (s, C(2)); 23,3 (q; 2 CH₃–C(2)).

4-Chlor-2,2-dimethyl-5-phenyl-2H-pyrrol (**12**):

Destilliert als farbloses Öl bei 60–70°/0,02 Torr. UV (Äthanol): λ_{\max} 224 (3,83), 247 (3,91); Schulter bei 275 (3,72); λ_{\min} 228,5 (3,71). IR (Film): 1612 (C=N). NMR (CDCl₃): 8,15–7,8 (m, 2 arom. H); 7,5–7,15 (m, 3 arom. H); 7,13 (s, H–C(3)); 2,42 (s, 2 CH₃–C(2)). MS: 205 (M⁺, 54), 204 (36), 190 (13), 170 (100), 154 (9), 145 (10), 129 (38), 104 (22), 103 (19), 77 (19).

trans-3-Chlor-5,5-dimethyl-2-phenyl-4-(p-tolylsulfonyl)-1-pyrrolin (**13**):

Farblose Kristalle aus Benzol, Smp. 130,3–131°. UV (Äthanol): λ_{\max} 210 (4,13), 230 (4,29), 245 (4,19); Schulter bei 272,5 (3,52); λ_{\min} 216,5 (4,09), 242 (4,18). IR (KBr): 1627 (C=N). NMR (CDCl₃): 8,0–7,65 (m, 4 arom. H); 7,6–7,3 (m, 5 arom. H); 5,60 (d, $J(3,4) = 6,8$ Hz, H–C(3)); 3,79 (d, $J(4,3) = 6,8$ Hz, H–C(4)); 2,46 (s, CH₃–C(4)); 1,76 (s, CH₃–C(5)); 1,72 (s, CH₃–C(5)). MS: 326 (9), 325 (5), 205 (24), 204 (20), 170 (100), 139 (12), 129 (35), 104 (24), 91 (40), 77 (31).

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