Mercury thiogermanate HgS-GeS_2 glasses: macroscopic, electric, and structural properties

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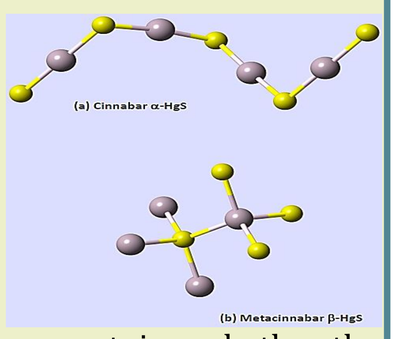
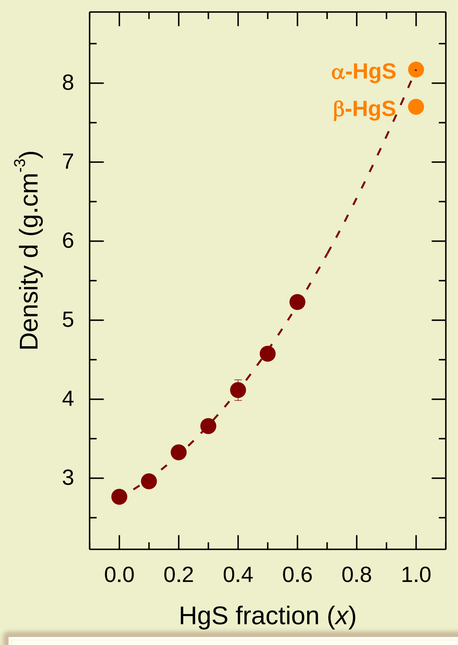
I. Introduction

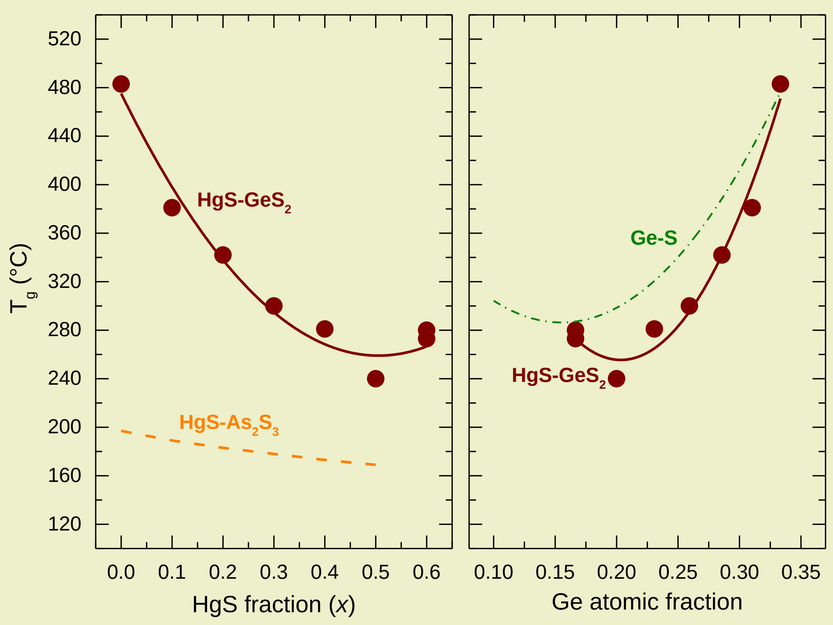


Crystalline mercury sulphide exists in two drastically different polymorphic forms in different domains of the P,T-diagram: red chain-like *cinnabar* α-HgS, stable below 344 °C, and black tetrahedral *metacinnabar* β-HgS, stable at higher temperatures. The question arises whether mercury will modify the terahedral network of the germanium chalcogenide glasses.

Dimorphism of HgS also opens discussions on local mercury environment, i.e., whether the two mercury bonding patterns are present simultaneously in mercury thiogermanate glasses $(HgS)_x(GeS_2)_{1-x}$ with $0.0 \leq x \leq 0.5$. The population and interconnectivity of chain-like and tetrahedral dimorphous forms determine both the structural features and fundamental glass properties (thermal, electronic, etc.).

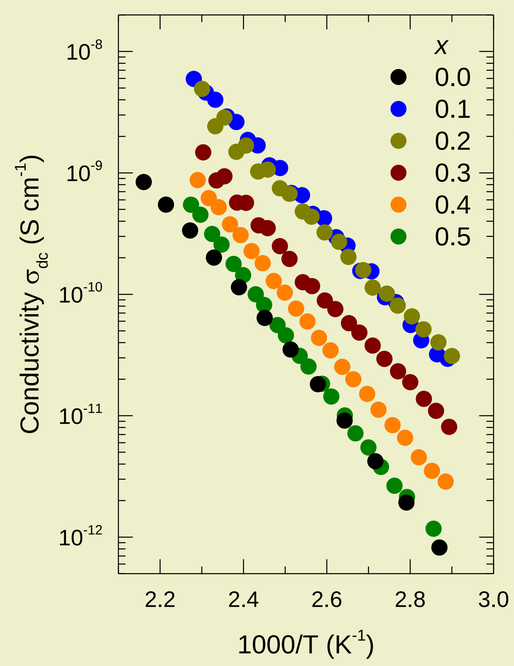
II. Macroscopic properties

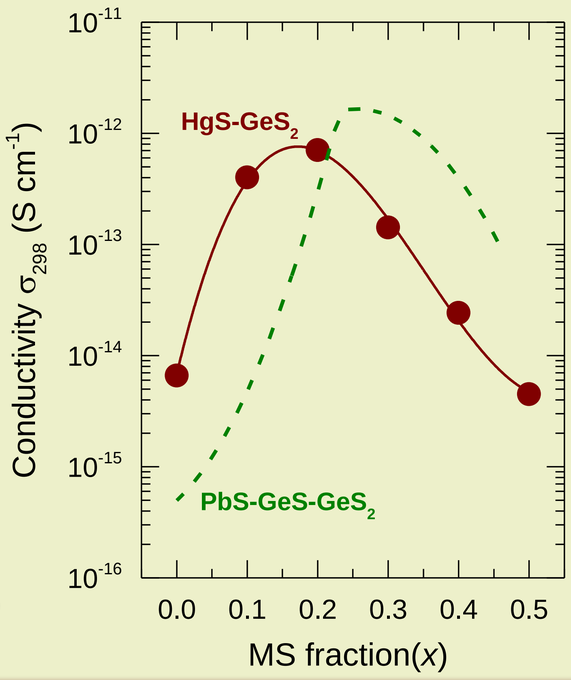




- ✓ The density increases monotonically with increasing HgS
- ✓ The reduced connectivity in the glasses seems to be responsible for T_g decease
- ✓ In Ge_yS_{1-y}, excessive sulphur species form S-S dimers and/or S oligomeric chains replacing bridging sulphur in CS-Ge_2S_7 tetrahedral ⇒ reduced network connectivity

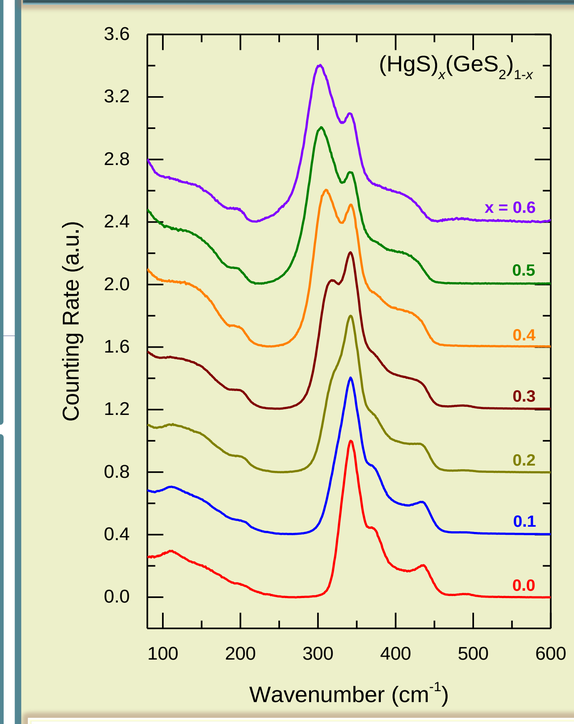
III. Conduction properties

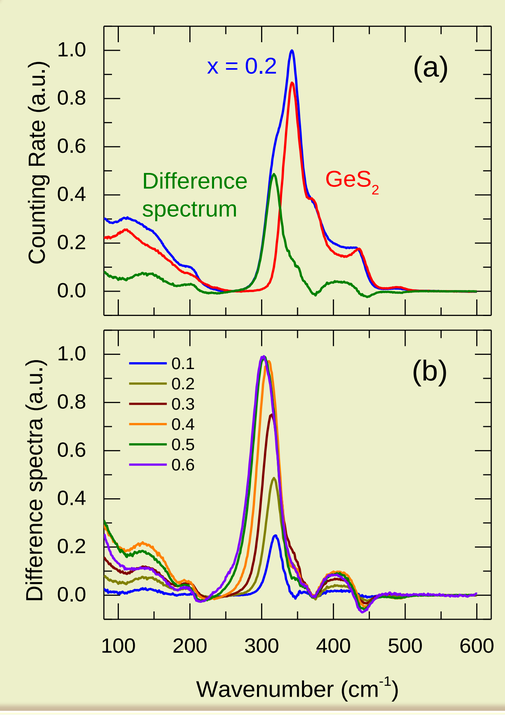




- ✓ The conductivity obeys the Arrhenius law: $\sigma_{dc} = \sigma_0 /T \exp(-E_a/kT)$
- ✓ The glasses are electronic insulators: $10^{-12} \leq \sigma_{298}$ (x) $\leq 10^{-15}$ S cm^{-1}
- ✓ The room-temperature conductivity σ_{298} exhibits a maximum

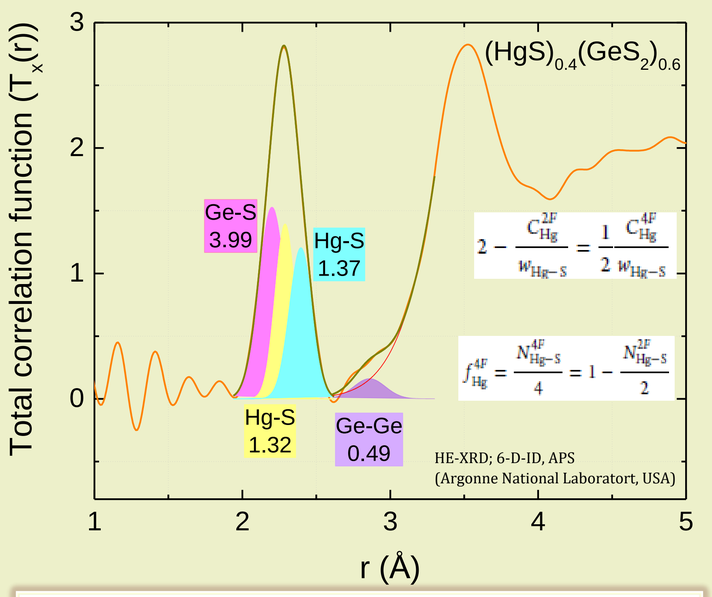
IV. RAMAN Studies

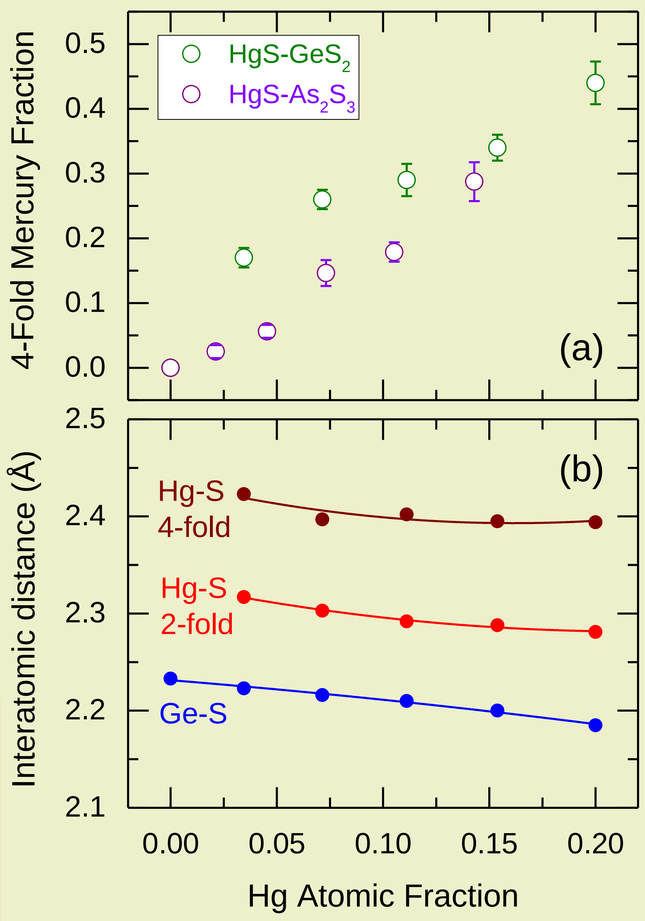




- ✓ GeS_2 ⇒ different Ge–S stretching modes : $GeS_{4/2}$, ES-Ge_2S_6, CS-Ge_2S_7
- ✓ Change is spectral shape of GeS_2 ⇒ evidenced by negative amplitude in difference spectra at ≈ 440 cm^{-1}
- ✓ Major and minor HgS-related modes at (i) 300-320 and (ii) 400 cm^{-1}
- ✓ Red shift of the major mode from 320 to 300 cm^{-1} ⇒ agglomeration of $(HgS_{2/2})_n$ fragments (increase of chain fragments ***n*** per $GeS_{4/2}$ units)
- ✓ Both modes are blue shifted with respect to α-HgS E-modes at 290 & 354 cm^{-1} ⇒ related to ***Hg-S chain/Ge-S tetrahedral motifs***

V. HE–XRD Studies





According to literature:

- ✓ r(Ge-S) ≅ 2.21-2.23 Å; N(Ge-S) ≅ 3.9-4.1
- ✓ $r(Hg_{2F}\text{-S}) \approx 2.38$ Å; N(Hg-S) = 2.00
- ✓ $r(Hg_{4F}\text{-S}) \approx 2.54$ Å; N(Hg-S) = 4.00

HgS fraction x	r(Ge-S) (Å)	$N_{Ge\text{-}S}$	$r(Hg_{2F}\text{-S})$ (Å)	N^{2F}_{Hg-S}	$r(Hg_{4F}\text{-S})$ (Å)	N^{4F}_{Hg-S}
0.0	2.23(1)	4.01				
0.1	2.22(1)	4.00	2.32(1)	1.65	2.42(1)	0.70
0.2	2.21(1)	4.00	2. 30(1)	1.47	2.39(1)	1.07
0.3	2.21(1)	4.01	2.29(1)	1.42	2.40(1)	1.16
0.4	2.20(1)	3.99	2.29(1)	1.32	2.39(1)	1.37
0.5	2.18(1)	3.99	2.28(1)	1.14	2.39(1)	1.74

- ✓ The Hg-S chains coexist with $GeS_{4/2}$ tetrahedral ⇒ intact local and IRO in the g-GeS_2
- ✓ f^{4F}_{Hg} fraction increases with HgS content reaching $f^{4F}_{Hg} \approx 0.44$ for the x = 0.5 composition
- ✓ The majority of mercury species is 2-fold coordinated ⇒ the hybrid chain/tetrahedral network is the main structural motif in mercury thiogermanate glasses

VI. Conclusion

- ✓ The glass-forming region accounts up to 50 mol% HgS
- ✓ T_g decrease is consistent with the gradual substitution of more rigid $GeS_{4/2}$, ES-Ge_2S_6, CS-Ge_2S_7 motifs by flexible $(HgS_{2/2})_n$ chain fragments
- ✓ Raman results reveal that the glasses form a hybrid Hg–S chain/Ge–S tetrahedral network evidenced by Hg–S stretching modes at 300 and 400 cm^{-1}
- ✓ Mercury sulphide appears to be dimorphous over the investigated glass composition
- ✓ The population of 4-fold coordinated $HgS_{4/4}$ minorities increases with x, but remain below 50%, i.e., $f^{4F}_{Hg} \approx 0.44$ for the x = 0.5 composition
- ✓ Further studies of High-temperature HgS-GeS_2 liquids will give a detailed and definitive answer