Thermal, Conductivity, Structural and Optical Properties of HgI_2-As_2X_3 (X = Se, Te) Chalcogenide Glasses

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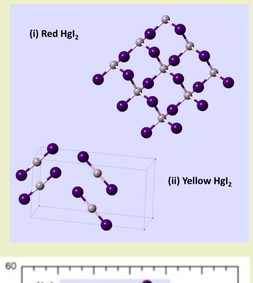
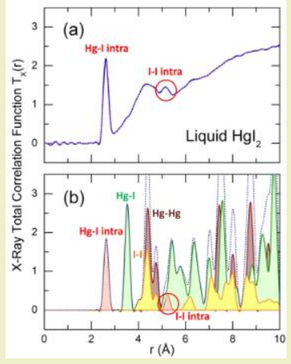
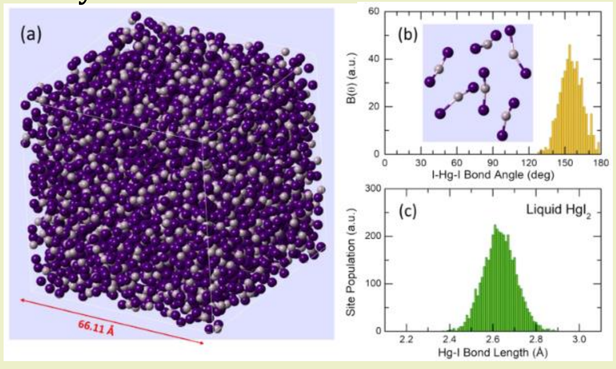
I. Introduction

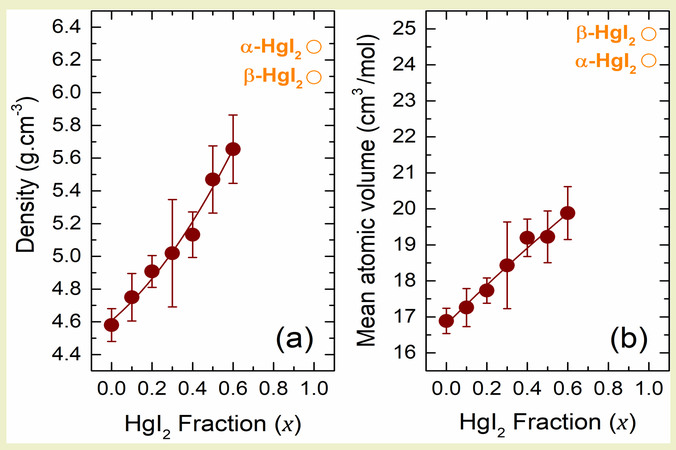
Crystalline mercury iodide HgI_2 exists in several polymorphs: (1) Layered red α-HgI_2 and metastable orange polymorphs build-up of centrosymmetric CS-HgI_4 tetrahedra, (2) Orthorhombic yellow β-HgI_2, existing above the α → β phase transition at 135 °C, composed of centrosymmetric quasi-linear HgI_2 triatomic molecules; ∠I–Hg–I = 178.3°, and (3) yellow^{HT} form consisting of non-centrosymmetric bent HgI_2 molecules; ∠I–Hg–I = 160°). The question arises whether (1) mercury will modify the trigonal networks of the As_2X_3 (X = Se, Te) chalcogenide glasses and (2) HgI_2 entities are non-centrosymmetric.

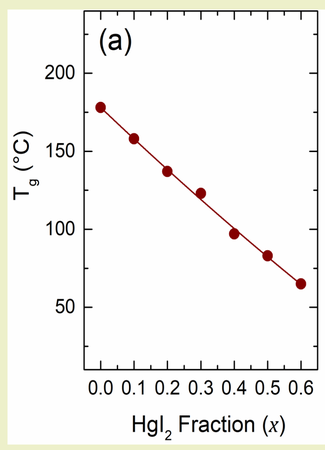


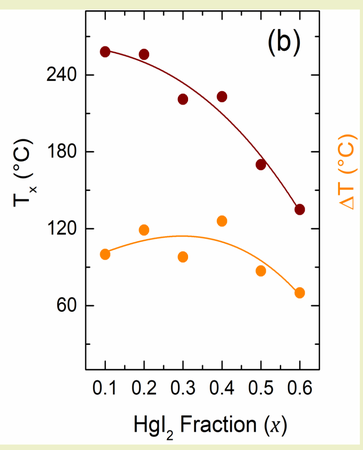




II. Macroscopic properties

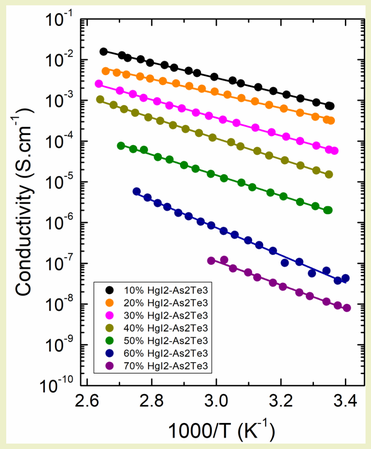


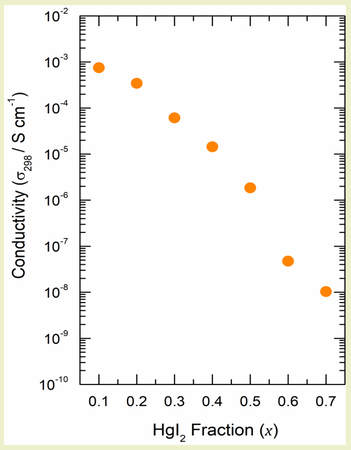


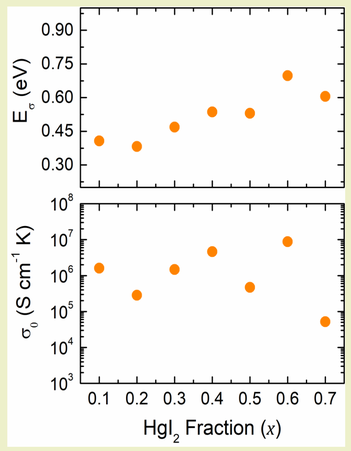


- ✓ The density & Mean atomic volume increase monotonically with increasing HgI_2
- ✓ The reduced network connectivity in the HgI_2–As_2Se_3 glasses seems to be responsible for T_g decease

III. Conduction properties

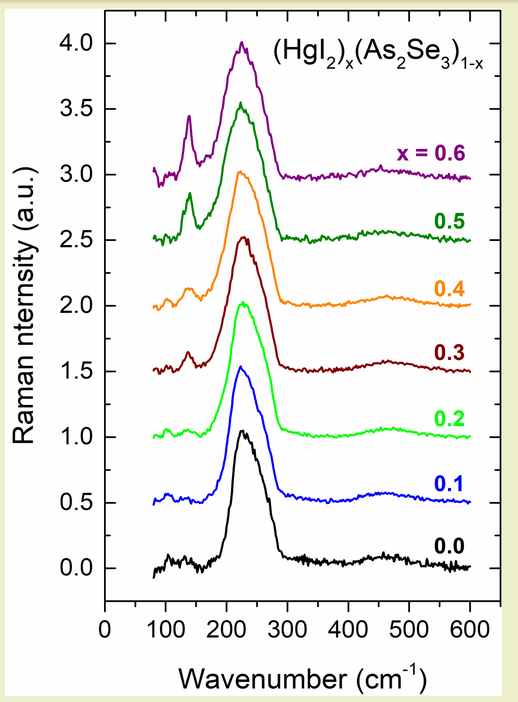


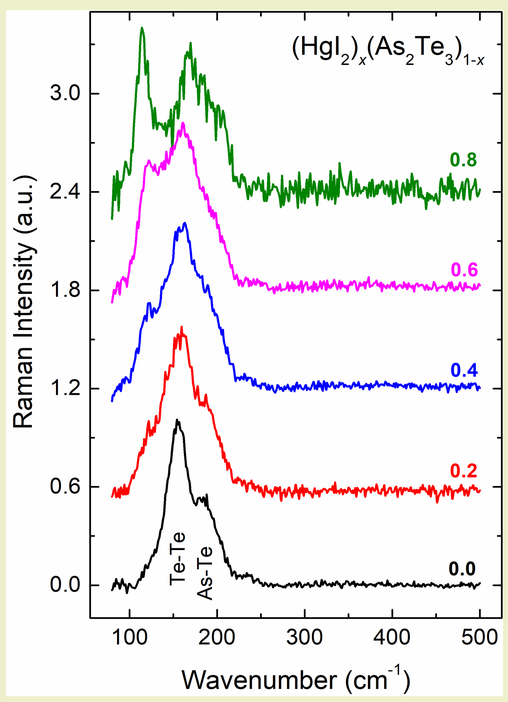


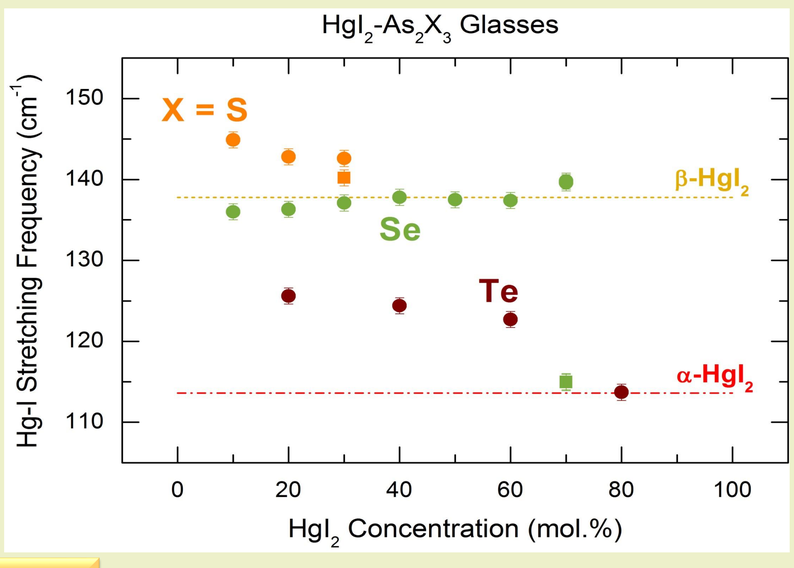


- ✓ The conductivity obeys the Arrhenius law: $\sigma = \sigma_0 /T \exp(-E_a/kT)$
- ✓ Highly energetic Te 5p lone pairs decreasing the gap is responsible for high electronic conductivity in telluride glasses
- ✓ Decreasing tellurium concentration with increasing *x* results in a gap widening and thus room-temperature σ_{298} (*x*) decrease
- ✓ Overall increase of activation energy with increasing *x*

IV. RAMAN Studies







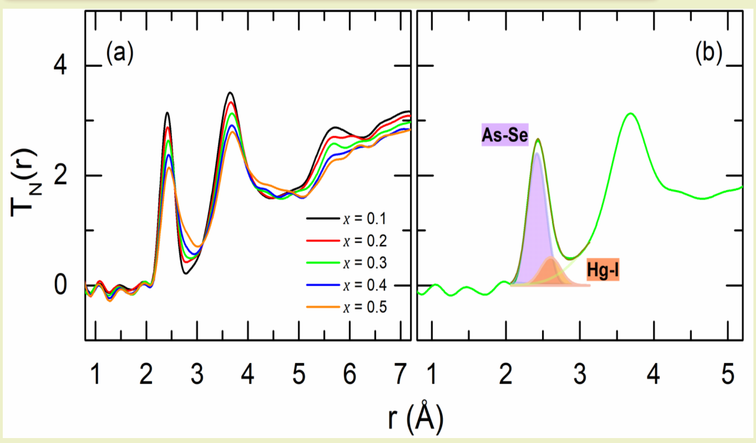
HgI_2-As_2Se_3:

- ✓ 227 cm^{-1} ⇒ stretching modes in **$AsSe_{3/2}$** trigonal units
- ✓ 270 cm^{-1} ⇒ **Se – Se** stretching modes of As-Se-Se-As units
- ✓ 139 cm^{-1} ⇒ similar to **A_{1g} symmetric Hg–I** stretching in **β–HgI_2**

HgI_2-As_2Te_3:

- ✓ 155 cm^{-1} ⇒ **Te – Te** related chains/fragments in the As-Te glass
- ✓ 190 cm^{-1} ⇒ stretching modes in **$AsTe_{3/2}$** trigonal units
- ✓ 114 cm^{-1} ⇒ **Hg–I** stretching in **α–HgI_2** / 123 cm^{-1} ($0.0 \le x \le 0.6$)

V. Neutron diffraction



Hypothesis:

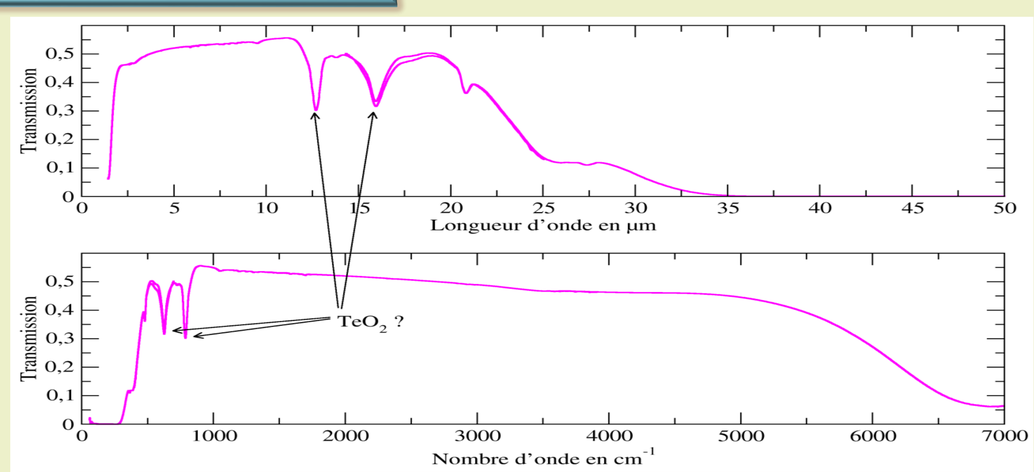
- ❑ two or more different mercury iodide local environments:

1) Hg–I molecular chains
2) tetrahedral $HgI_{4/4}$–related motifs
3) a mixture of both

HgI_2 Fraction *x*	*r*(As–Se) (Å)	N_{As-Se}	*r*(Hg–I) (Å)	N_{Hg-I}
0.0	2.41(1)	2.95(10)	–	–
0.1	2.41(1)	3.05(10)	2.58(2)	2.85(10)
0.2	2.41(1)	3.03(10)	2.57(2)	2.62(10)
0.3	2.41(1)	3.01(10)	2.60(2)	2.82(10)
0.4	2.42(1)	2.95(10)	2.64(1)	3.00(10)
0.5	2.42(1)	3.00(10)	2.67(1)	3.36(10)

VI. Optical properties

HgI_2-As_2Te_3:



- ✓ long infrared spectral range up to 35 µm

VII. Perspective

- ✓ DFT modelling of the Raman spectra
- ✓ High-energy X-ray diffraction (HE-XRD) for the HgI_2-As_2S_3 glasses
- ✓ Structural studies of the HgI_2-As_2Te_3 glasses using neutron diffusion (ND) and HE-XRD
- ✓ First-Principle Molecular Dynamics (FPMP) to decipher the structural motifs within the glass network
- ✓ Infrared optical measurements