HgY_2-GeS_2 (Y = Cl, Br, I) chalcogenide glasses: structural, macroscopic and electric properties

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Introduction

- Chalcogenide glasses containing **heavy metals** are well-established materials for **optical** and **photonic** applications related to low phonon density of state, wide transmission range, high linear and non-linear refractive indices.
- **Mercury**-containing **ion-conducting** glasses exhibit **high sensitivity to Hg^{2+} traces** in aqueous solutions, important for **chemical sensors** applications.
- Very little is known about their structure and properties.

AIM:

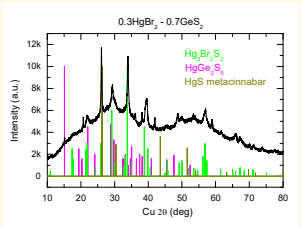
Synthesis and characterization of the bulk glasses in the HgY_2-GeS_2 (Y = Cl, Br, I) system.

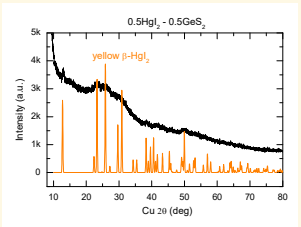
Synthesis and Macroscopic properties

Glass synthesis

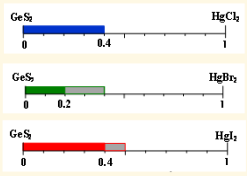
Melt quenching technique

- ✓ **Starting materials**: HgY_2 (4 N), and Ge, S elements (5 N), **sealed up** in silica tube **under vacuum**
- ✓ **Heated slowly in furnace** up to 950°C, **quenched** in air or in water

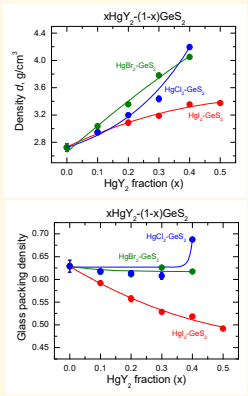


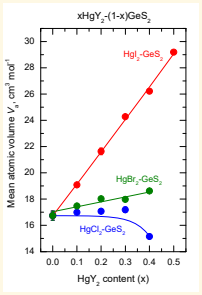


Vitreous domain



Density and mean atomic volume



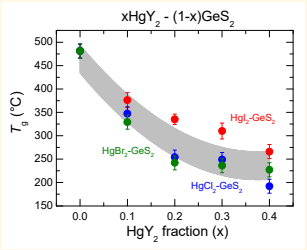


d↑ and V_m↑ with the HgY_2 addition

$d(HgCl_2) = 5.43\ g.cm^{-3}$
$d(HgBr_2) = 6.03\ g.cm^{-3}$
$d(HgI_2) = 6.36\ g.cm^{-3}$

Thermal properties

Glass transition temperature (T_g)

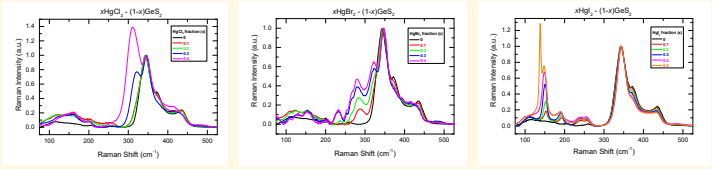


- **one T_g** ⇒ homogeneous glasses
- **T_g ↓ with HgY_2 addition** ⇒ host glass fragmentation and decrease of network connectivity

Glass structure

Raman spectroscopy

Appearance of the **new low-frequency features** with HgY_2 addition related to Hg-Y stretching

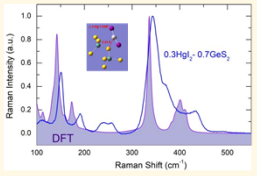


Y = Cl:
at ≈ **322 cm^{-1}** (for x = 0.3)
at ≈ **311 cm^{-1}** (for x = 0.4)

Y = Br:
287 cm^{-1} (x = 0.1) → **280 cm^{-1}** (x = 0.4)
at ≈ **322 cm^{-1}** (for x = 0.3 and 0.4)

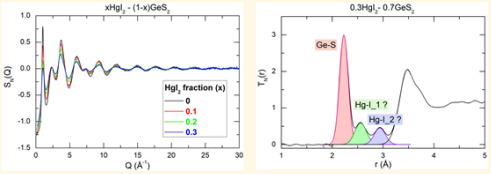
Y = I:
153 cm^{-1} (x = 0.1) → **148 cm^{-1}** (x = 0.5)
at ≈ **138 cm^{-1}** (for x = 0.5) => c-HgI_2

DFT modelling



Bent HgI_2 molecules in GeS_2 glass ⇒ intrinsic optical nonlinearity of the second order

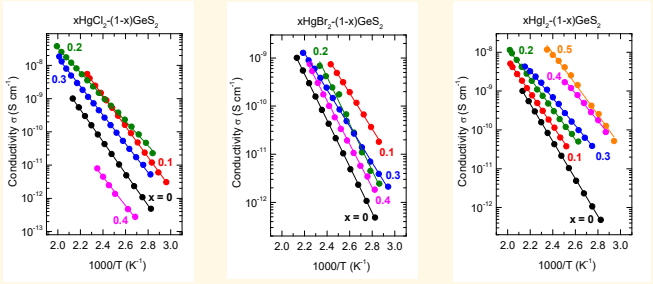
Neutron diffraction



HgI_2 fraction	r_{Ge-S} (Å)	N_{Ge-S}	r_{Hg-I} (Å)_1	N_{Hg-I}_1	r_{Hg-I} (Å)_2	N_{Hg-I}_2
0	2.22	3.99				
0.1	2.23	4.24	2.55	0.78	2.90	2.03
0.2	2.23	3.99	2.56	1.26	2.94	1.00
0.3	2.23	4.07	2.56	1.00	2.94	0.87

Electrical conductivity

Arrhenius-type behaviour: $\sigma = \sigma_0 T^{-1} \exp(-E_\sigma/kT)$



HgY_2-GeS_2 glasses are **electronic insulators**: $10^{-15}\ S.cm^{-1} \le \sigma_{298}(x) \le 10^{-12}\ S.cm^{-1}$

Conclusion

- **Glass-forming region**: up to 0.4 HgY_2 (Y = Cl, I) and 0.2 $HgBr_2$ fraction;
- **Thermal properties**: **T_g decreases** significantly with **HgY_2 addition;**
- **Electrical transport properties**:
  - glasses are electronic **insulators** ($10^{-15}\ S.cm^{-1} \le \sigma_{298}(x) \le 10^{-12}\ S.cm^{-1}$);
  - **σ_{298} increases** with the **increase** of **mercury iodide** concentration;
  - **σ_{298}** changes **non-monotonically** with **mercury chloride and bromide** concentration;
- **Structural features**: hypothesis of **bent asymmetric HgI_2 molecules** in the GeS_2 glass.

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