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Development of glass formulations for sealing applications in High-Temperature steam Electrolysis

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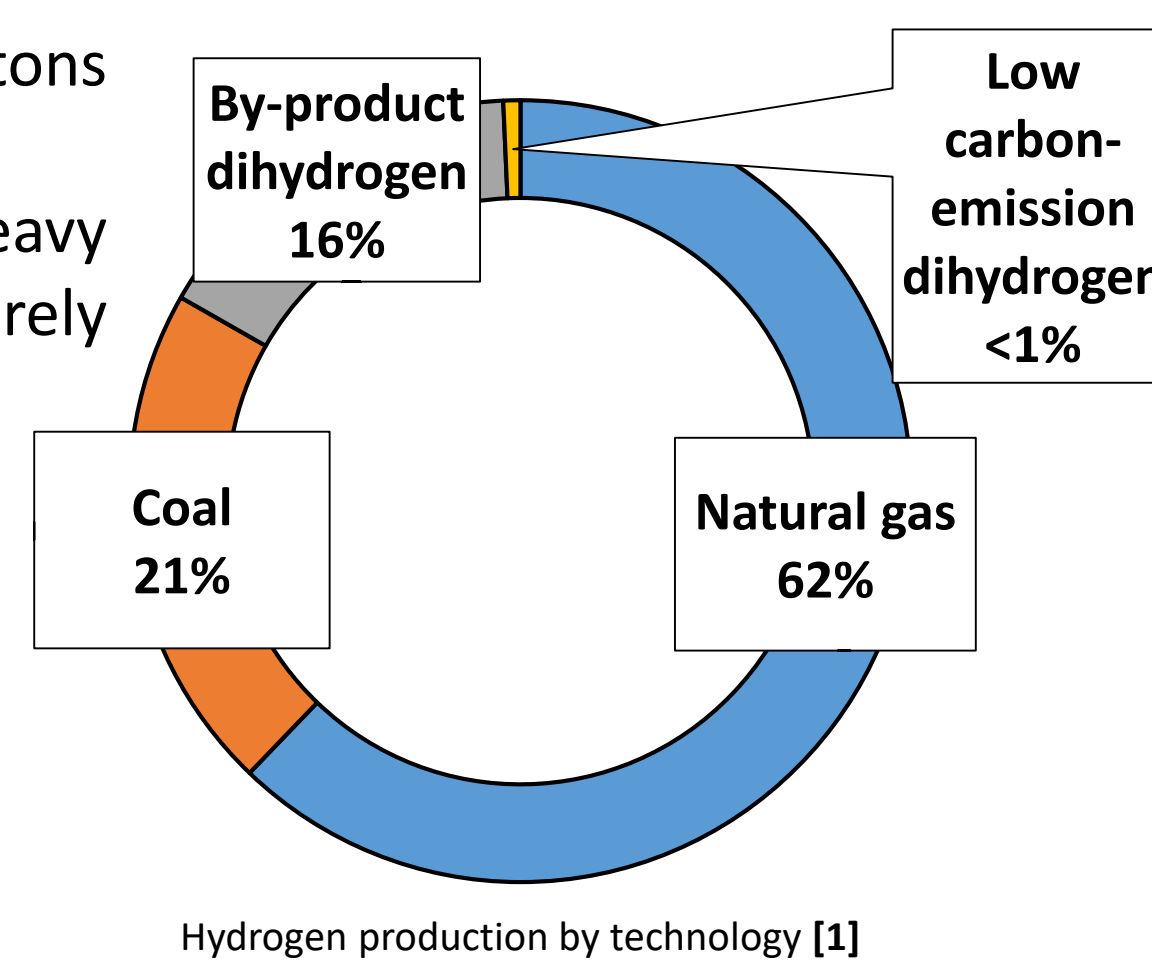
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CONTEXT: HIGH-TEMPERATURE STEAM ELECTROLYSIS

Global dihydrogen (H₂) demand reached more than 95 million tons in 2022 [1]
H₂ production processes, mainly using hydrocarbons, are heavy greenhouse gas emitters. Low carbon-emission H₂ is almost entirely produced from processes using fossil fuels with CCUS*

Thus, low-carbon H₂ production processes need to be developed

One possibility for low-carbon dihydrogen production is
High-Temperature Electrolysis of steam

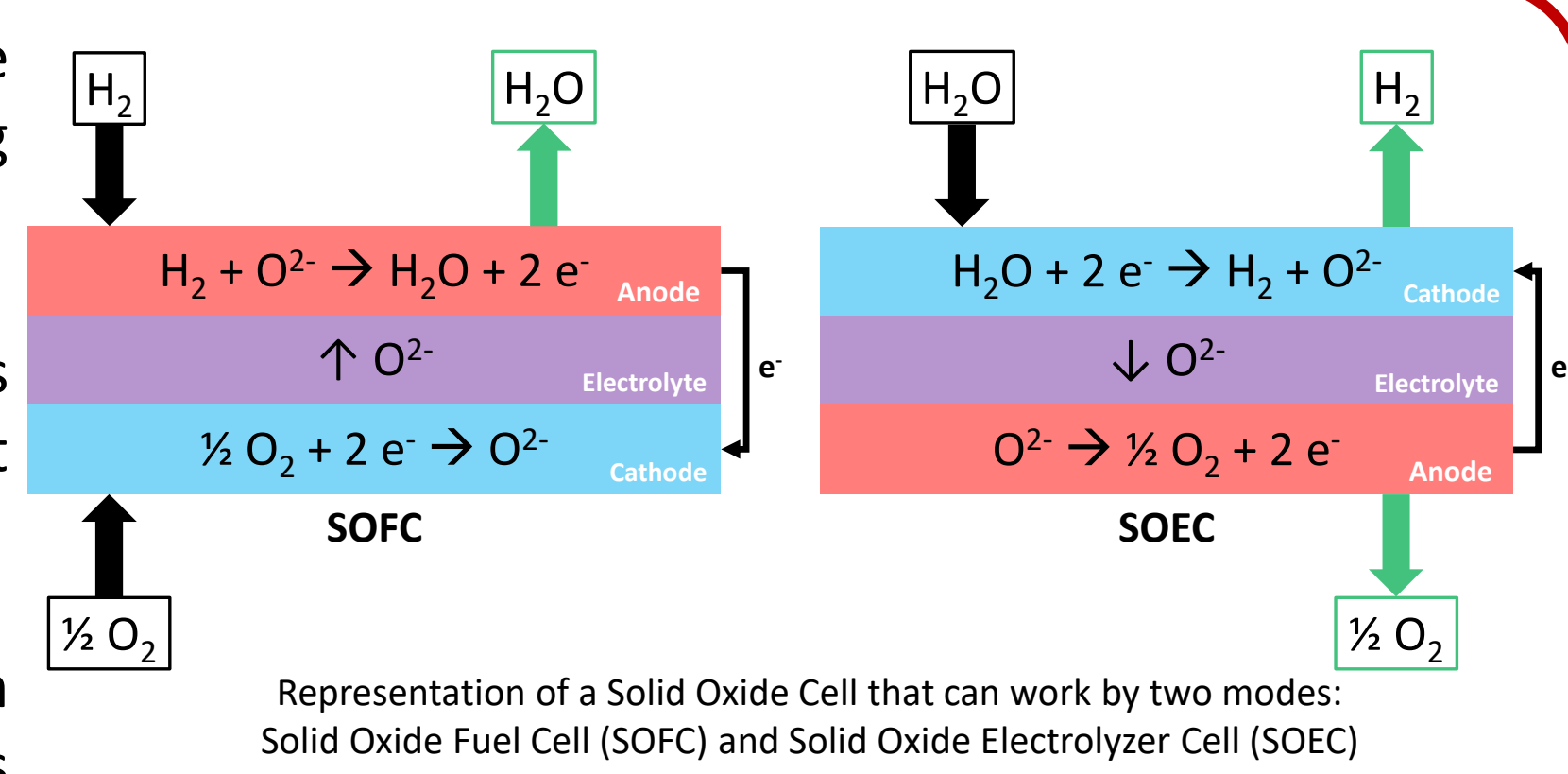


CCUS: Carbone Capture, Utilization and Storage

High Temperature Electrolyzers (HTE) are made of stacked Solid Oxide Cells (SOC) usually working between 700 - 850°C

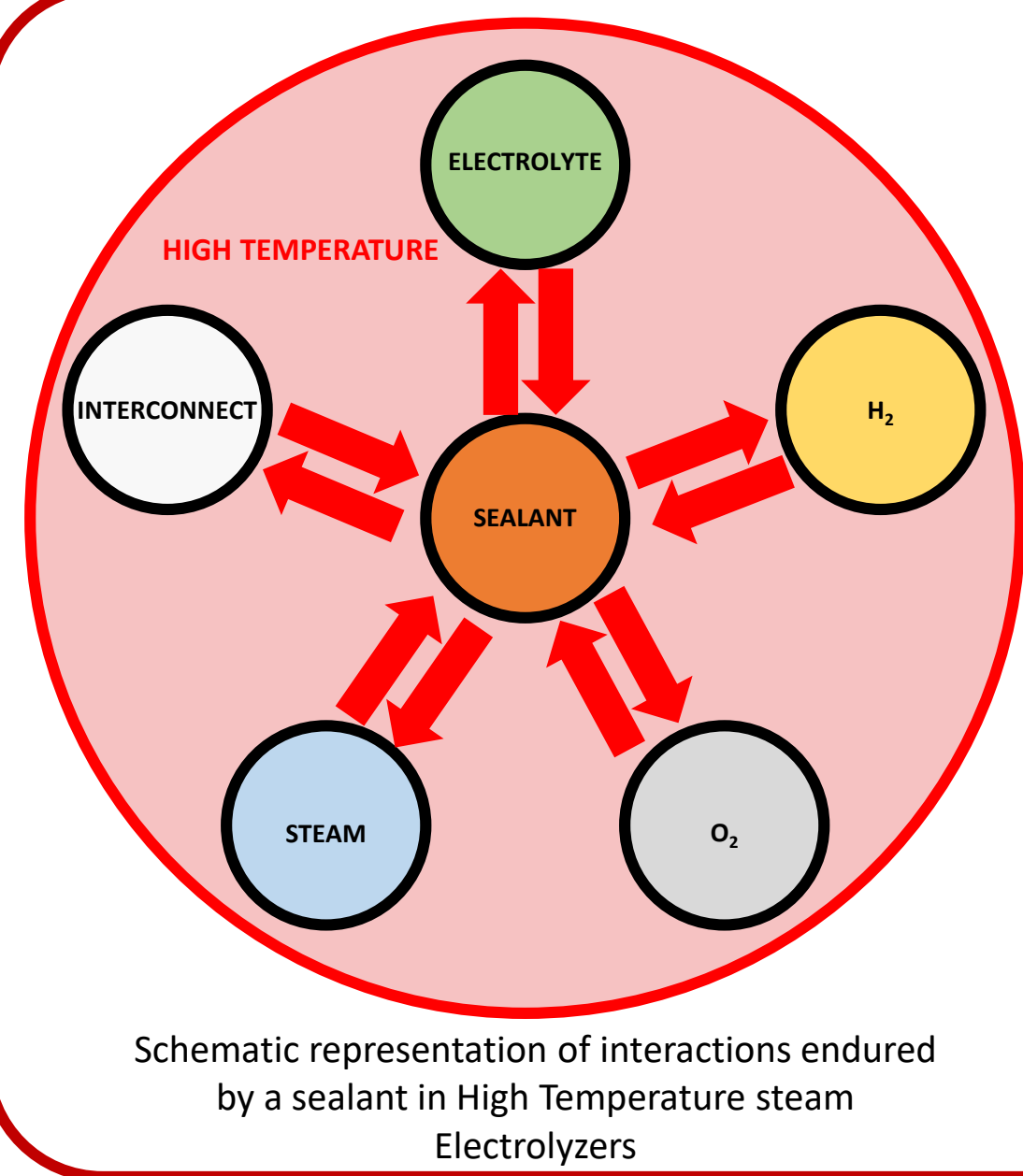
High-temperature electrolysis of steam produces dihydrogen (H₂) and dioxygen (O₂), to be efficient the system needs to be **gas-tight**

Ensuring the sealing of this structure is of high importance but also very challenging as a gas leak could lead to the degradation of the system



Necessity of a very specific sealant

GLASS & GLASS-CERAMIC SEALANTS FOR SOLID OXIDE CELLS



HTE involves very specific working conditions for a sealing material :

- Various materials directly in contact
- Several atmospheres with extreme properties
- High-temperature working conditions (700 - 850°C)
- Long working durations (40 000 hours)

The sealant's technical specifications are highly restrictive: literature shows that **glass and glass-ceramic sealants** are widely developed due to their **high adaptability** [2] [3]

Current sealing solution for HTE developed at CEA is a glass-ceramic encountering various problematics:

- Fast crystallization inducing high amount of **remaining porosity**
- Possible formation of **BaCrO₄** at the interconnect interface, inducing possible **delamination**
- Deleterious phases crystallization exhibiting very different TEC possibly implying strain-induced **cracking**

OBJECTIVE: Investigate the impact of composition variations on the crystallization behavior of the current sealing material

METHODOLOGY

- Multiple glass systems are elaborated by melt-quenching method
 - Oxide mix in Pt/Rh crucible
 - 1300°C for 3h and 2nd melting for 2h
- Several systematical substitutions of BaO by Al₂O₃ are studied
- Sieved glass powder is thermally treated at chosen temperatures for variable durations to obtain glass-ceramic samples
 - Pt/Au crucible
 - 1g of sieved glass powder (20 - 40 μm)

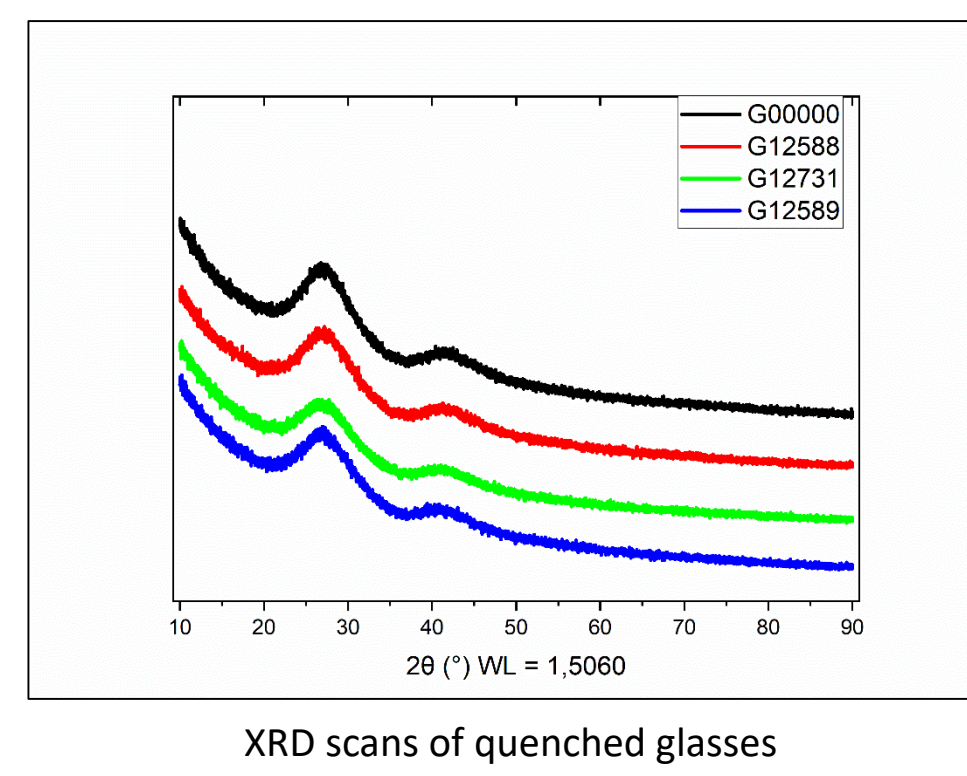
Glasses and glass-ceramics samples are characterized by various methods:

- Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS)
 - Imagery + Chemical quantifications
- X-Rays Diffraction (XRD) → Crystalline phases identifications
- Dilatometry measurements → Thermal Expansion Coefficient (TEC) measurements
- Differential Thermal Analysis (DTA) → Glass-transition temperature (T_g) measurements and exothermic behavior (crystallization) observations

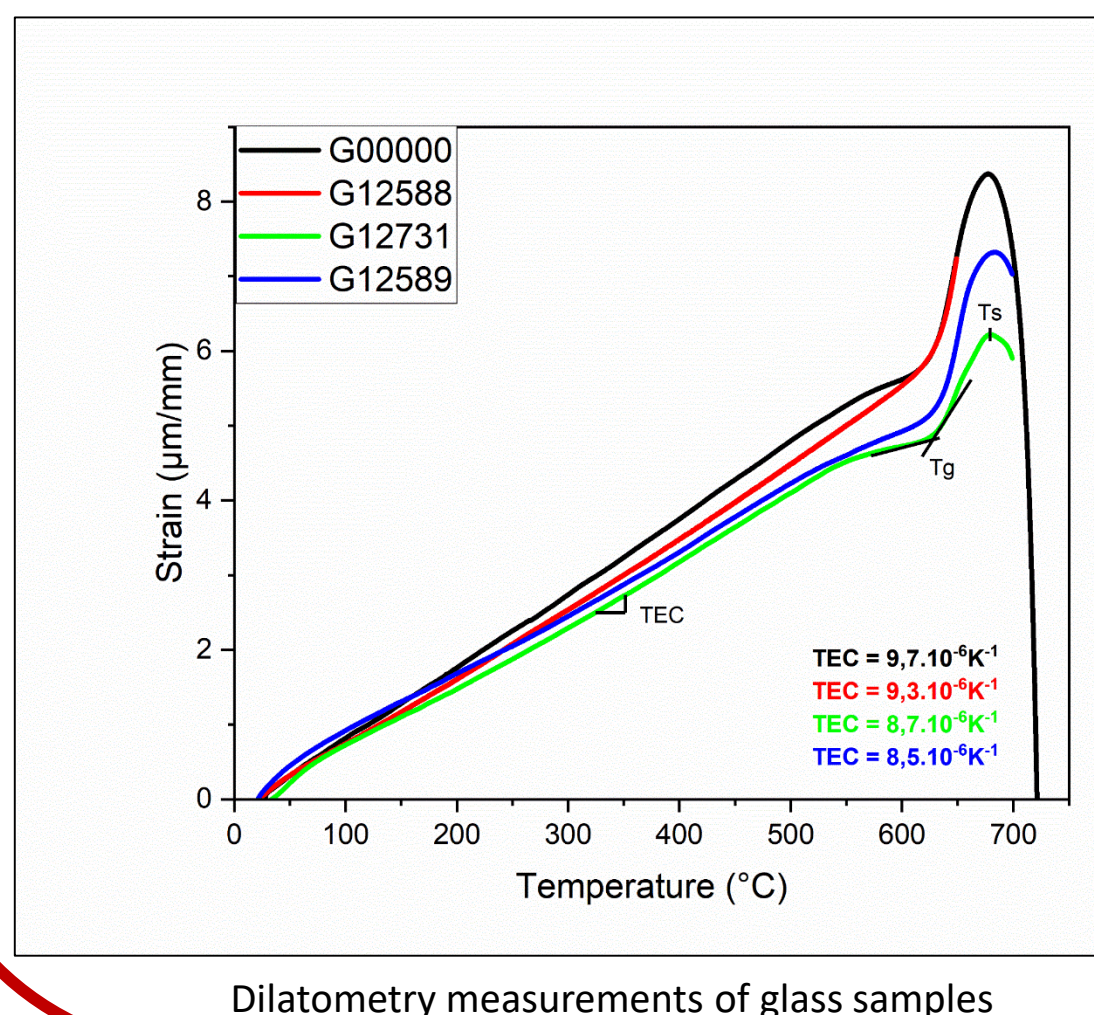
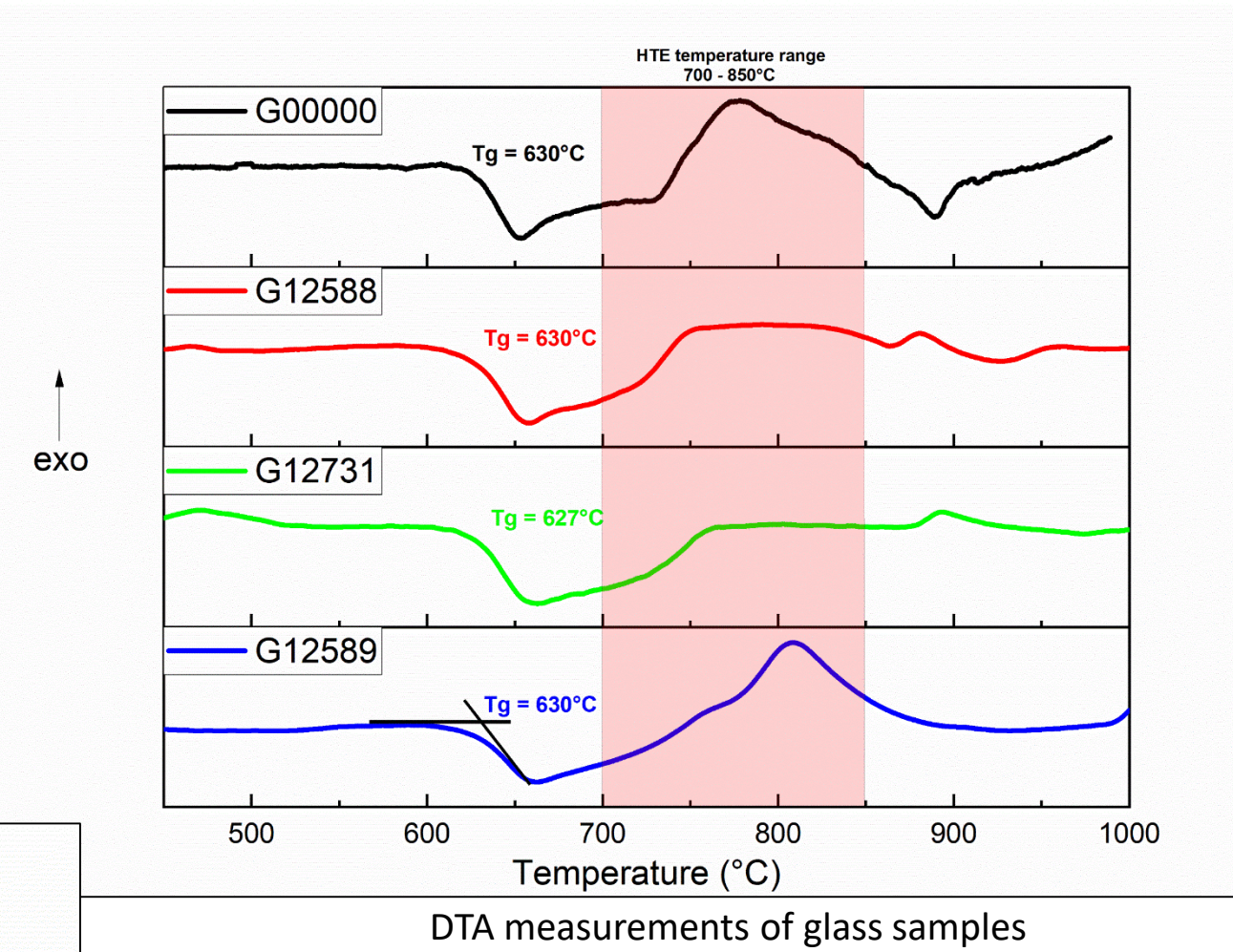
RESULTS

- SEM-EDS characterization of quenched glasses show compositions near expected values

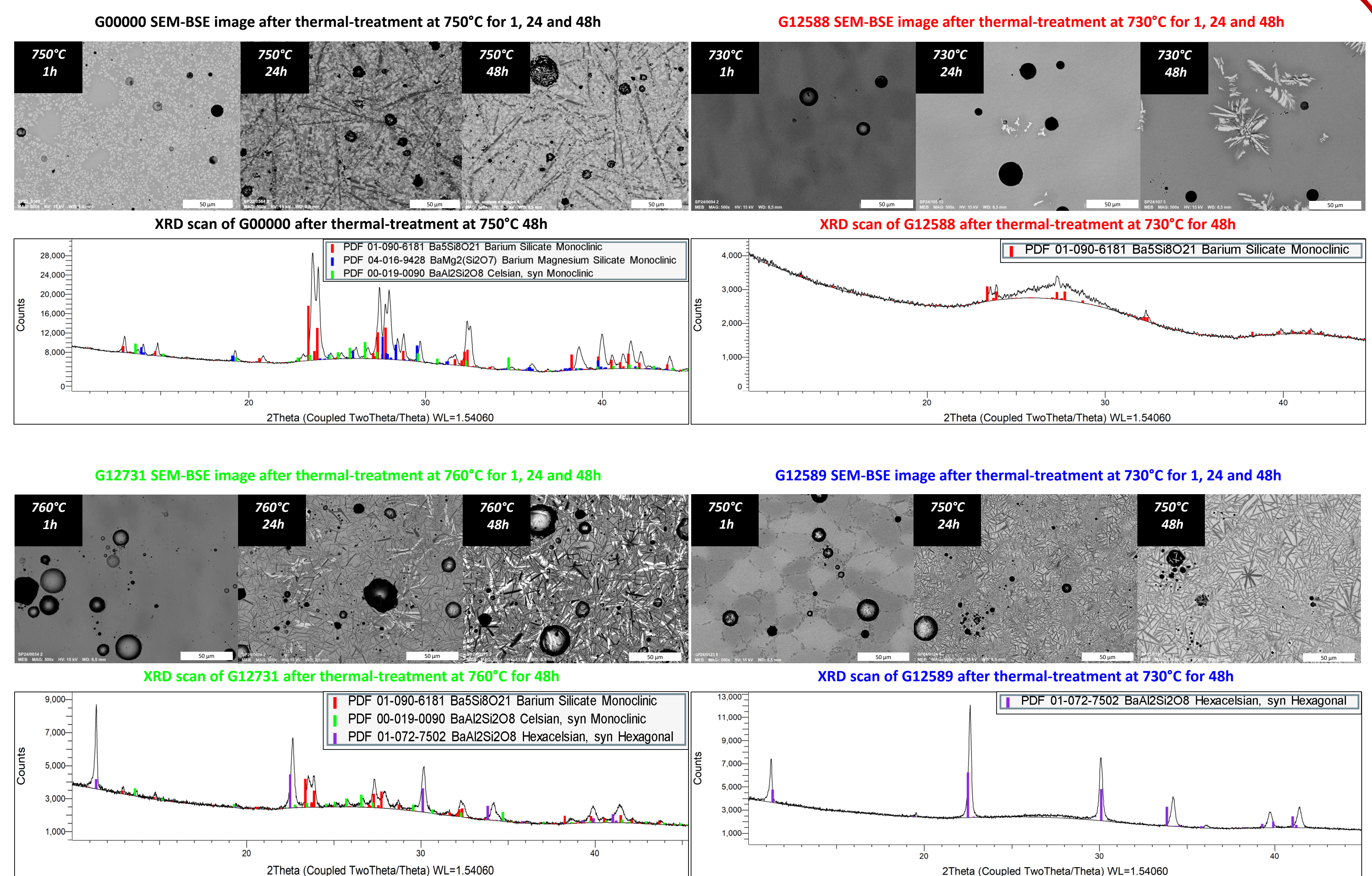
| Glass composition (%mass) | BaO | Al ₂ O ₃ | SiO ₂ + B ₂ O ₃ | MgO |
|---------------------------|------|--------------------------------|--|-----|
| Nominal G00000 | 55,3 | 1,7 | 38,8 | < 5 |
| EDS G00000 | 57,4 | 1,7 | 37,1 | < 5 |
| Nominal G12588 | 53,2 | 3,4 | 39,2 | < 5 |
| EDS G12588 | 52,3 | 3,7 | 40,0 | < 5 |
| Nominal G12731 | 51,1 | 5,1 | 39,6 | < 5 |
| EDS G12731 | 53,6 | 5,2 | 37,2 | < 5 |
| Nominal G12589 | 48,9 | 6,9 | 39,9 | < 5 |
| EDS G12589 | 50,0 | 6,6 | 39,6 | < 5 |



- Sieved glass powder (20 - 40 μm) is analyzed by DTA
- No evolution in glass-transition temperature (T_g) has been measured
- Glasses exhibit very different exothermic (crystallization) behavior in HTE temperature range



- Monolithic glass samples are prepared to carry out dilatometry analysis
- Glasses Thermal Expansion Coefficient (TEC) is decreasing with the %BaO decreasing
- T_g measured values are consistent with DTA measurements
- Softening temperatures (T_s) aren't greatly changed



| Phase | System | TEC (.10 ⁻⁶ K ⁻¹) | Reference |
|--|------------|--|-----------|
| Ba ₃ Si ₆ O ₂₁ | Monoclinic | 12,5 | [4] |
| BaMg ₂ Si ₂ O ₇ | Monoclinic | 11,0 | [5] |
| BaAl ₂ Si ₂ O ₈ | Hexagonal | 8,0 | [6] |
| BaAl ₂ Si ₂ O ₈ | Monoclinic | 2,0 | [6] |

Individual TEC of identified crystalline phases

- Very different crystallization behavior is witnessed in studied systems
- G12588 seems to be less crystallized after these specific thermal-treatments at 730°C
- Presence of possible deleterious phases is confirmed by SEM-EDS and XRD measurements

CONCLUSION & PROSPECTS

- 4 glass systems have been prepared with various BaO substitutions by Al₂O₃
- Thermal properties (T_g, T_s, TEC) of said glasses have been measured
- Variations in TEC of glasses have been reported to be consistent with BaO concentration
- Glass-ceramics samples have been elaborated and characterized
- Possible deleterious crystalline phases crystallization have been observed

- Crystallization in this glass-ceramic systems must be further examined:
 - Determination of the crystallization range of identified phases
 - Study of longer thermal-treatments to assess crystalline phases microstructural behavior
- Determination of the impact of crystallization on thermomechanical properties of the material must be studied
- Study of the interconnect/sealant interface after thermal treatment will be conducted

ACKNOWLEDGMENTS

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