Élaboration, structure et caractérisation mécanique de verres et de vitrocéramiques oxyazotés mécanoluminescentes du système $BaO-SiO_2-Si_3N_4$

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Journées VERRE 2024 Dijon

–

Prix de thèse USTV 2023

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Two joined investigations

Oxynitride glasses

- Literature review
- Elaboration
- Structure
- Mechanical properties

→ Structure/properties relationship

Mechanoluminescence

- Of crystals and glass-ceramics
- Study of the mechanisms
- Combined experimental and theoretical study

→ Study mechanical phenomena through light emission

Introduction

Luminescence and mechanoluminescence

Material formulation

Luminescence

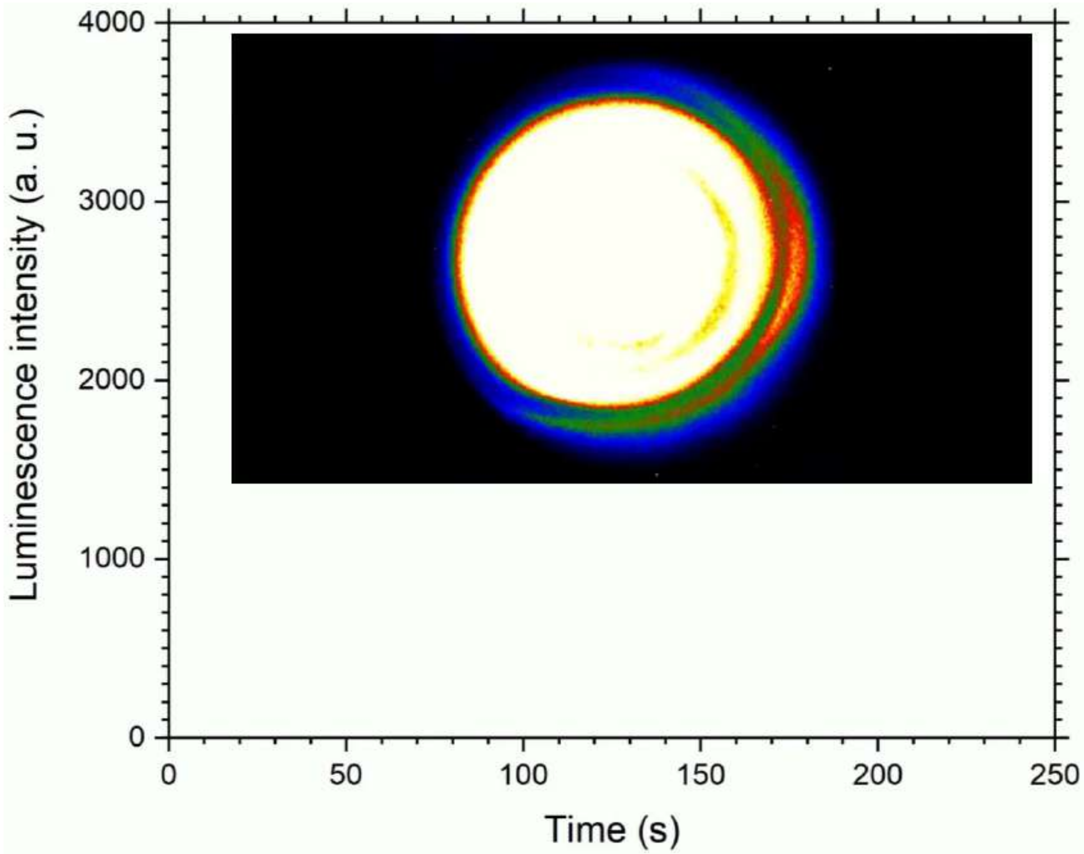
Introduction

Luminescence:

- **Light emission** resulting from an **excitation**

Various types of **luminescence** depending on the **excitation source**:

- **Electroluminescence** (electric field)
- **Cathodoluminescence** (electronic bombardment)
- **Photoluminescence** (electromagnetic radiation)



Luminescence

Mechanism

- Focus on **photoluminescence** induced by a **luminescent center (Eu^{2+})**

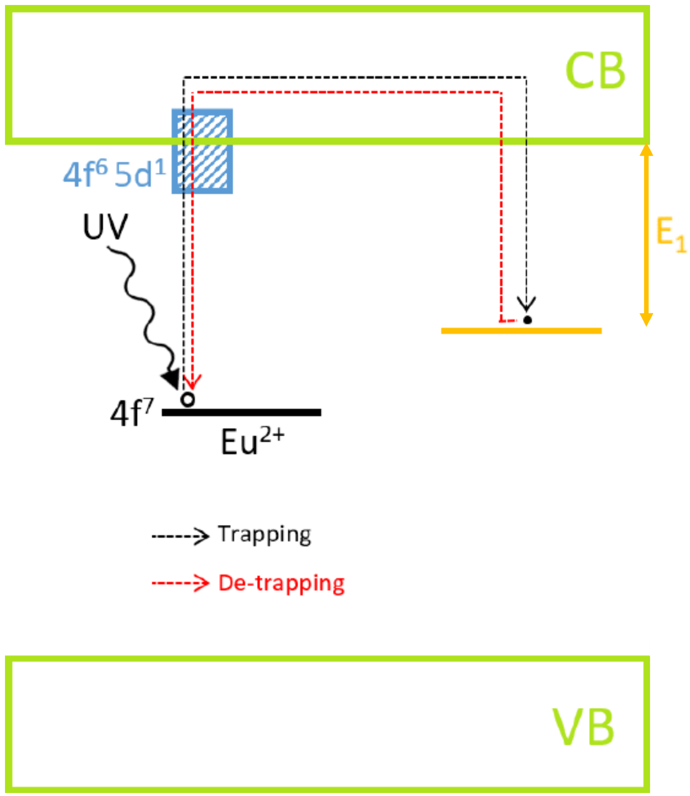
Step 1: UV irradiation

- **Eu^{2+} electronic configuration change**: $4f^7 \rightarrow 4f^6 5d^1$
- $5d^1$ **electron escapes** to the **conduction band** (leaving a **hole** behind)
- Then **falls** in the E_1 **energy level (= trap) associated** to **defects** in the **crystal structure**

Step 2: Light emission

- With **time**, the **electron returns to** the $4f^7$ **ground state** along **with light emission:**
- **Deeper energy levels: lifetime ↗**

$$I(t) = I_0 exp\left[-ste^{-\frac{E}{k_B T}}\right]$$



Introduction

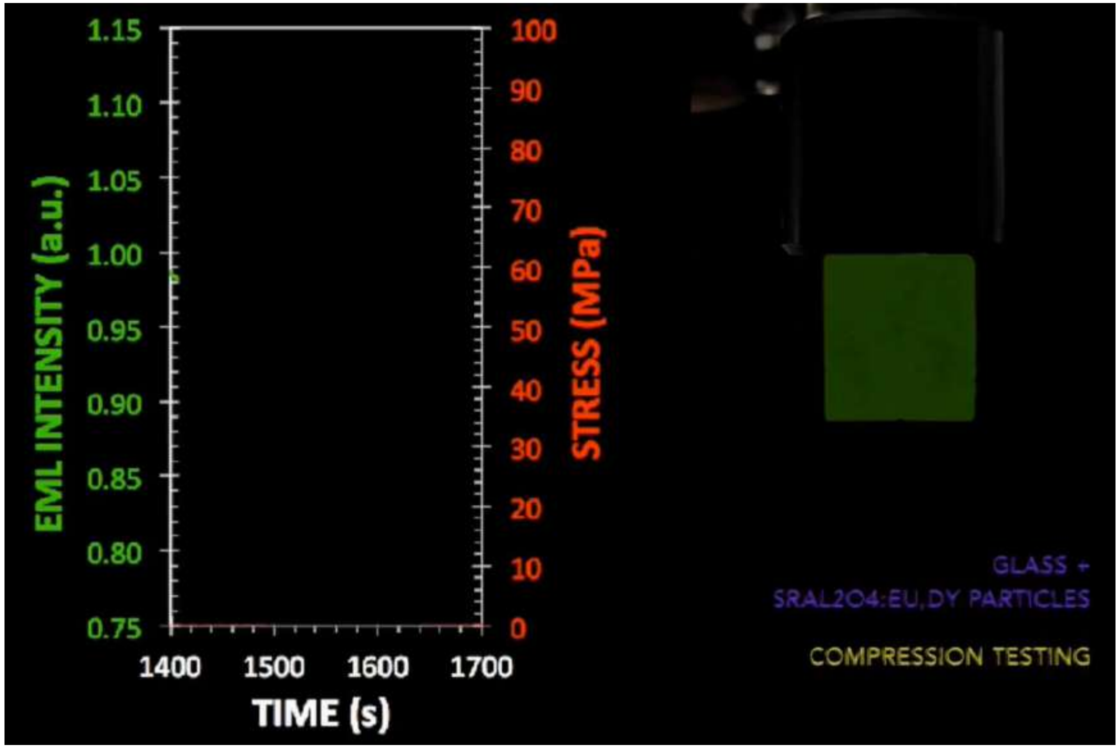
Mechanoluminescence:

- **Emission** of **light** of a **crystalline material** as a **response** to a **mechanical stimuli**
- **Focus** on **elastico-mechanoluminescence** (elastic deformation)

→ **Changes** the **position** of the **energy levels**, *i.e.* **charge carriers recombination kinetics**

This **PhD** is **in line** with the **PhD** of **M. Dubernet**, realized at the **Glass Mechanics lab** in **2016**:

- It **focused** on a **glass/particles composite** **($SrAl_2O_4:Eu^{2+}$, Dy^{3+})**



https://www.youtube.com/watch?v=TGTBg8M4JRg

[1]Dubernet M, Bruyer E, Gueguen Y, et al. Mechanics and Physics of a Glass/Particles Photonic Sponge. Sci Rep. 2020;10(1):1–10. https://doi.org/10.1038/s41598-020-75504-9

Mechanoluminescent material formulation…

…to investigate mechanical phenomena

To **study mechanical phenomena** (crack propagation, etc.) **through** a **light emission**:

- Need a **bulk** and **crystalline material**

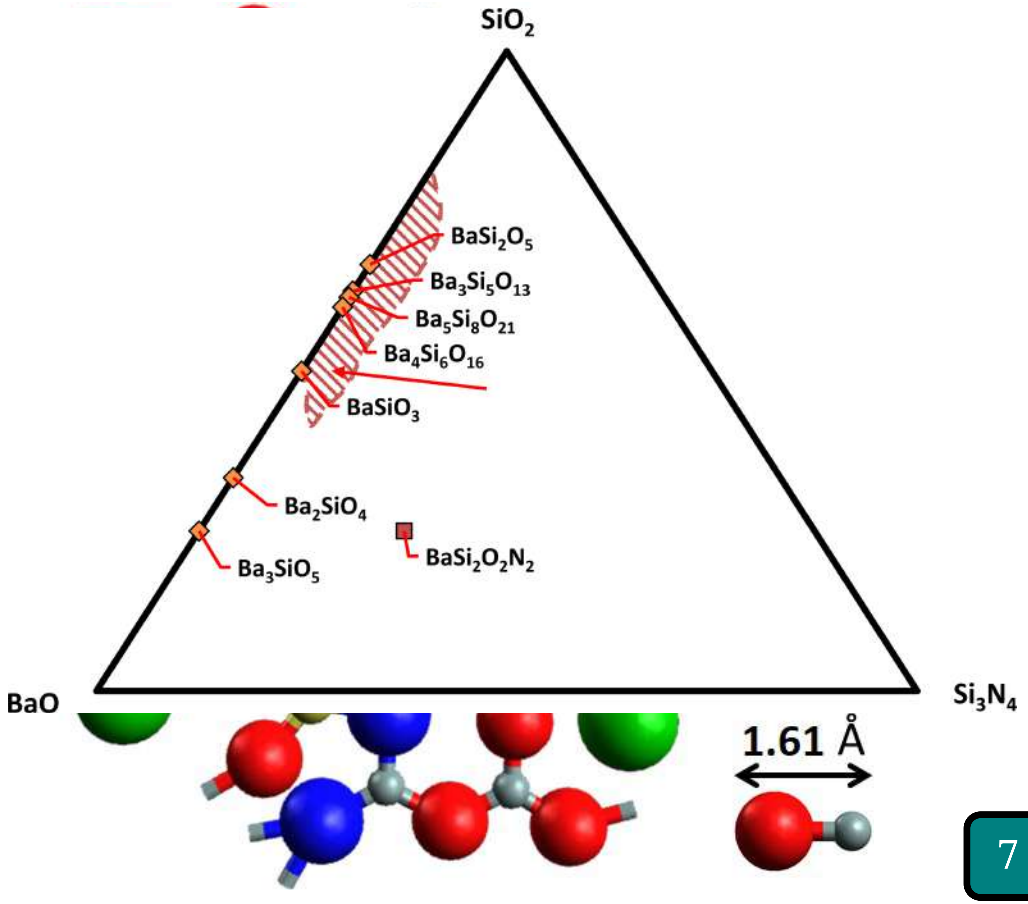
→ Start from a **glass**

To achieve **mechanoluminescence** in a **bulk glass-ceramic**, we looked for:

- a **mechanoluminescent crystalline phase**
- that **can form** a **glass**
- with a **composition close to** that of the **glass** so as **to favor** a **congruent crystallization**

$Ba_4Si_6O_{16}$

Oxynitride glasses:



$Ba_4Si_6O_{16}$

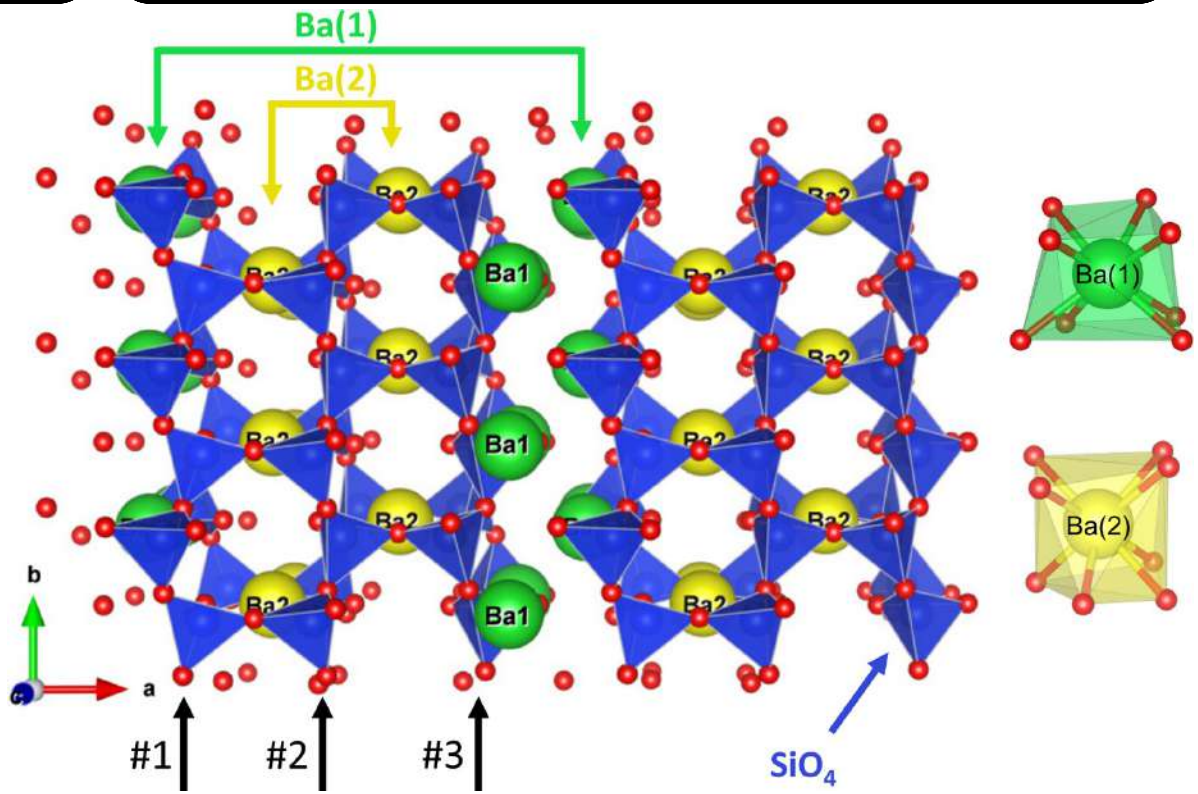
Mechano-luminescence properties

However, **$Ba_4Si_6O_{16}$:Eu^{2+}:**

- (very) **small mechanoluminescence intensity**
- **Too small** to properly **analyze** the **signal**

While the **(mechano-)luminescence properties** of **several crystals** are **known:**

- **$SrAl_2O_4$:Eu^{2+}, Dy^{3+}**
- **ZnS:Cu^+**
- **$BaSi_2O_2N_2$:Eu^{2+}**



Those of $Ba_4Si_6O_{16}$:Eu^{2+}, *RE* (*RE* = rare earth) were **not** (or scarcely) **reported**

→ **Study** of the **(mechano-)luminescence properties** with **compositional changes**

→ **Incidence** of ***RE***

Composition-dependent luminescence and mechanoluminescence (powdered crystals)

Composition dependence

Mechanisms

Composition-dependent (Mechano-)luminescence

Study of the **luminescence** and **mechanoluminescence properties** of **$Ba_4Si_6O_{16}$:Eu^{2+}** , ***RE*** powdered **crystals** with **compositional changes:**

- **Rare-earths co-doping**
- ***RE*:Eu^{2+} ratio** and **quantity**

→ **Coupling thermally stimulated luminescence** and **mechanoluminescence** experiments

Composition-dependent

Thermally stimulated luminescence

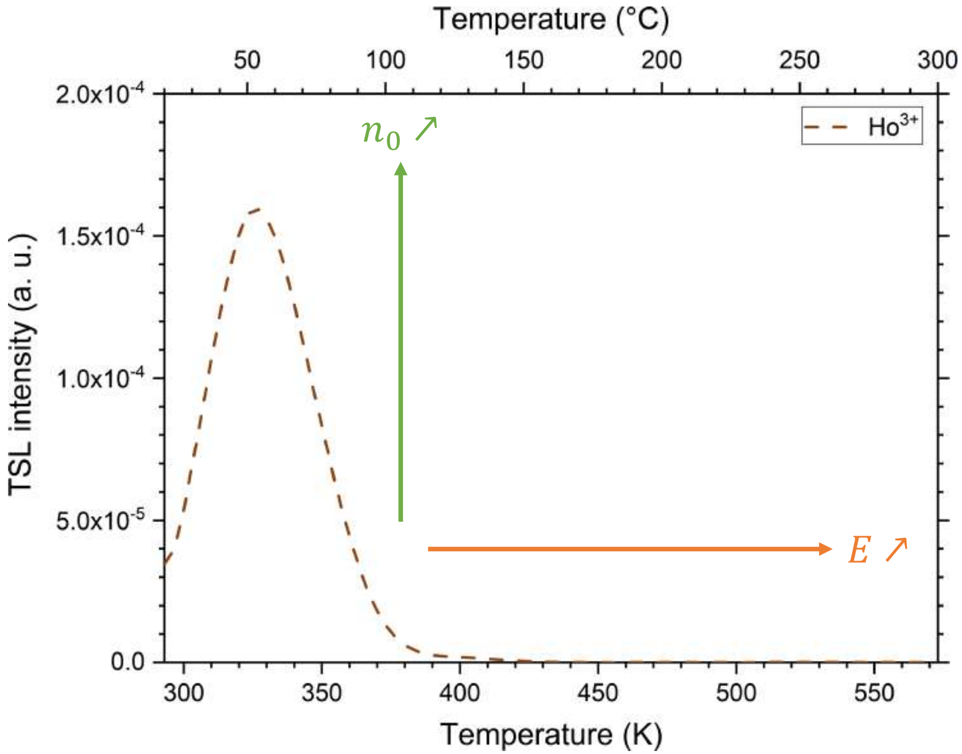
Insights of the **energy levels depths** E and **concentrations** n_0 from **thermally stimulated luminescence:**

$$I(T) = sn_0 \exp\left(-\frac{E}{k_B T}\right)\left[\left(\frac{(l-1)s}{\beta}\right) \times \int_{T_0}^{T} \exp\left(-\frac{E}{k_B T}\right) dT + 1\right]^{-\frac{l}{l-1}}$$

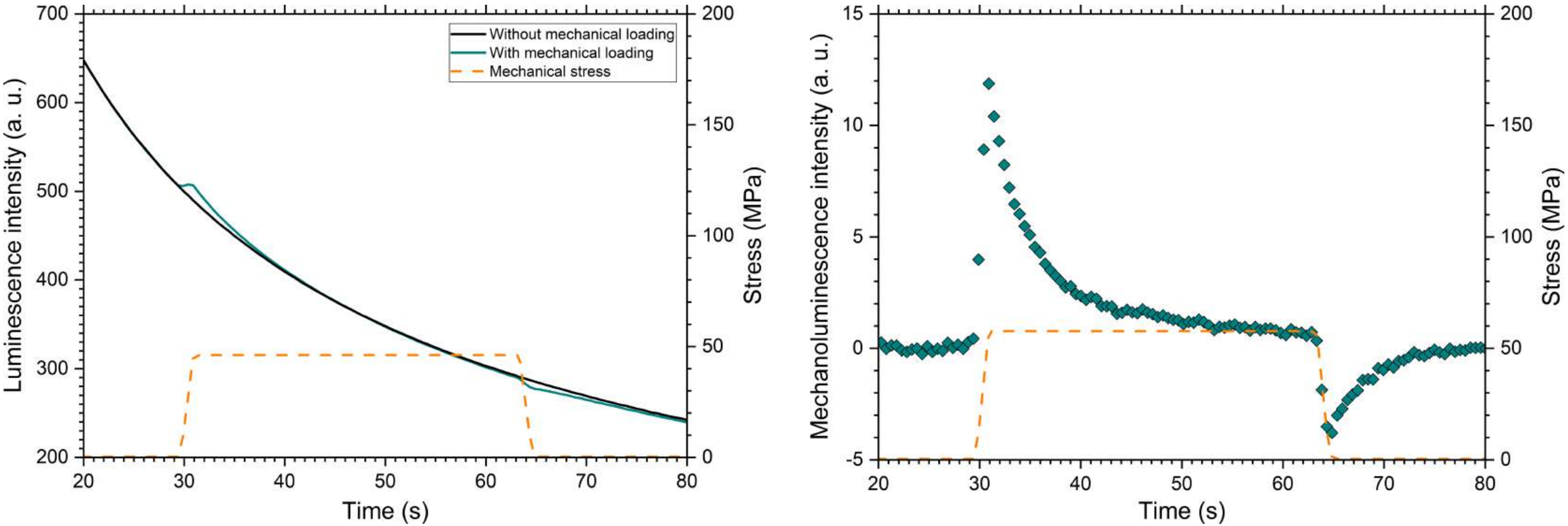
- 1st step: **UV irradiation**
- 2nd step: after a few s, **heating** of the **sample** (1 K · s^{-1})

Presence of ≥ 1 **peak**:

- **T_{max} ↗: deeper trap (E ↗)**
- **Intensity ↗: n_0 ↗**



Mechanoluminescence measurement: Diametral compression tests on powder/epoxy composites



Mechanoluminescence behavior independent from ***RE* co-doping**

- **Mechanoluminescence** intensity ↗ during **loading**
- **Mechanoluminescence** intensity ↘ during **unloading**

Composition-dependent (Mechano-)luminescence

Study of the **luminescence** and **mechanoluminescence properties** of **$Ba_4Si_6O_{16}$:Eu^{2+}** , ***RE*** powdered **crystals** with **compositional changes:**

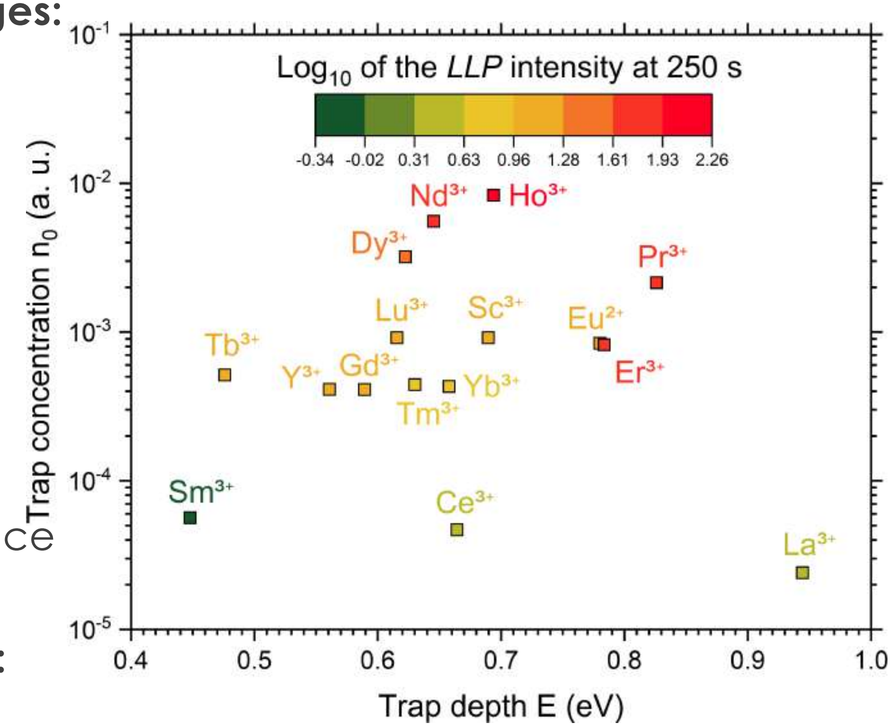
- **Rare-earths co-doping**
- ***RE*:Eu^{2+} ratio** and **quantity**

→ **Coupling thermally stimulated luminescence** and **mechanoluminescence** experiments

→ The **(mechano-)luminescence intensity changes** by several **orders** of **magnitude depending** on the ***RE* co-doping**

→ **Rare-earths dependent local structural rearrangements** induce **changes** in **concentrations** and **trap depths** of **energy level**

→ **Largest luminescence and mechanoluminescence intensity:** **$Ba_{3.5}Eu_{0.3}Ho_{0.2}Si_6O_{16.1}$** (20 % as intense as $SrAl_2O_4$:Eu^{2+}, Dy^{3+})



Composition-dependent luminescence and mechanoluminescence powdered (crystals)

[2]Duval A, Suffren Y, Benabdesselam M, Houizot P, Rouxel T. Luminescence and Mechanoluminescence of $Ba_4Si_6O_{16}$:Eu^{2+}, RE Phosphors. *J Chem Phys*. 2023;159(13):134501. https://doi.org/10.1063/5.0167222

Composition-dependent

Thermally stimulated luminescence

Two important things to **build** the **mechanoluminescence mechanism:**

- **I.** The **luminescence** and the **mechanoluminescence intensity** are **proportional**

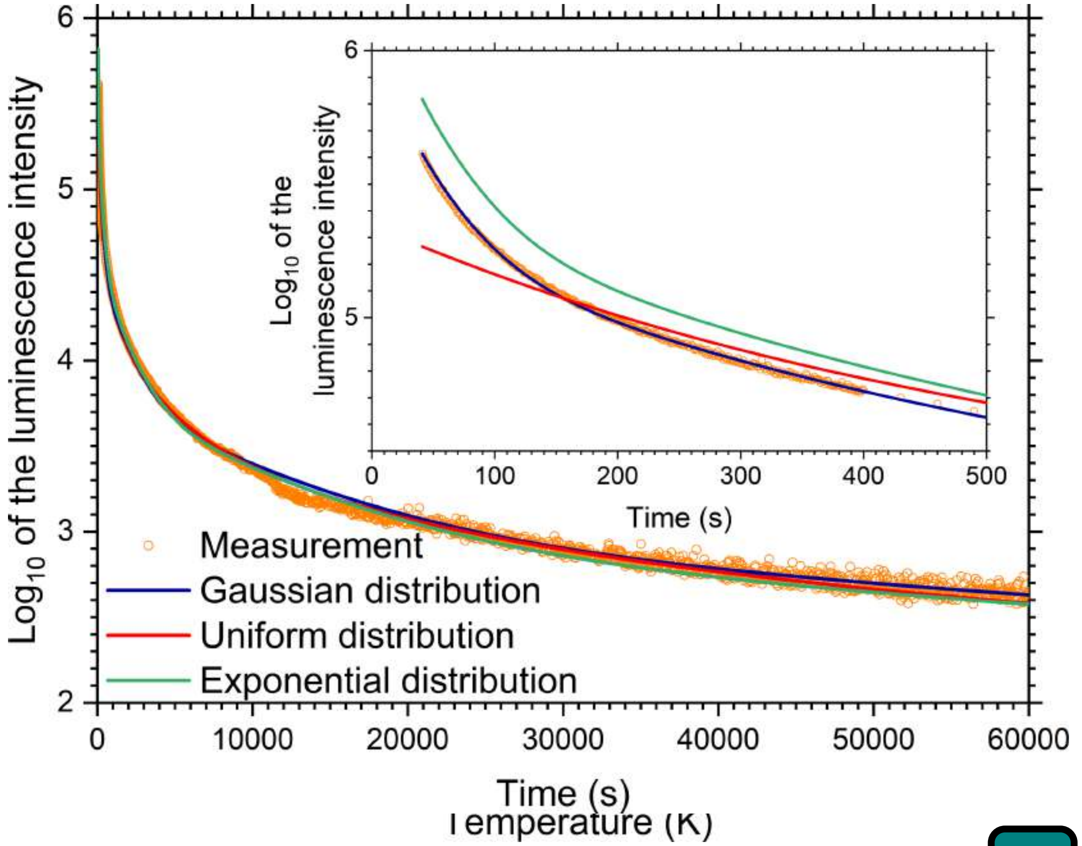
→ **Charge carriers involved** with **luminescence** are also **involved** with **mechanoluminescence**

With *RE* = Ho^{3+}:

- **II.** Gradual **shift** in **T** of the peak with ↗ **delay** time

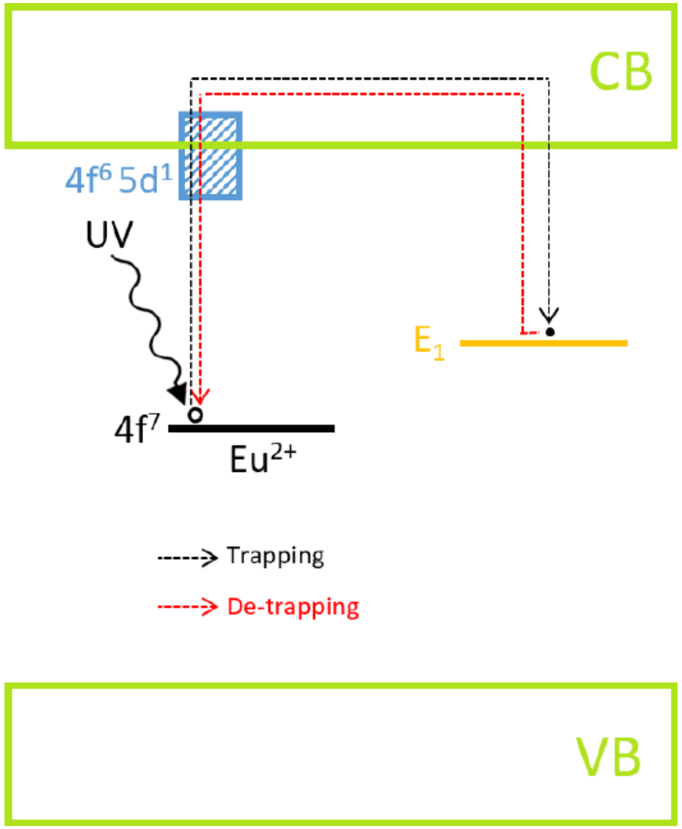
→ There is **at least ≥ 2 energy levels**

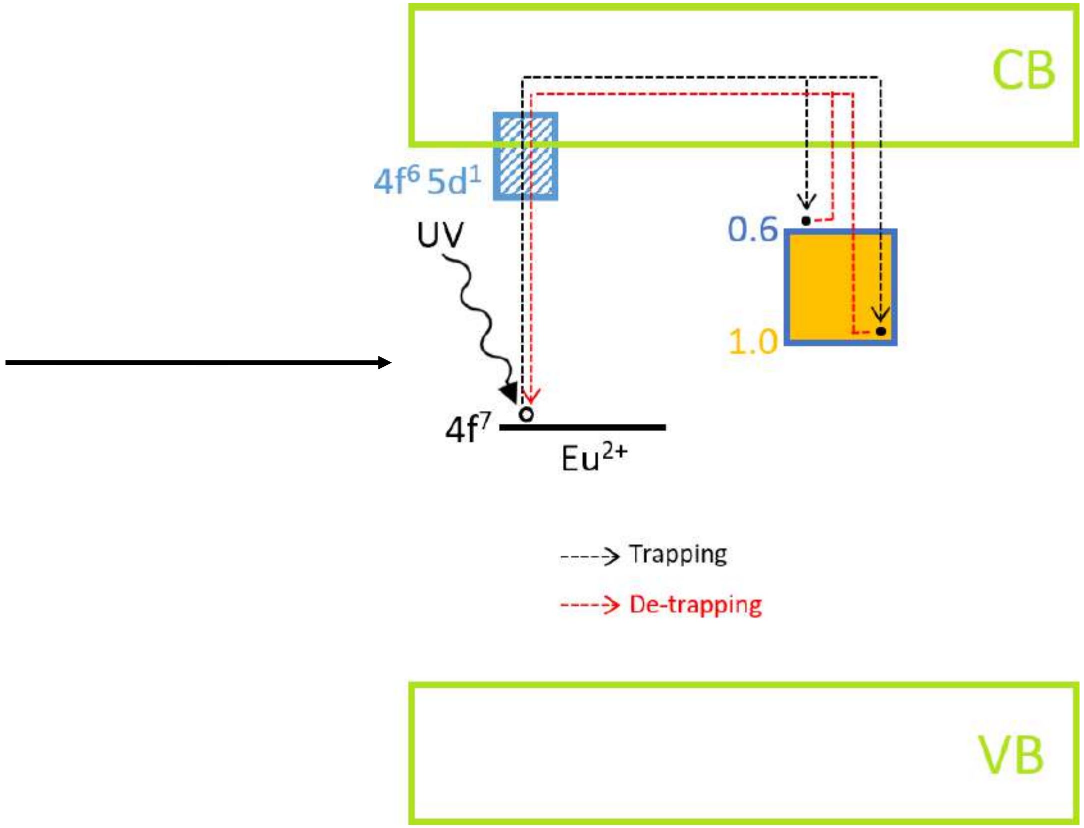
→ The **study** of the **luminescence decay** (up to 16 h) **suggests** a continuous **distribution** of **energy levels**



Mechanisms

Luminescence





Composition-dependent luminescence and mechanoluminescence powdered (crystals)

Mechanisms

Mechanoluminescence

Large trap distribution from ≥ **0.6** to ≥ **1.0 eV**

It is believed that **mechanical stress** induces a **change** of the **trap depths**

Step 1: **mechanical stress** ↗

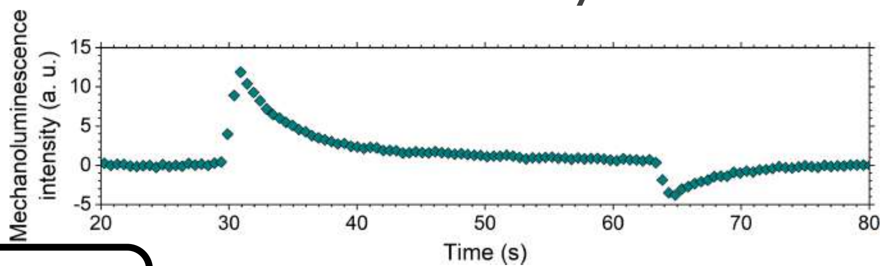
- The **trap depth** ↘

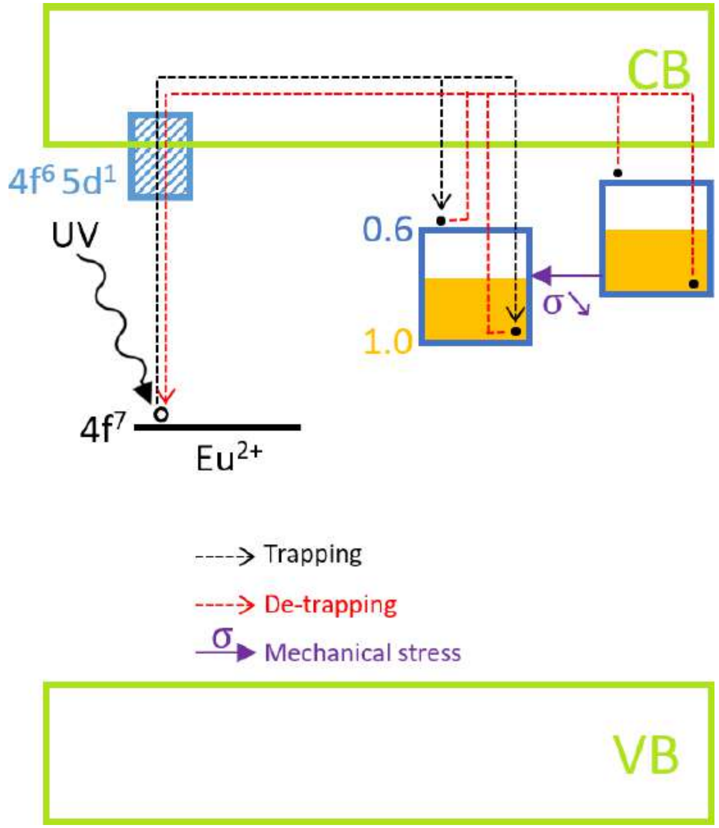
→ **Mechanoluminescence intensity** ↗

Step 2: **mechanical stress** ↘

- The **trap depth returns** to its **initial state** but with ↘ **electrons**

→ **Mechanoluminescence intensity** ↘





Composition-dependent luminescence and mechanoluminescence powdered (crystals)

Mechanisms

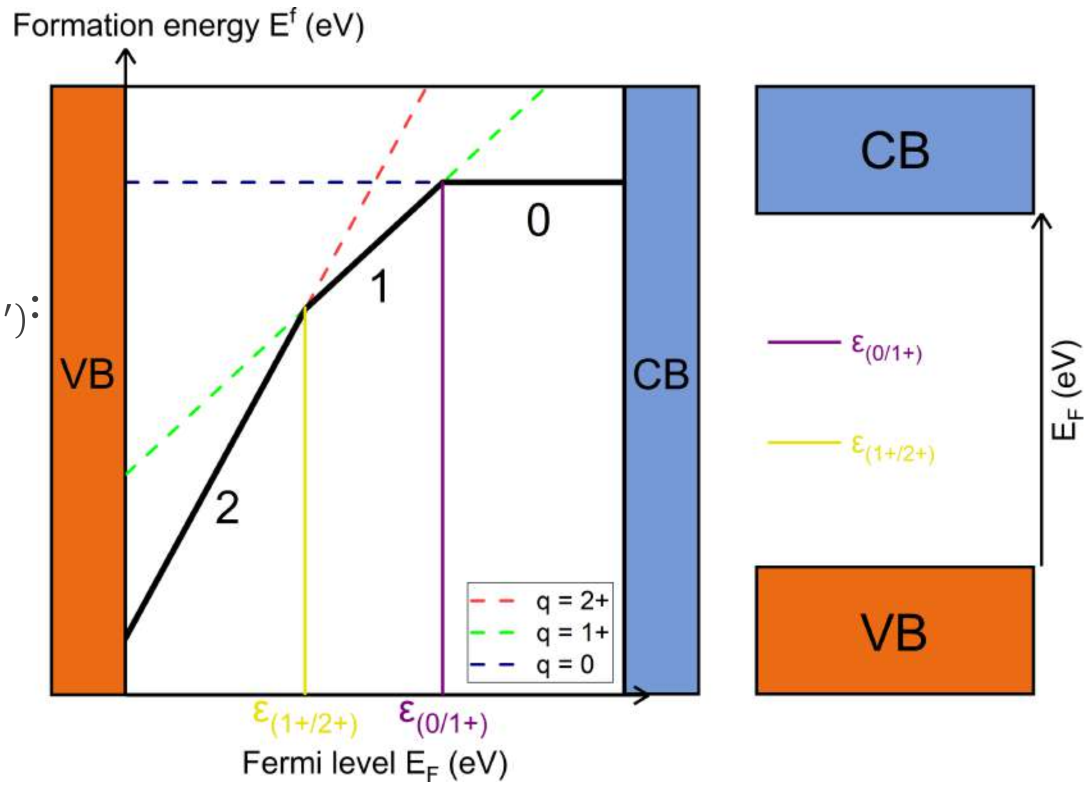
Nature of the point defects

***DFT* investigation:**

- **Calculate formation energy** of various **defects** with different **effective charges q**
- **Oxygen vacancy** with **2 trapped electrons: q = 0**
- **Oxygen vacancy** with **0 trapped electrons: q = 2+**
- We **calculate thermodynamic transition levels** $\varepsilon_{(q/q')}$:

$$\varepsilon_{(q/q')} = \frac{E^f(D^q; E_F = 0) - E^f\left(D^{q'}; E_F = 0\right)}{q' - q}$$

→ **Transition** of an **effective charge q to q'**



Composition-dependent luminescence and mechanoluminescence powdered (crystals)

Mechanisms

Nature of the point defects

Review of several potential **point defects:**

- **Cationic** and **anionic vacancies: Ba^{2+}, Si^{4+}, O^{2-}**
- **Complex point defects: substitution, adjacent vacancies**

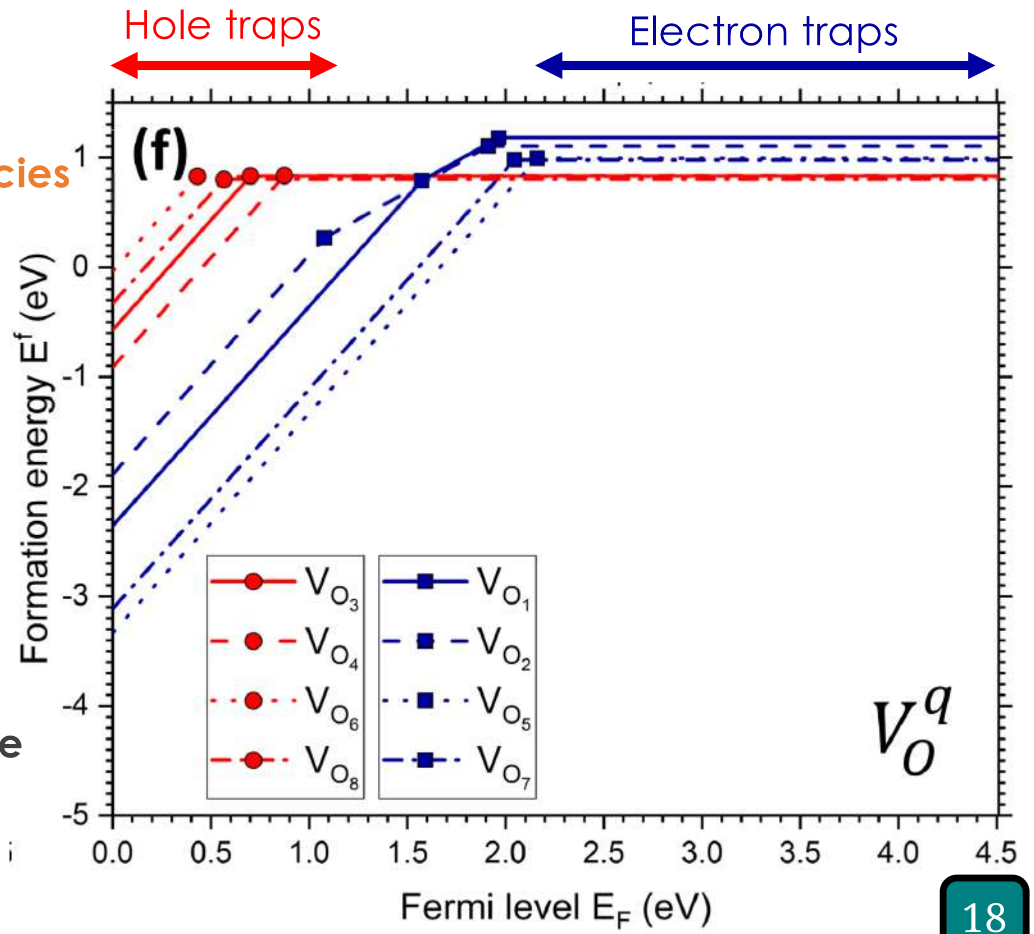
We discarded:

- **Large formation energies**
- **Too deep/shallow energy levels**

→ **Oxygen vacancies act as hole traps**

→ **Several energy levels distributed from 0.4 to 1.1 eV**

→ This hole-trapping **mechanism for the $Ba_4Si_6O_{16}$ silicate** was **already observed in a-SiO_2** (Si-Si bond breaking)



Composition-dependent luminescence and mechanoluminescence powdered (crystals)

Stress-dependent mechanoluminescence (bulk glass-ceramic)

Elaboration

Stress-dependent mechanoluminescence

Elaboration of the glass-ceramic

Europium reduction rate

To **obtain** a **bulk glass-ceramic:**

→ **Start** from an **oxynitride glass**

Nitrogen has a **strong incidence** on:

- **Mechanical, optical** and **electrical properties**

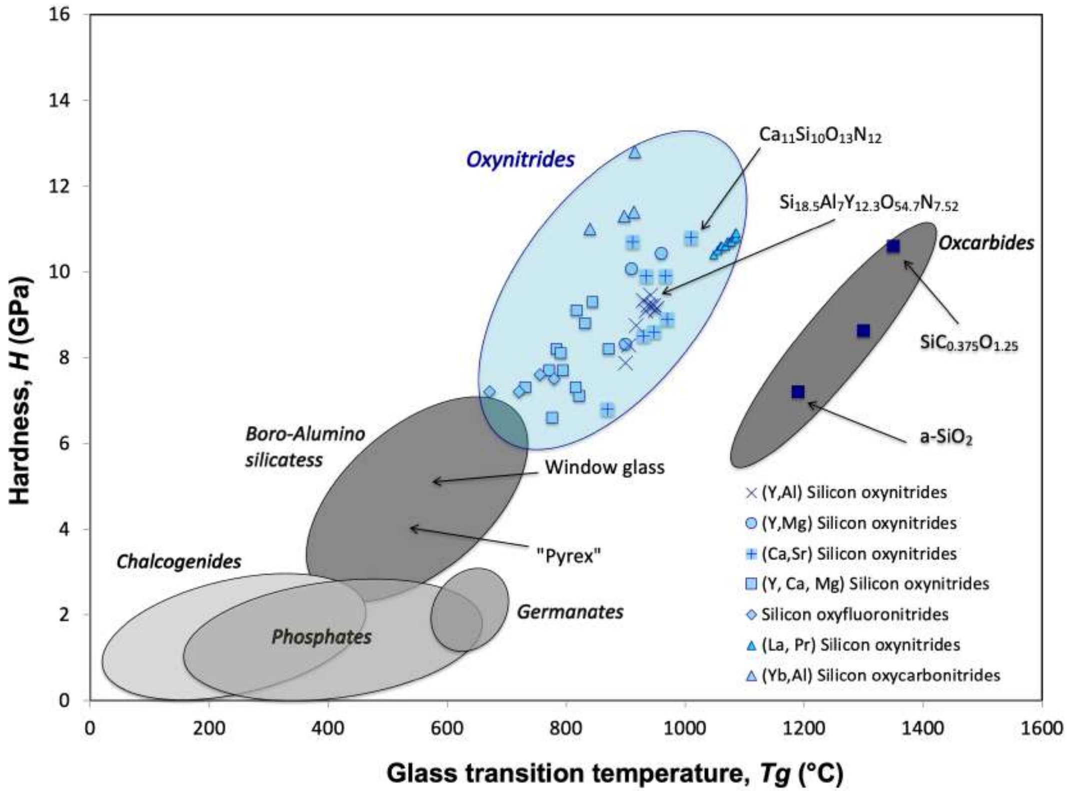
Purpose of **oxynitride glasses** in this study:

- We **need** Eu^{2+} to **observe mechanoluminescence**
- But **mostly** Eu^{3+} in **oxide glasses**

Si_3N_4 is a **reducing agent:**

$$Si_3N_4 + 6\ Eu_2O_3 \rightarrow 3\ SiO_2 + 12\ EuO + 2\ N_2$$

→ **Control** Eu^{2+} **content through** Si_3N_4 **addition**



Stress-dependent mechanoluminescence (bulk glass-ceramic)

[3]Duval A, Houizot P, Rouxel T. Review: Elaboration, Structure, and Mechanical Properties of Oxynitride Glasses. J Am Ceram Soc. 2022;106(3):1611–1637. https://doi.org/10.1111/jace.18824

Elaboration of the glass-ceramic

Europium reduction rate

To **quantify** both **Eu^{2+}** and **Eu^{3+}:**

→ **Mössbauer spectroscopy**

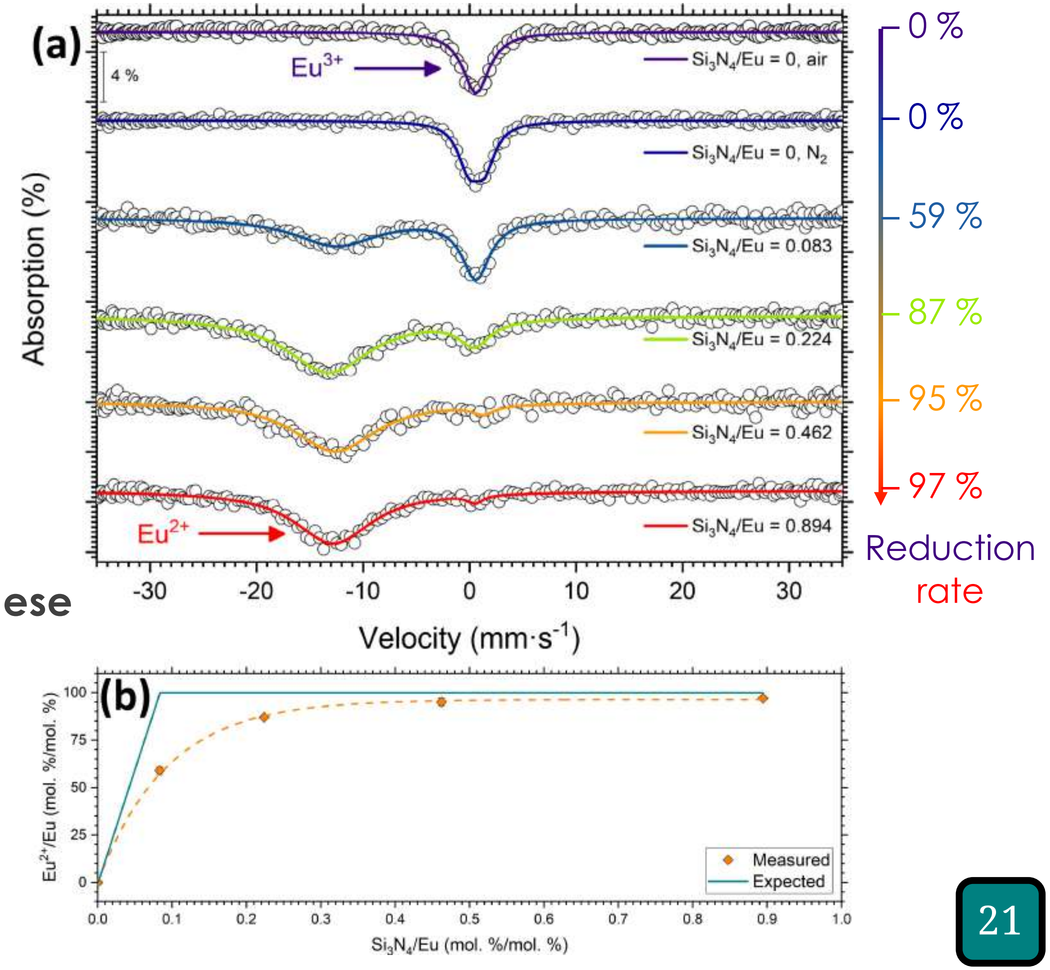
Si_3N_4 over-stoichiometry (~ 2.5 at. % N) to:

- **Reduce > 95 %** of **Eu^{3+} into Eu^{2+}**
- **Free** the **melt** of **N_2 bubbles:**

$$Si_3N_4 + 6\ Eu_2O_3 \rightarrow 3\ SiO_2 + 12\ EuO + 2\ N_2$$

→ So as to **obtain homogeneous bulk specimens**

→ And finally **perform diverse mechanical testing** on **these**



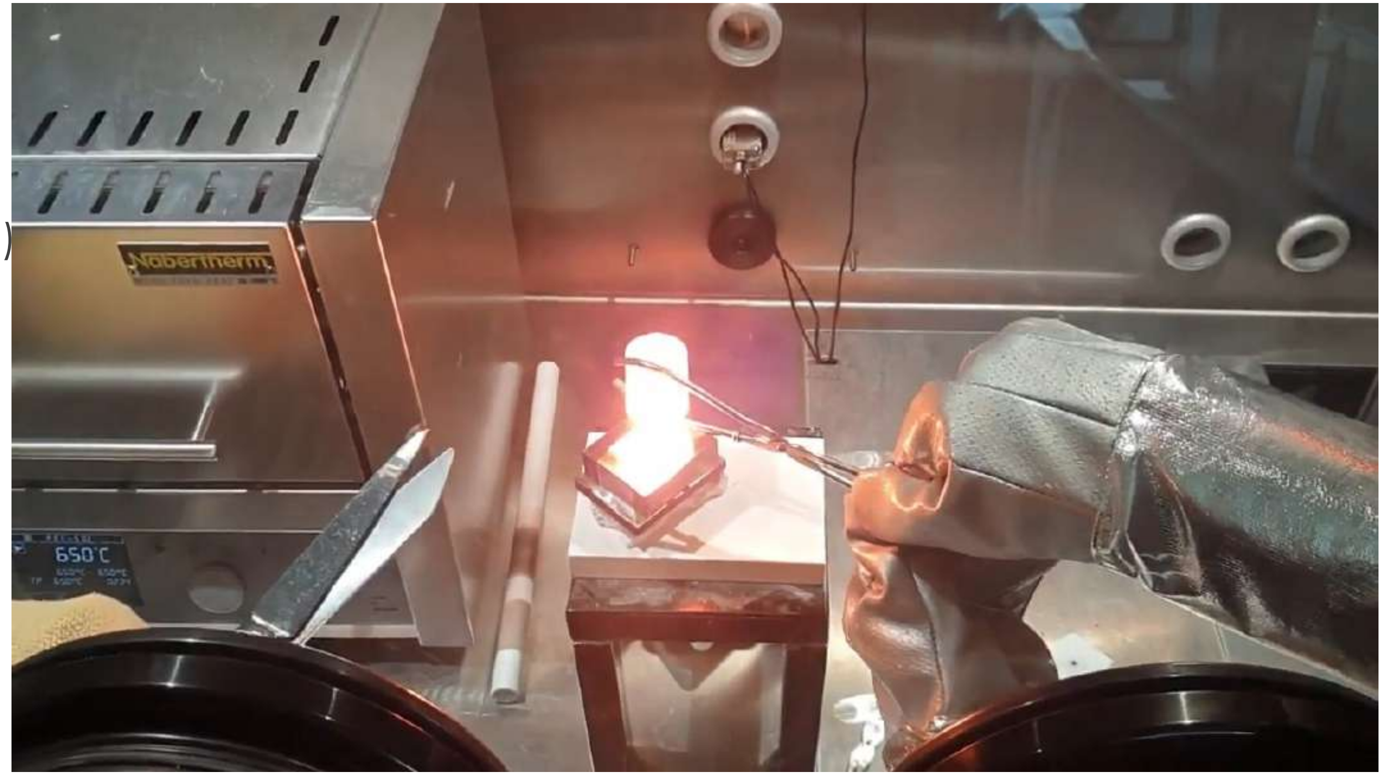
Elaboration of the glass-ceramic

Melt-quench synthesis of the base glass

Synthesis of the **base glass:** 36.7 BaO – 57.6 SiO_2 – 1.7 Si_3N_4 – 3.0 EuO – 1.0 Ho_2O_3 (mol. %)

In a **glove box**:

- **Controlled atmosphere** (N_2)
- **High temperature furnace** (1800 °C)
- **Annealing furnace**
- **Automated crucible uploader**



https://www.youtube.com/watch?v=bwIJ2q4Vw0M&

Elaboration of the glass-ceramic

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In a **glove box**:

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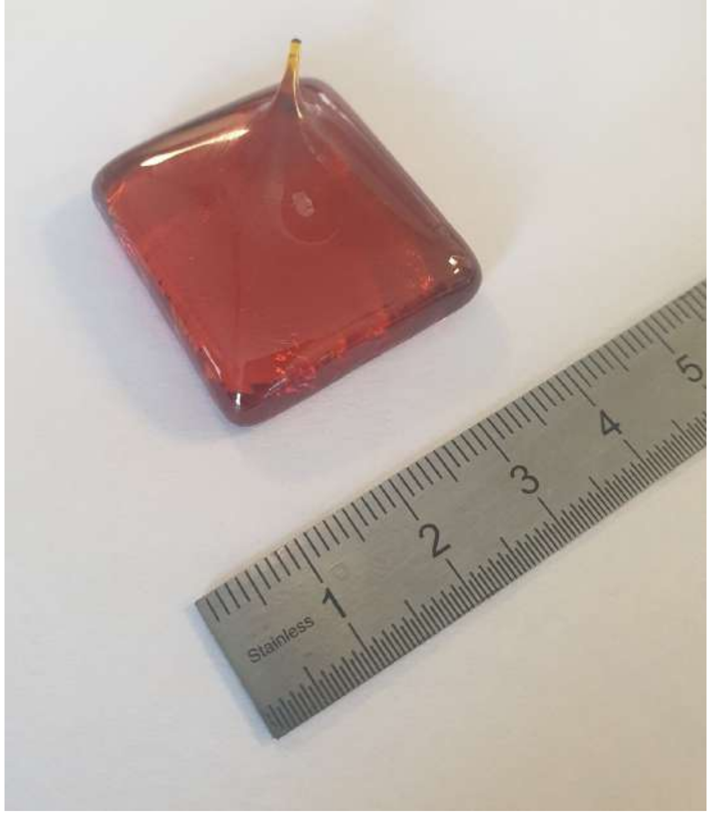
→ **~ 40 g** per **batch**



Elaboration of the glass-ceramic

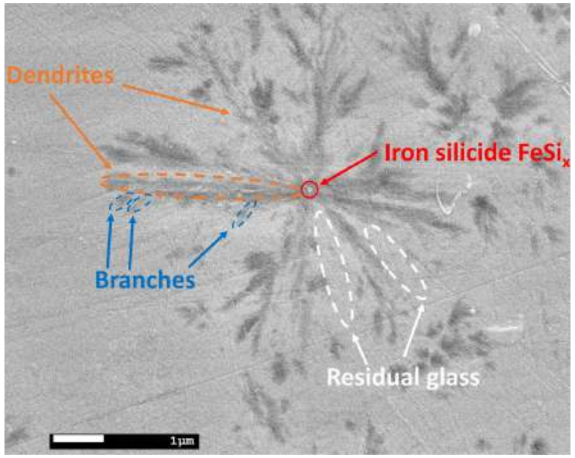
Parent glass crystallization

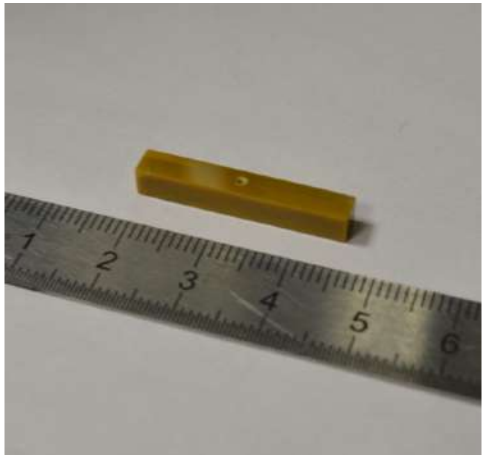
During oxynitride glasses synthesis:

- ○ **Si_3N_4 decomposes partly** into **Si** + **N_2**
- → **Formation** of **Si** and **$FeSi_x$ particles** (10 nm – 10 µm)
- → **Homogeneously distributed**

These **act** as **crystallization points:**

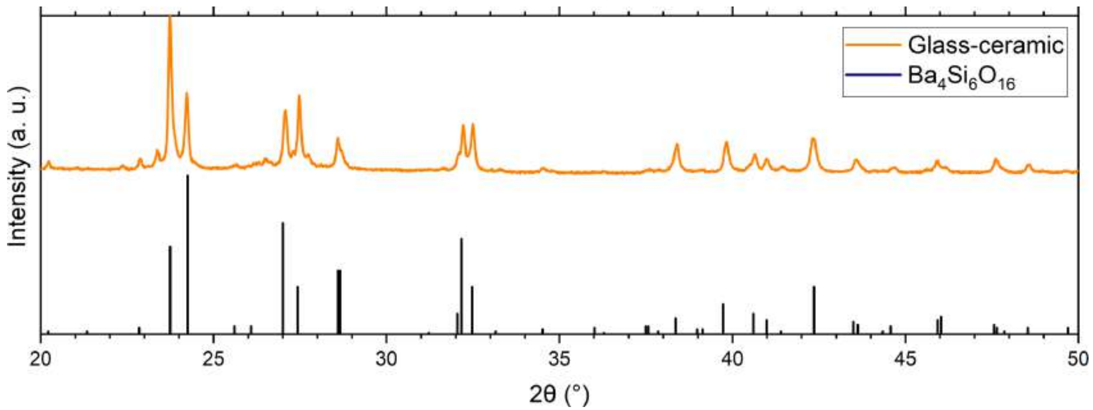
- → A **homogeneous** and **volumetric crystallization**





Crystallization of the **glass: 10 minutes** at **1200 °C**

- ○ **Congruent crystallization ($Ba_4Si_6O_{16}$)**
- ○ **Large crystallization rate** (56 ± 10 %)
- ○ **cm³ large specimens, easy** to **shape**
- → **Mechanical test** on **bulk specimens**



Stress-dependent mechanoluminescence (bulk glass-ceramic)

[4]Duval A, Houizot P, Rocquefelte X, Rouxel T. Mechanoluminescence of (Eu, Ho)-Doped Oxynitride Glass-Ceramics from the BaO-SiO_2-Si_3N_4 Chemical System. *Appl Phys Lett*. 2023;123(1):011905. https://doi.org/10.1063/5.0149749

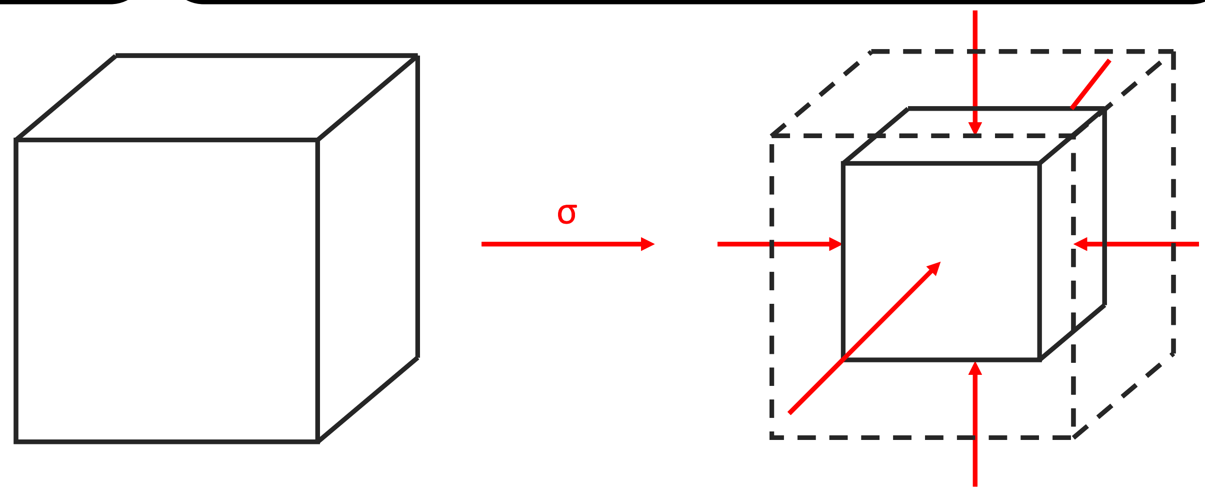
Stress-dependent mechanoluminescence

Introduction

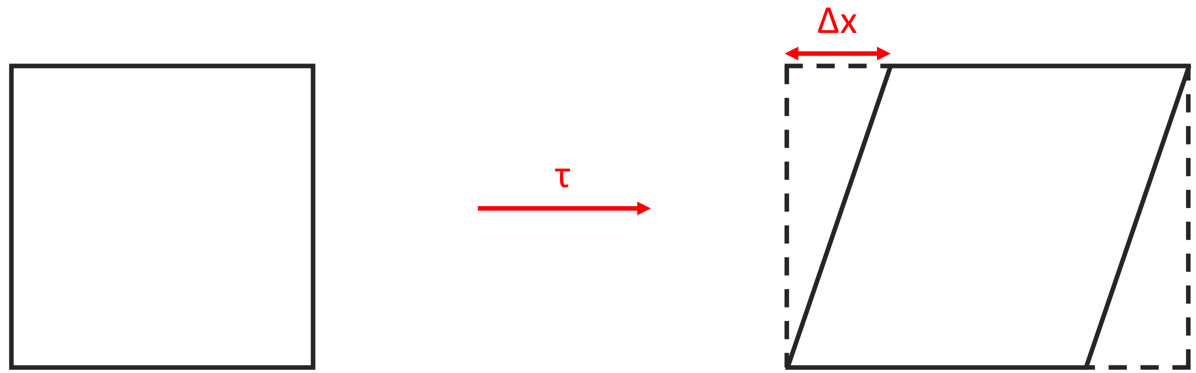
- **Investigation** of **mechanoluminescence** through **various mechanical tests**

Hydrostatic stress: volume change

- **Compressive stress** (volume ↘)
- **Tensile stress** (volume ↗)



Shear stress: shape change



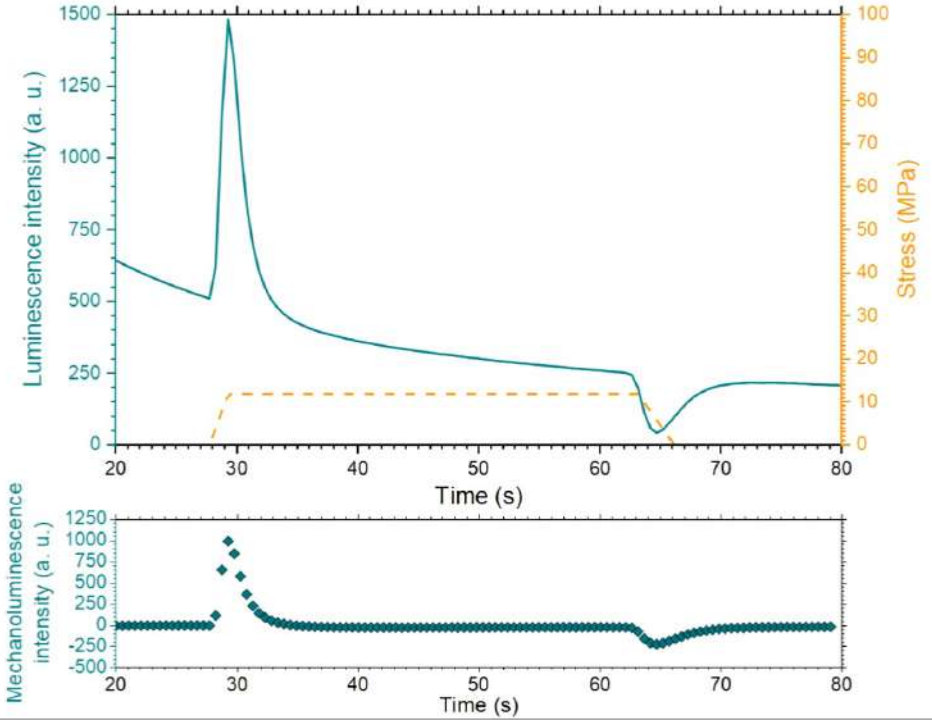
Stress-dependent mechanoluminescence

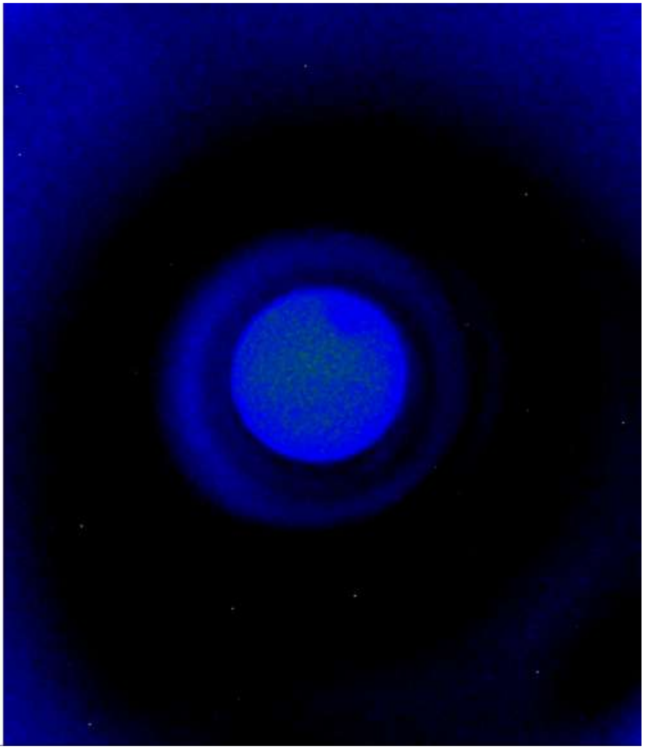
Isostatic pressure

Isostatic pressure test: hydrostatic stress

Gas introduced in a **gas tank**

- **Control** of **stress** σ
- **Control** of **stress rate** $\dot{\sigma}$



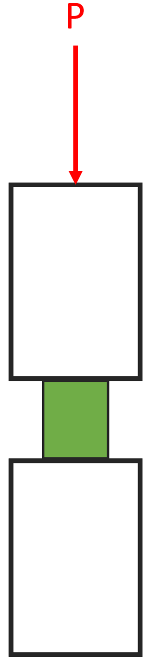


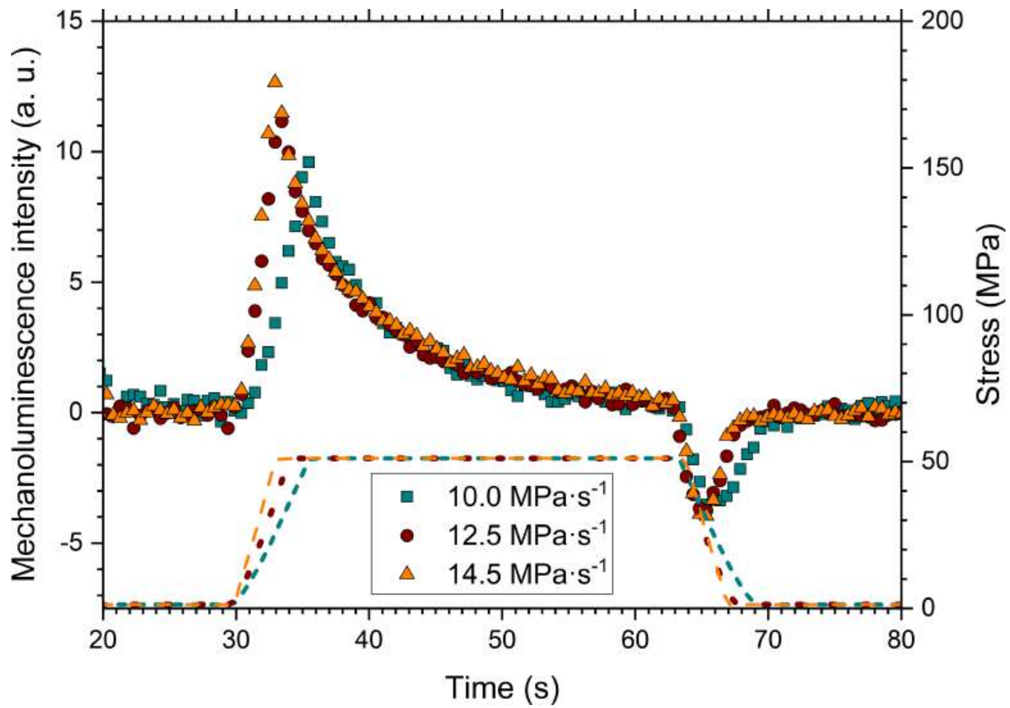
Mechanoluminescence intensity: ~ 1000 a. u.

Uniaxial compression

Uniaxial compression test: hydrostatic stress + shear stress

- With **similar σ** and $\dot{\sigma}$ as **isostatic pressure** tests: **mechanoluminescence intensity ↘ (100 times !)**





Mechanoluminescence intensity: ~ 10 a. u.

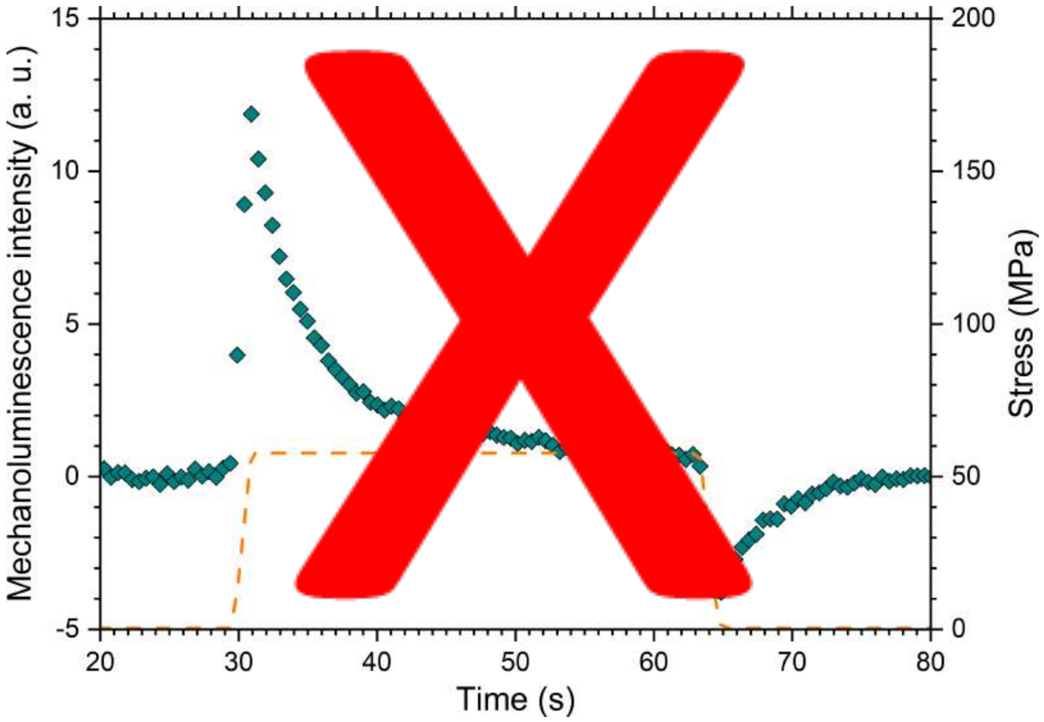
Stress-dependent mechanoluminescence

Torsion

Torsion test: shear stress

- **Up to τ = 40 MPa** and **$\dot{\tau}$ = 40 MPa · s^{-1}**

→ **No mechanoluminescence**
(observed with **σ = 50 MPa** and **$\dot{\sigma}$ = 5 MPa · s^{-1})**

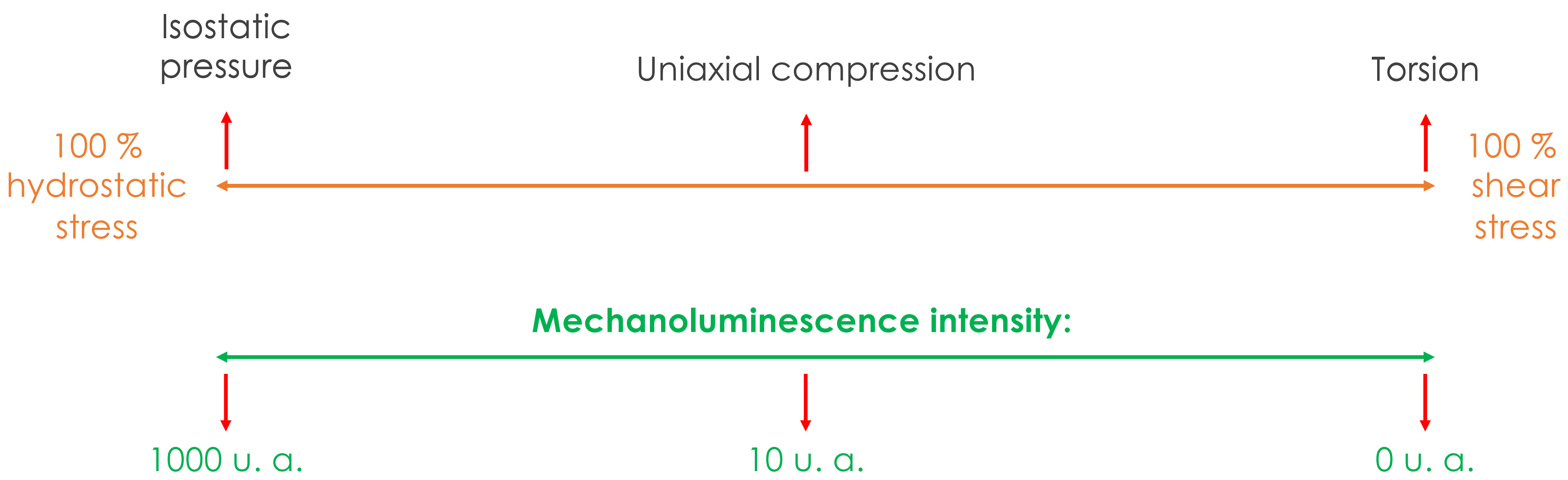


Mechanoluminescence intensity: 0 a. u.

Summary

Summary:

- **Identical mechanoluminescence behavior whatever** the **mechanical test**
- But **change** in **mechanoluminescence intensity**

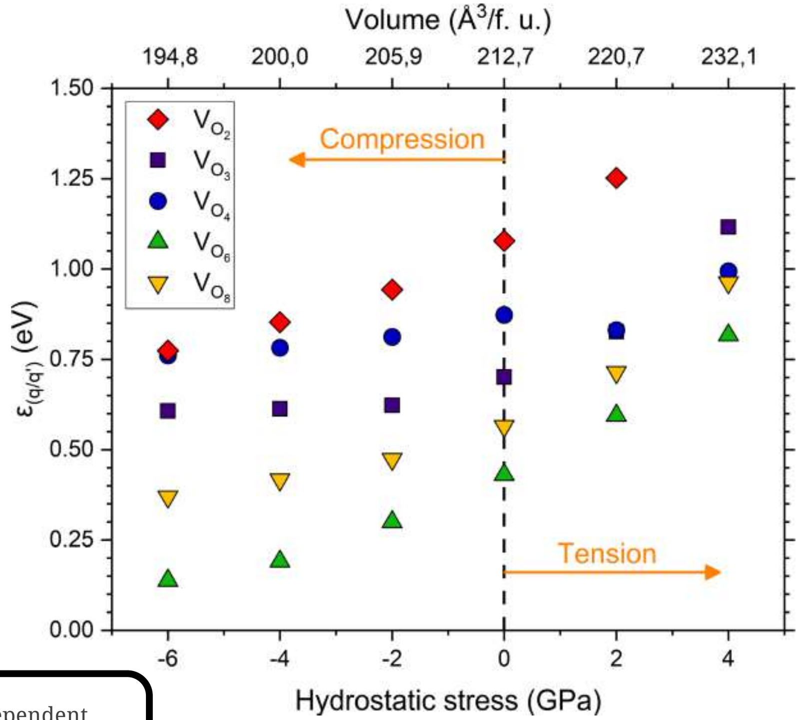


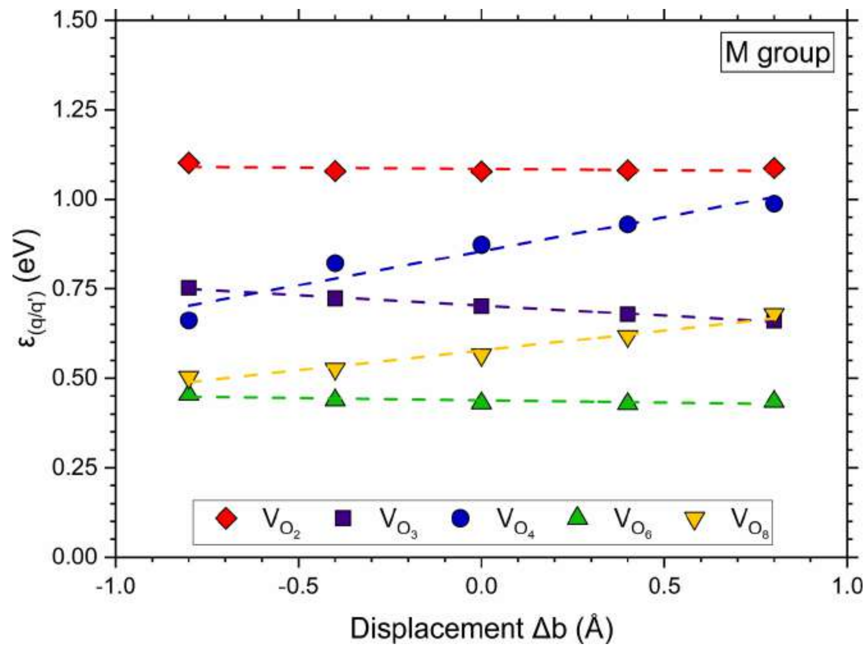
Stress-dependent mechanoluminescence

Theoretical investigation

We considered the **5 identified energy levels** (oxygen vacancies) and **applied various stresses to $Ba_4Si_6O_{16}$:**

- **Hydrostatic stresses | The trap depth** of every **energy levels ↘ with ↗ mechanical stress**
- **Shear stresses | Multiple trends: trap depth either ↗, ↘, or remains unchanged. ↘ changes** in **compared** to **hydrostatic stress (with similar stresses)**





→ **Agreement with the experiment**

Stress-dependent mechanoluminescence

Theoretical investigation

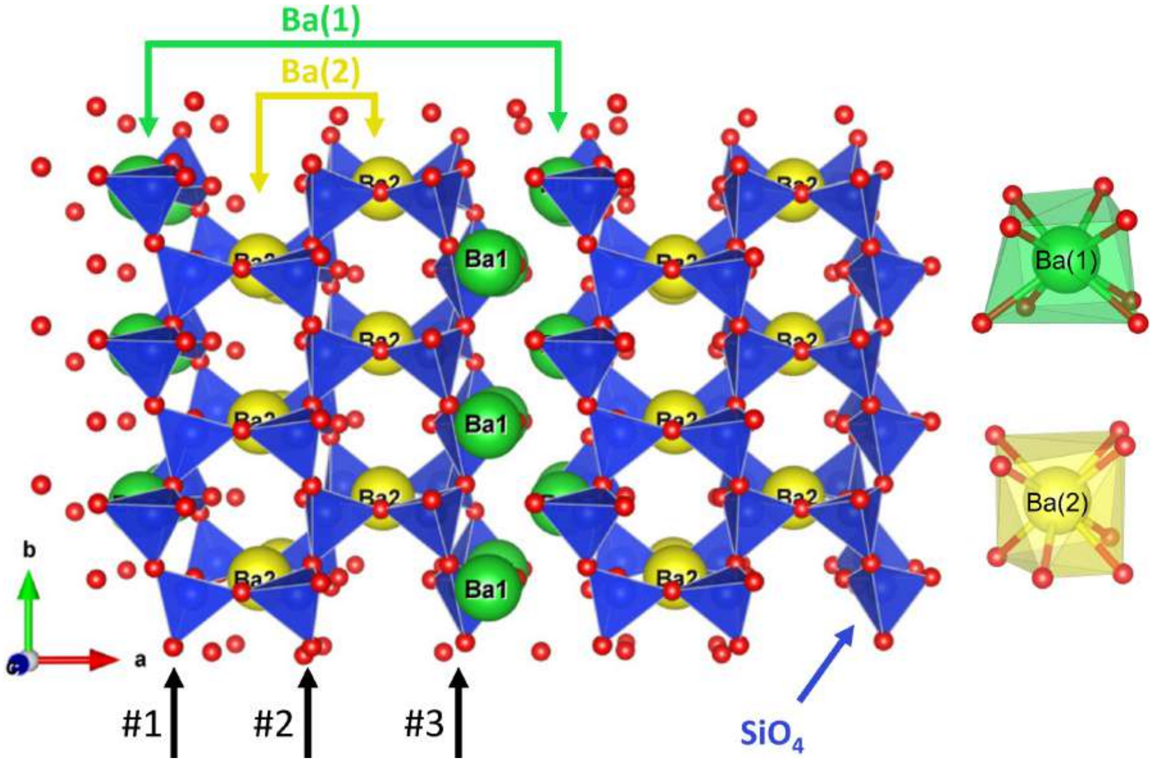
$Ba_4Si_6O_{16}$ is a **2D structure:**

- **Silicate chains** in **between BaO_8 sheets**
- **Point defects associated** with **luminescence: oxygen vacancies**

(a, b) plane along b: gliding of **silicate chains**

→ **Slight changes** of the **oxygen environment**

→ **Small changes** in **trap depth**



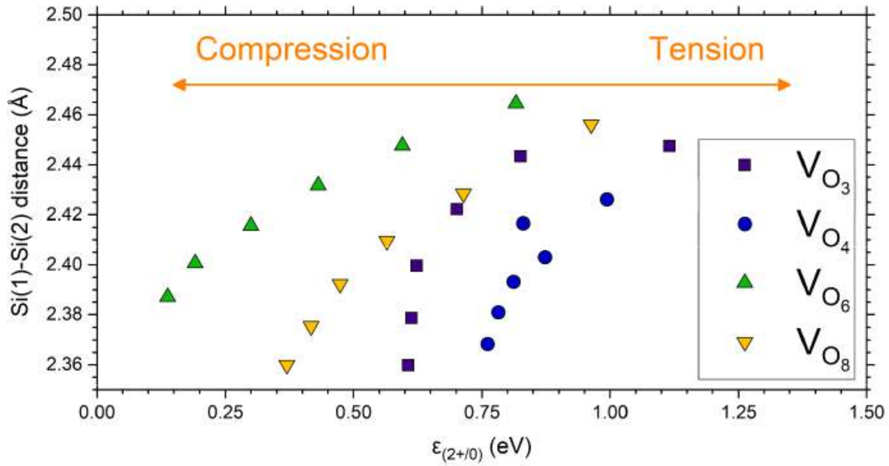
Stress-dependent mechanoluminescence

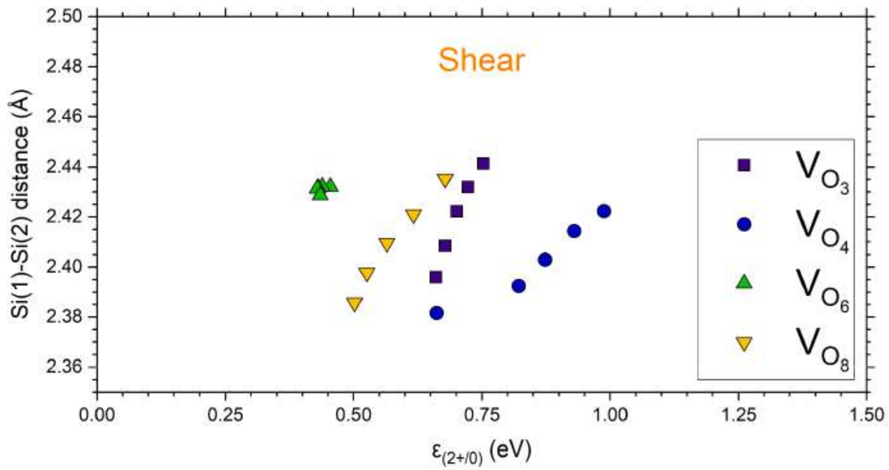
Theoretical investigation

Plot of **Si-Si distance against** the **trap depth:**

- **Mechanoluminescence** results from **changes** in the **trap depth** upon **mechanical loading**
- These **changes** stem from the **structural reorganization** of **point defects** as a **response** to the said **stress**
- **Si-Si distance ↘: energy level depth ↘**
- **Oxygen vacancies** are **more sensitive** to **hydrostatic stress** than **shear stress (even** for **similar Si-Si distances)**

→ **Mechanoluminescence intensity** ↗ when **hydrostatic stress** ↗





Summary

Conclusions

Perspectives

Conclusions

Study of the **composition-dependent luminescence** and **mechanoluminescence** of **$Ba_4Si_6O_{16}$:Eu^{2+}, *RE***:

- **Role** of $\boldsymbol{E}$ and $\boldsymbol{n_0}$
- **Role** of **oxygen vacancies** in the **luminescence mechanism**

Elaboration of **bulk mechanoluminescent glass-ceramics**:

- **Control** of the **europium reduction rate**
- **Control** of the **crystallization rate**

Study of the **stress-dependent mechanoluminescence** of **$Ba_4Si_6O_{16}$:Eu^{2+}, Ho^{3+}**:

- **Experimental** and **theoretical study**
- **Separate role** of **hydrostatic stress** and **shear stress**

Proposition of a **mechanoluminescence mechanism**:

- **Changes** in **trap depth** stem solely from the **structural reorganization** of the **point defects** as a **response** to the **mechanical stress**

Conclusions

Perspectives

Applications:

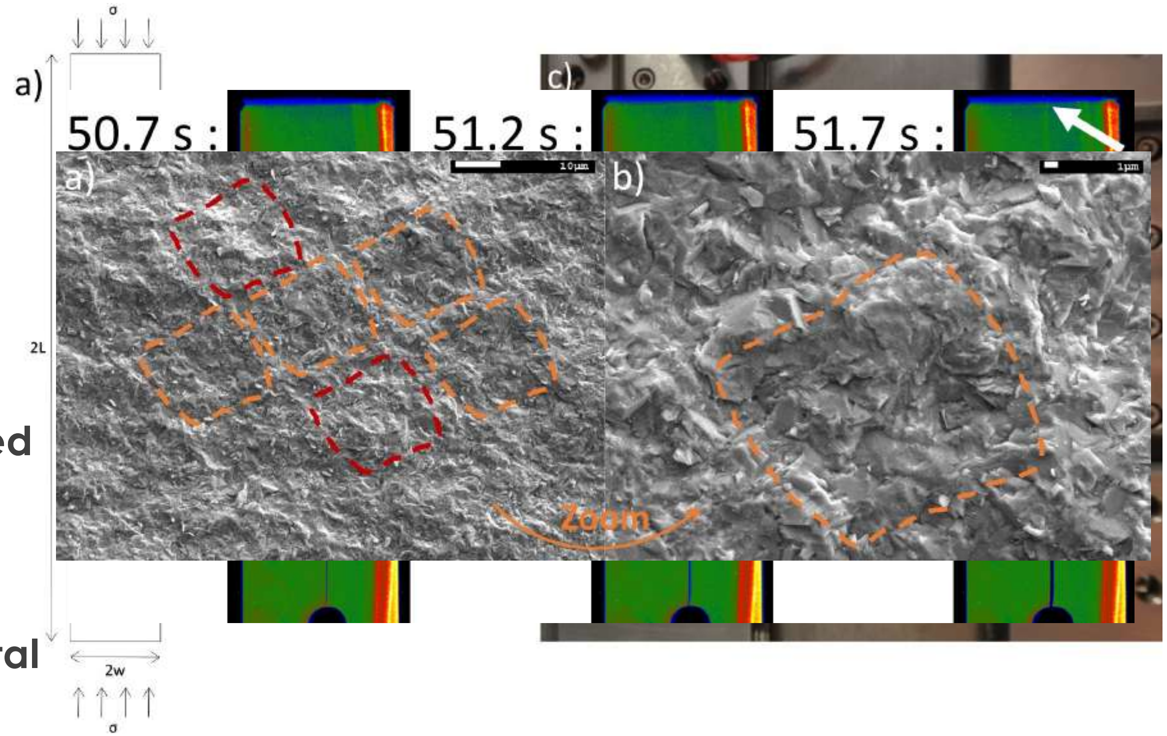
- **Stress sensing**
- **Energy storage**
- **Light sources responsive** to **mechanical stress**

Study of **mechanical phenomenon** through **light emission (crack propagation):**

- **No fracto-mechanoluminescence** was **observed**
- The **crack front avoids** the **crystals** in the **path**

→ **Crystallization rate** ↗

→ **Change** to another **mechanoluminescent crystal (start** the **study over again)**



Thank you !