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1 Mechanoluminescence of (Eu, Ho)-doped oxynitride glass-ceramics from 2 the BaO-SiO₂-Si₃N₄ chemical system

3

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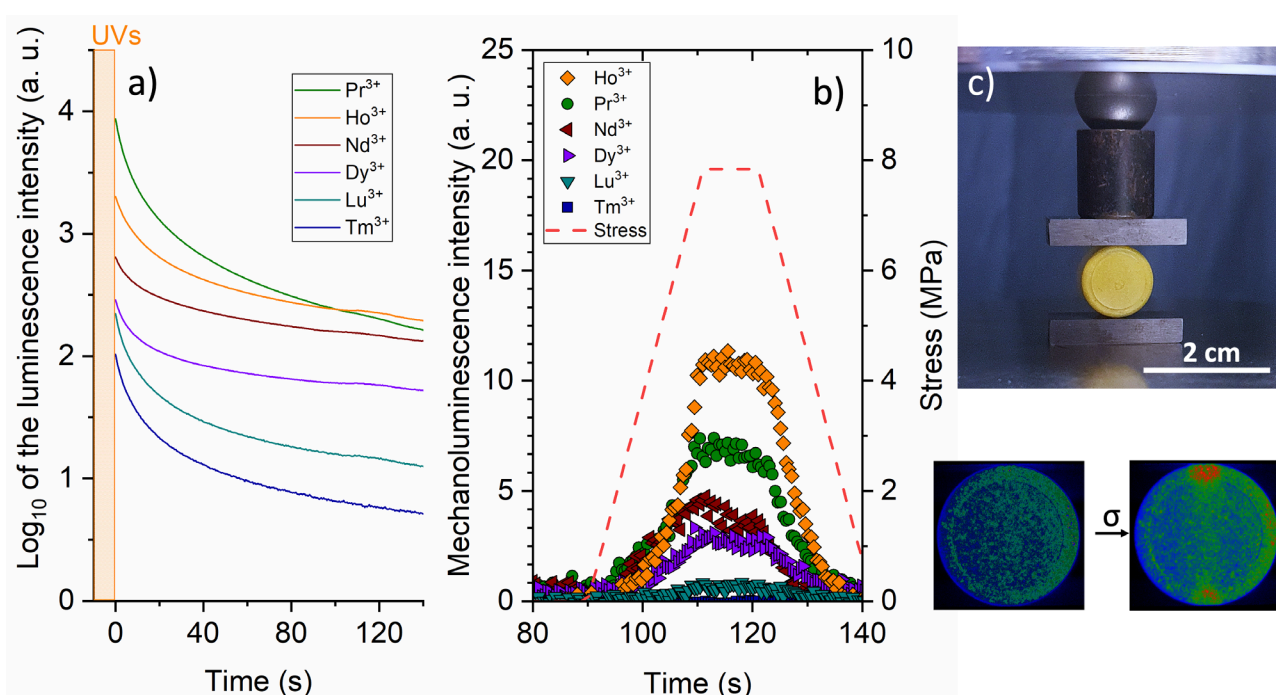
10 **Abstract** — Mechanoluminescence is observed in oxynitride glass-ceramics from the BaO-SiO₂-
11 Si₃N₄ chemical system, doped with Eu and Ho. Light emission was investigated by means of uniaxial
12 compression experiments on disks and parallelepipedic bars with constant loading rates ranging from
13 0.3 to 300 MPa.s⁻¹ up to about 500 MPa. In agreement with previous reports on SrAl₂O₄-based
14 materials^{1,2}, the mechanoluminescence intensity is found proportional to the mechanical power.
15 Nevertheless, in contrast with SrAl₂O₄, no gain in the intensity is observed at the onset of the
16 unloading stage, but a drop of the photoluminescence intensity during unloading. This stems from
17 different electron trapping populations and associated energy levels for the Ba₄Si₆O₁₆ phase (the
18 dominant crystallized phase in the present glass-ceramics), which are discussed in the light of *DFT*
19 calculations.

20 Various materials, organic³ and inorganic⁴, are known to emit light when submitted to a
21 mechanical loading. For example, this is the case of Eu-doped SrAl₂O₄ whose luminescence and
22 mechanoluminescence properties were studied in the 1990s^{5,6}. This phenomenon is referred to as
23 mechanoluminescence, and includes elastico-mechanoluminescence, plastico-
24 mechanoluminescence, and fracto-mechanoluminescence⁷. In general, mechanoluminescence is
25 observed by grinding or compressing a composite material containing the active crystallized phase
26 after exposure to *UV* light^{1,2,6}. Mechanoluminescence was recently reported in a germanate-based
27 glass-ceramic doped with Cr³⁺ by means of ball-dropping experiments performed on powder⁸, and in
28 Pr³⁺-doped borate-based glass-ceramic/epoxy composites using compression experiments⁹. The
29 mechanoluminescence of Eu²⁺-doped ceramics such as BaSi₂O₂N₂¹⁰ or BaAl₂Si₂O₈¹¹ has been known
30 for about three decades. Several studies were dedicated to the luminescent properties of
31 Ba₄Si₆O₁₆:Eu²⁺, *RE* (*RE* = rare-earth) ceramics^{12,13,14,15}. In these crystalline phases, *RE* substitutes for
32 Ba thanks to close ionic radii¹⁶, so as to keep the (Ba+Eu+*RE*)/Si ratio constant and equal to 2/3.

33 Interest in the $\text{Ba}_4\text{Si}_6\text{O}_{16}$ composition also lies in its ability to vitrify and further result in a glass-
34 ceramic through a congruent crystallization of the parent glass¹⁷. In the present study, we show that
35 the $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}, \text{Ho}^{3+}$ crystal, while being centrosymmetric, exhibits mechanoluminescence.

36 In this work, a barium-silicate glass was doped with a mixture of (Eu, RE) elements, and some
37 nitrogen is further incorporated to control the oxidation state of europium. The doped-glass was
38 further crystallized by heat-treatment and the mechanoluminescence intensity was then studied by
39 means of compressive experiments on centimeter size bulk specimens. The RE element was chosen
40 so as to optimize the mechanoluminescence intensity of the main crystallized phase, namely
41 $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}, \text{RE}$. In order to reach this objective, $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}, \text{RE}$ containing 3 cat. % Eu and
42 2 cat. % RE (RE = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu) ceramics were
43 first synthesized, starting from dried BaCO_3 (Sigma-Aldrich, 99%), Gd_2O_3 , Lu_2O_3 , Dy_2O_3 , Sc_2O_3 ,
44 Eu_2O_3 (Sigma-Aldrich, 99.9%), SiO_2 (Sigma-Aldrich, 99.5%), Pr_2O_3 and Sm_2O_3 (Fischer 99.9 %),
45 Tb_4O_7 (Fischer 99.998 %), Tm_2O_3 (Alfa Aesar 99.9 %), Yb_2O_3 , La_2O_3 , CeO_2 , Nd_2O_3 (Rhône-Poulenc
46 99.99 %), Y_2O_3 (Acros 99.99 %), and Ho_2O_3 Er_2O_3 (Rhône-Poulenc 99.999%). These RE
47 concentrations were selected so as to optimize the intensity of the mechanoluminescence.
48 Stoichiometric amounts were weighted and hand-grounded during 15 minutes with a small amount
49 of ethanol in an agate mortar, and then fired 6 h at 1300 °C in a $\text{N}_2:\text{H}_2 = 94:6$ reducing atmosphere in
50 order to favor europium in the 2+ oxidation state. The obtained ceramic powders were added to an
51 epoxy resin with a final ceramic content of 20 wt. % (≈ 6 vol. %), and ceramic/epoxy composites
52 disks, 11.5 mm diameter and 6 mm thick, were shaped. Then, an oxynitride glass with a $36.7\text{BaO}-$
53 $57.6\text{SiO}_2-1.7\text{Si}_3\text{N}_4-3.0 \text{EuO}-1.0\text{Ho}_2\text{O}_3$ molar composition was synthesized, starting from dried
54 precursors. The oxide powders were mixed together and dried at 1200 °C for 5 h. The resulting
55 mixture (about 40 g) was grounded with a Si_3N_4 powder (Sigma-Aldrich, 99.9%) in an agate mortar.
56 The mixture was then heated in a BN crucible placed inside an atmosphere-controlled apparatus
57 containing both furnaces for melting and annealing, with a nitrogen pressure of 1 atm (see ref.¹⁸ for
58 details). The powder mixture was melted at 1600 °C and further annealed at T_g-50 °C ($T_g = 737$ °C)
59 for 3 h. Note that the glass was crushed and re-melted thrice to get a homogeneous glass batch. Glass-
60 ceramics were obtained by heat-treating the glass in a nitrogen atmosphere at temperatures between
61 857 and 1200 °C, as is discussed further in relation to the optical properties. The X-ray diffraction
62 (XRD) patterns were recorded using a PANalytical X'pert Pro diffractometer using Cu-K α radiation
63 (1.5418 Å). Mechanical experiments were performed on the ceramic/epoxy composite disks
64 (diametral compression test) and on 4x4x5 mm³ parallelepipedic specimens, mirror-polished (1 μm
65 diamond suspension), for the glass-ceramics, using a Shimadzu-AGS-X testing machine equipped
66 with a 10 kN load cell and a SiC pusher. In the case of diametral compression, the maximum tensile

67 stress is located at the center of the composite and is expressed as $\sigma = \frac{2P}{\pi dh}$, where P is the load, d is
68 the diameter and h is the thickness of the cylindrical composites¹⁹. Although the “elastic” stress at -
69 and immediately adjacent to - the contact areas with the SiC plates is larger (see the red dots at the
70 bottom right of Fig. 1c), the stress gradient is too large and the contact area is too small to attribute
71 the light emitted in this region to a particular stress value. Nevertheless, this requires additional
72 investigations because it is not excluded that the compressive and tensile stresses lead to different
73 phenomena. The luminescence intensity was measured using a Zyla 5.5 sCMOS Andor Technology
74 high sensitivity camera. Samples were irradiated for 2 minutes with a 365 nm *UV* light prior to each
75 measurement. The Density Functional Theory (*DFT*) calculations on the Ba₄Si₆O₁₆ crystal ($a =$
76 $12,477 \text{ \AA}$, $b = 4,685 \text{ \AA}$, $c = 13,944 \text{ \AA}$ and $\beta = 93.54^\circ$ ²⁰) were performed at ambient pressure using
77 the *VASP* code (Vienna ab-initio Simulation Package; www.vasp.at)^{21 22}. This code allows to
78 determine the ground state properties of a given compound based on *DFT* calculations and is based
79 on a plane wave based Projector Augmented Wave (*PAW*) approach. The semi-local Perdew–Burke–
80 Ernzerhof (*PBE*) functional²³ on a (a,3b,c) supercell containing 156 atoms was used to identify the
81 defect energy levels responsible for the detrapping processes. The wavefunctions were expanded in
82 plane waves up to a kinetic energy cut-off of 500 eV, and the k-point sampling was chosen sufficiently
83 fine to ensure the numerical convergence of all the calculated properties. In particular, the accurate
84 calculation of the total energy for all defect models (155 atoms supercell) was carried out using a $6 \times$
85 6×6 k-point mesh. The geometry was optimized until the forces on all the atoms were less than $3 \cdot 10^{-2}$
86 eV \AA^{-1} .



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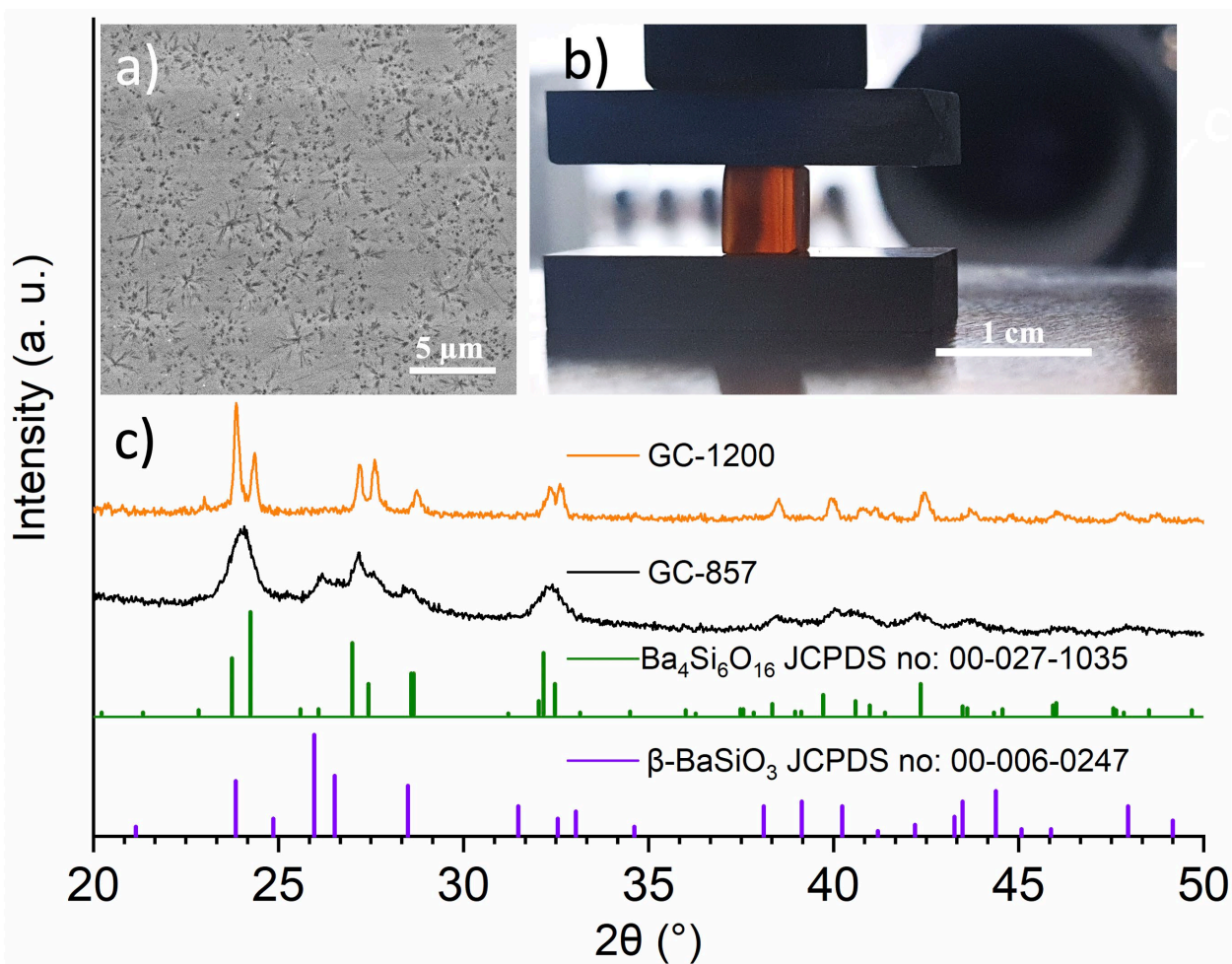
88 **FIG. 1.** a) Luminescence decay and b) mechanoluminescence of some of the synthesized
89 $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}$, RE ceramic/epoxy composites, c) photograph of the experimental setup and camera
90 photograph of the composite before and during the diametral compression test. The
91 mechanoluminescence is evidenced by a stronger luminescence. Note that for sake of clarity, curves
92 obtained on grades containing Sc, Y, La, Ce, Sm, Eu, Gd, Tb, Er, or Yb were not drawn.

93 In a first stage, the $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}$, RE ceramic/epoxy disks were irradiated with a UV light for
94 2 min and were further submitted to diametral compression experiments, 90 s later, following the
95 same experimental procedure for each grade. Results regarding the phosphorescence decay following
96 the irradiation show that Pr, Ho and Nd are the three best candidates in terms of luminescence
97 intensity (Fig. 1a). However, the mechanoluminescence signal observed after 90 s as a mechanical
98 loading cycle is applied gives a clear advantage to Ho co-doping (Fig. 1b). The spatial distribution of
99 the mechanoluminescence signal is consistent with the stress field associated with a diametral
100 compression specimen, i.e. with a maximum tensile stress in the center of the disk and maximum
101 compressive stresses beneath the area of contact with the upper and lower pistons (Fig. 1c). In regard
102 of these preliminary investigations, a barium-silicate glass containing europium and holmium with a
103 $(\text{Ba}+\text{Eu}+\text{Ho})/\text{Si}$ ratio equal to 2/3, as in the $\text{Ba}_4\text{Si}_6\text{O}_{16}$ crystal, was synthesized in a second stage.
104 Nevertheless, in order to promote Eu in the 2+ oxidation state, some nitrogen is incorporated using
105 Si_3N_4 as a starting powder. This results in a more durable, harder and stiffer glass with the following
106 composition: 36.7 BaO-57.6 SiO_2 -1.7 Si_3N_4 -3.0 EuO-1.0 Ho_2O_3 , or $\text{Ba}_{13.6}\text{Si}_{23.3}\text{Eu}_{1.12}\text{Ho}_{0.75}\text{O}_{58.7}\text{N}_{2.53}$.
107 The increase of the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio with the nitrogen content was already observed by Ramesh et al.²⁴,
108 and confirmed both by LECO measurements and by measuring the emission spectra of the glass,
109 where the characteristic broadband emission of Eu^{2+} was outlined²⁵. The chemical reaction involved
110 in this process is written as



111 and is thermodynamically feasible above 1480 K^{26,27}. The obtained glass is homogeneous to the naked
112 eyes and has an amber color (Fig. 2), which is typically observed in glasses with over 0.2 at. % of
113 europium in its divalent state²⁵. A nitrogen content of 6 eq. % N is required to reach a nearly complete
114 reduction of Eu^{3+} . The nucleation and growth of crystals from an oxide-glass having the same cationic
115 composition as the presently prepared oxynitride glass was previously studied¹⁷. The density of
116 crystals, which is of the order of 10^{12} crystals·m⁻³ within a few hours, increased slightly with the
117 holding time at T_g+20 °C. In the case of silicon oxynitride glasses, the partial decomposition of silicon
118 nitride into metallic silicon (or silicides with impurities) and molecular nitrogen leads to the formation
119 of homogeneously distributed metallic Si-based nano-size particles^{28,29,25}. This situation promotes a
120 uniform crystallization process from these particles, resulting in the growth of dendrites from the

121 metallic nuclei (Fig. 2a) and in a considerably larger density of crystals (about 10^{15} crystals·m⁻³) than
122 in the parent oxide glass. Besides, a nucleation step is no more necessary as, in general, oxynitride
123 glasses appear to be self-nucleating²⁶. Nitrogen in the glass network induces i) the reduction of Eu³⁺
124 into Eu²⁺, which is of primary importance to observe the long-lasting phosphorescence and
125 mechanoluminescence of the glass-ceramics, ii) the formation of micro and nano-sized intermetallic
126 particles tremendously increasing the ease for a uniform crystallization, and iii) the improvement of
127 the corrosion resistance and the mechanical properties.



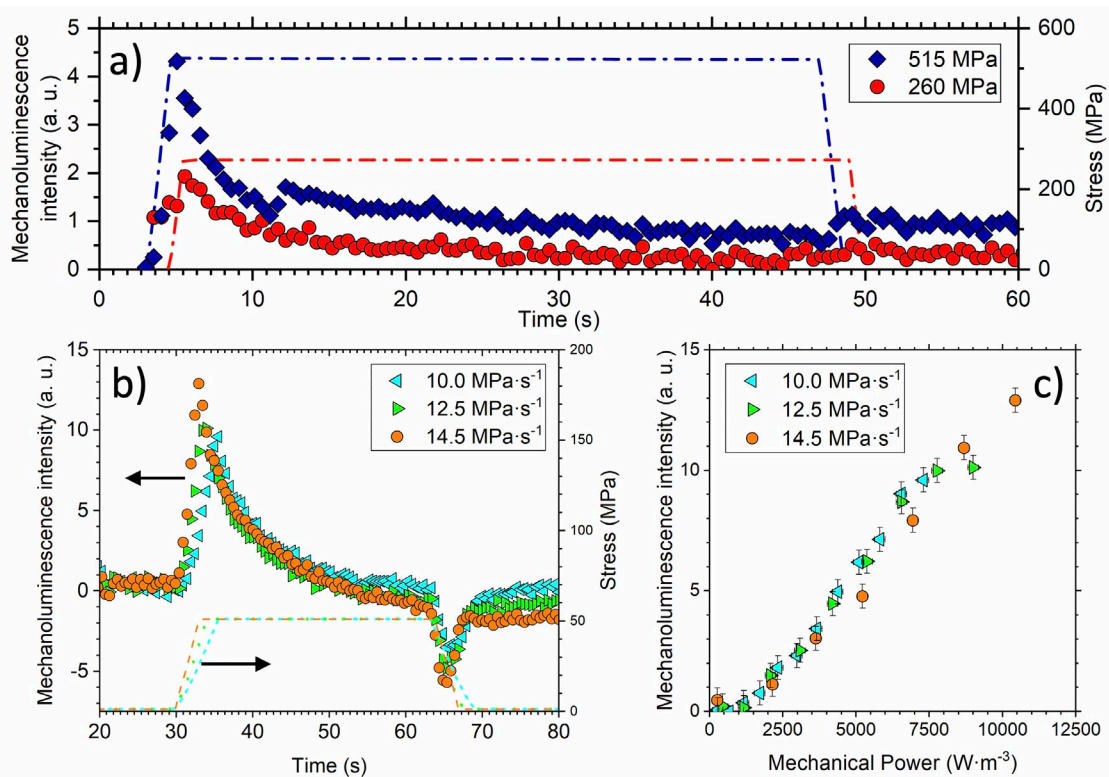
147 **FIG. 2.** a) SEM micrograph of GC-857 b) Photograph of the experimental setup with GC-857 c) XRD
148 patterns of GC-1200 (orange), GC-857 (black), Ba₄Si₆O₁₆ (green) and β-BaSiO₃ (purple).

149 Different heat-treatment temperatures and durations were investigated in order to develop glass-
150 ceramics with different levels of transparency and different fraction of crystallized phases with a
151 direct incidence on the mechanoluminescence intensity. The main outcomes of these lengthy
152 experimental campaigns is that, on the one side, a heat-treatment of 3 h at T_g+20 °C (sample GC-857)
153 allows to observe mechanoluminescence while maintaining the transparency of the glass-ceramic
154 (Fig. 2b), whereas on the other side heat-treatments at higher temperature lead to a more intense

155 mechanoluminescence response but to opaque yellowish/greenish samples. In this latter case, an
156 optimum was observed for a heat-treatment of 10 min. at 1200 °C, that is well above the
157 crystallization temperature but below the melting temperature of Ba₄Si₆O₁₆ (sample GC-1200).
158 Longer treatment times were found to induce the degradation of the surface of the material (a few
159 tens of microns porous layer forms at the surface). The major crystalline phase in the glass-ceramics
160 as identified by means of *XRD* on powders (after grounding the glass-ceramics) is Ba₄Si₆O₁₆ (space
161 group P2₁/c) (Fig. 2c). This confirms the congruent crystallization of the glass. The presence of a
162 minor amount of β-BaSiO₃²⁷ in GC-857 is attributed to a side surface crystallization process. The
163 amount of residual glassy phase in GC-857 remains important according to the width of the *XRD*
164 peaks and to the *SEM* micrograph, where the glassy phase (light grey) is dominant. In the case of GC-
165 1200, well-defined peaks corresponding to the Ba₄Si₆O₁₆ phase are observed and the material is
166 almost fully crystallized.

167 Non-destructive elasto-mechanoluminescence was observed by loading parallelepipedic
168 glass-ceramic specimens in compression at a rate of 300 MPa·s⁻¹. The specimens were *UV*-irradiated
169 prior to testing and mechanically loaded 4 and 30 s later for the GC-857 and GC-1200 grades
170 respectively (Fig. 3). The mechanoluminescence intensity was obtained by subtracting the
171 photoluminescence decay background as obtained on the same specimen in the absence of mechanical
172 loading. The mechanoluminescence intensity gradually decreases i) with increasing delay times
173 before applying the mechanical stress ii) during cyclic compression tests (Supplementary data 1).
174 This suggests that the charge carriers involved in the mechanoluminescence mechanisms are slowly
175 recombining with the luminescent centers with time, but also that mechanical stress increases the
176 recombination kinetics. For a given loading rate, an increase of the intensity of the
177 mechanoluminescence peak is observed with an increase of the maximum stress, consistently with
178 the fact that as the applied stress is increased the release of the charge carriers becomes easier
179 (faster)^{1,10}. Then, the mechanoluminescence intensity decreases continuously during the stress
180 plateau. Mechanoluminescence is more pronounced in GC-1200 than in GC-857 thanks to a larger
181 fraction of “active” crystallized phase, and can thus be detected in GC-1200 even at relatively low
182 loading rates. As a result, the weakening of the mechanoluminescence phenomenon during the
183 unloading stage is easier to follow (Fig. 3b). As far as mechanoluminescence is under scrutiny, the
184 loading-rate is of paramount importance. The mechanoluminescence intensity was found previously
185 in the case of the SrAl₂O₄:Eu²⁺, Dy³⁺ compound to be proportional to the mechanical power, $P_m =$
186 $\frac{\sigma \dot{\sigma}}{E}$, where $\dot{\sigma}$ is the stress-rate and E the Young’s modulus of the material¹. However, the
187 mechanoluminescence behavior of Ba₄Si₆O₁₆:Eu²⁺, Ho³⁺ differs from the one of SrAl₂O₄:Eu²⁺, Dy³⁺
188 in that the luminescence intensity drops rapidly upon unloading. In the case of SrAl₂O₄:Eu²⁺, Dy³⁺, a

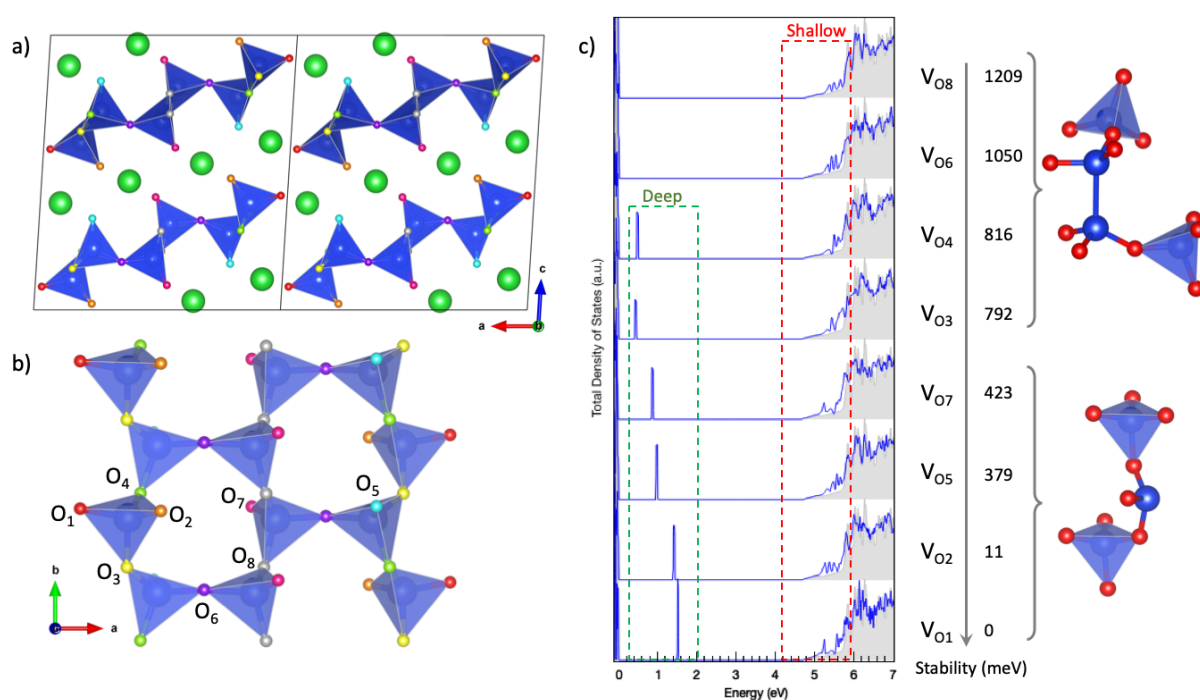
189 mechanism for the mechanoluminescence based on the existence of three discrete trap levels in the
 190 crystal structure was proposed and sustained by experiments conducted in hydrostatic pressure, in
 191 compression and in shear and by *DFT* calculations^{1,2}.



202 **FIG. 3.** a) Mechanoluminescence behavior of the GC-857 glass-ceramics under different stress
 203 condition: b) Mechanoluminescence behavior of the GC-1200 glass-ceramics for loading cycles with
 204 different loading and unloading rates c) Mechanoluminescence intensity as a function of the
 205 mechanical power for the GC-1200 glass-ceramics.

206 In Ba₄Si₆O₁₆:Eu²⁺, Ho³⁺, defects such as oxygen vacancies are likely to play an important role
 207 in the luminescence and mechanoluminescence mechanisms. There are eight non-equivalent oxygen
 208 sites in the corresponding crystal structure. Therefore, eight models were investigated by means of
 209 *DFT* to account for the effect of creating a specific oxygen vacancy in a Ba₄Si₆O₁₆ crystal.
 210 Nevertheless, these eight possible configurations lead (after optimization) to only two types of local
 211 atomic arrangement at the defect sites, which are associated with the two types of oxygen atoms,
 212 namely those internal with respect to the silicate ribbon, and those external (Fig. 4b). While the
 213 external oxygen atoms are connected to only one silicon atom, the internal ones are bonded to two
 214 silicon atoms. As a consequence, the formation of an oxygen vacancy is more favorable on the edges
 215 of the ribbon (O₁, O₂, O₅ and O₇) than inside the ribbon (O₃, O₄, O₆ and O₈), and leads to SiO₃ and
 216 Si₂O₆ entities, respectively. It is interesting to notice that the latter defect exhibits Si-Si distances of
 217 2.59, 2.58, 2.49 and 2.44 Å, respectively for V_{O3}, V_{O4}, V_{O6} and V_{O8}, for which the relative energies
 218 are 792, 816, 1050, and 1209 meV, respectively. In other words, the formation of oxygen vacancies

219 inside the ribbon is clearly unfavorable and a shorter Si-Si distance leads to increase the instability of
 220 the related Si_2O_6 defect. The incidence of the eight different oxygen vacancies on the density of states
 221 (DOS) was evaluated and is shown in Fig. 4 along with the DOS of the defect-free supercell. A band
 222 gap value of 4.7 eV is found, similar to the one reported by Li et al. (4.6 eV)¹². Both deep and shallow
 223 defect levels originating from the removal of the oxygen atom were identified. Unlike the case of
 224 SrAl_2O_4 ², the shallow defect levels of $\text{Ba}_4\text{Si}_6\text{O}_{16}$ are rather diffuse. This is believed to have a strong
 225 incidence on the mechanoluminescence behavior of this crystal. Nevertheless, further experimental
 226 and theoretical investigations are needed to reach a complete understanding of the response of the
 227 $\text{Ba}_4\text{Si}_6\text{O}_{16}:\text{Eu}^{2+}, \text{Ho}^{3+}$ compound to a specific mechanical loading cycle.



228
 229 **FIG. 4.** a) Schematic representation of the atomic structure of $\text{Ba}_4\text{Si}_6\text{O}_{16}$, which is built on ribbons of
 230 corner-sharing SiO_4 tetrahedra (in blue) separated from each other by Ba^{2+} ions (in green). b) The
 231 eight inequivalent oxygen positions in a ribbon can be classified in two categories, namely external
 232 ($\text{O}_1, \text{O}_2, \text{O}_5$ and O_7) and internal ($\text{O}_3, \text{O}_4, \text{O}_6$ and O_8) to ribbon. c) The total densities of states ($TDOS$)
 233 corresponding to formation of an oxygen vacancy containing one electron (blue line) on each
 234 inequivalent oxygen sites ($V_{\text{O}i}$) are compared to the defect-free $TDOS$ (in grey). Energies for $TDOS$
 235 are given with respect to the E_{F} . Deep and shallow defect energy range regions with respect to the
 236 conduction band are highlighted. The relative energy, i.e. the related stability of the defect, is given
 237 in meV. The atomic arrangements resulting from the removing of external and internal oxygen atoms
 238 are shown.

239 In conclusion, mechanoluminescence was observed in glass-ceramics from the $\text{BaO}-\text{SiO}_2-\text{Si}_3\text{N}_4$
 240 chemical system containing 4 mol. % ($\text{EuO}, \text{Ho}_2\text{O}_3$). The crystallized phase of interest, e.g.

241 Ba₄Si₆O₁₆:Eu²⁺, Ho³⁺, was obtained through a congruent crystallization of a glass with the same
242 composition. Large (cm scale) batches of homogeneous parent glasses and glass-ceramics were
243 elaborated. The intensity of the mechanoluminescence response observed after loading, post-UV
244 irradiation, scales with the mechanical power (i.e. with the loading-rate). However, some major
245 differences were noticed with the behavior of SrAl₂O₄:Eu²⁺, Dy³⁺, which result from the differences
246 in the energy levels induced by the oxygen vacancies.

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249

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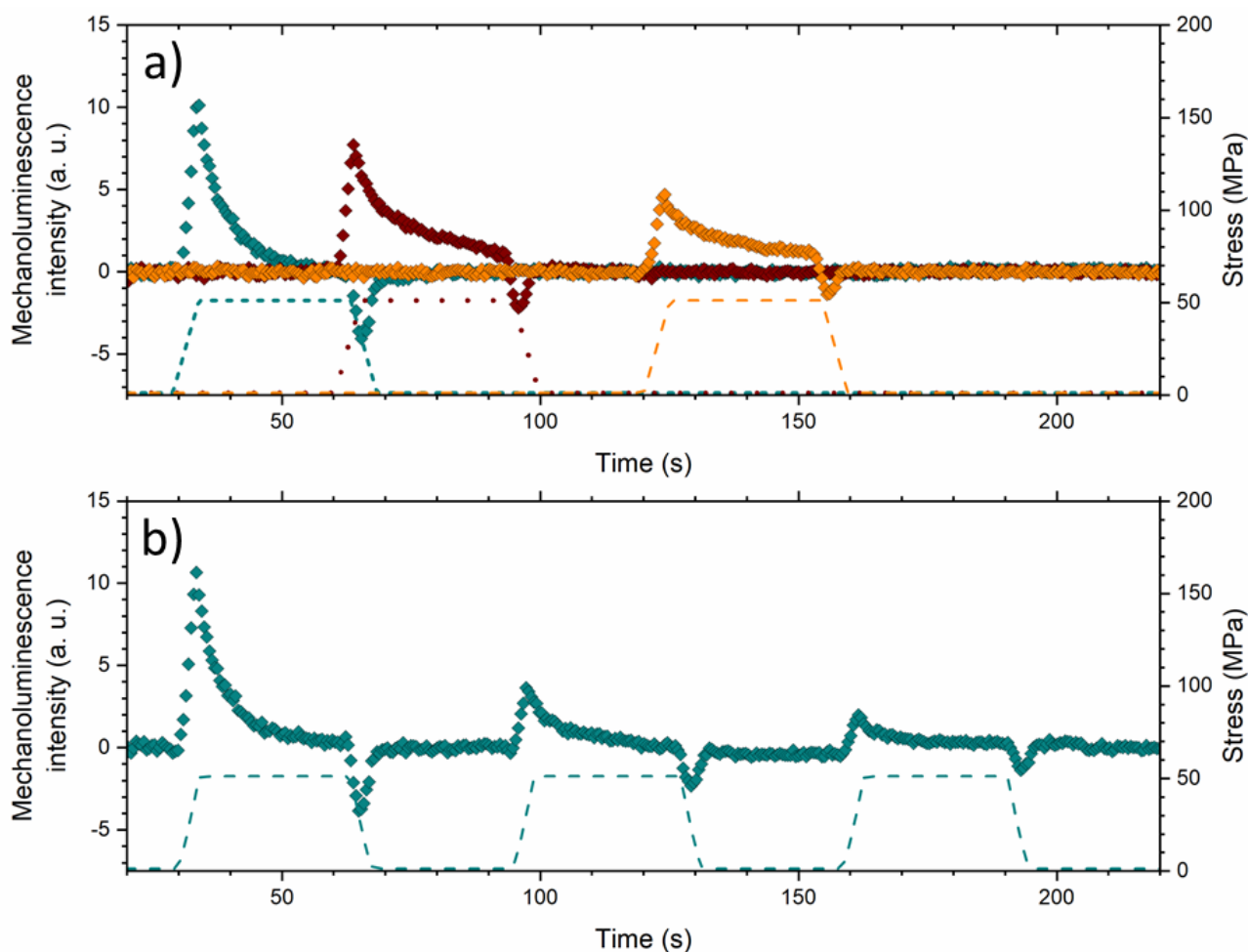
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SUPPLEMENTARY DATA



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294 **SUPPLEMENTARY DATA 1.** a) Mechanoluminescence of GC-1200 a) with different delay times

295 b) under cyclic compression tests.