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# 1                    **Extending the potential of plasma-induced luminescence** 2                    **spectroscopy**

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## 17   **Abstract**

18   In the context of laser-induced breakdown spectroscopy (LIBS), plasma-induced luminescence (PIL)  
19   may be observed by tuning the temporal acquisition parameters (delay and gate). This approach  
20   provides useful information about minor elements in a sample. The broad range of excitation  
21   resulting from the laser-induced plasma enables the simultaneous observation of multiple  
22   luminescence emission bands. However, PIL results in damage to the sample due to laser ablation.  
23   Moreover, time resolution only enables the separation of emission signatures with different decay  
24   times; as a consequence, only luminescence signatures with long decay times may be observed  
25   separately from plasma emissions. In this study, we propose a new experimental approach to extend  
26   the potential of PIL spectroscopy. Our main idea is to generate a laser-induced plasma on a separate  
27   ablation target adjacent to the luminescent sample, which is hence protected from laser ablation.  
28   Moreover, the ablation target can be selected to ensure a stable plasma for PIL excitation. We also  
29   show that this setup enables the further study of the excitation mechanisms of PIL itself by varying  
30   the nature of the excitation source of PIL. Finally, we propose a new experimental setup that enables  
31   the study of the luminescence features of short decay times. We successfully tested this new  
32   approach on both artificial and natural crystals, showing luminescence emission bands of varying  
33   decay times.

34

## 35 1. Introduction

36 Plasma-induced luminescence (PIL) is the name given to the phenomenon of luminescence emission  
37 after excitation by a plasma. To the best of our knowledge, it was first studied in the context of cold  
38 plasma treatment [1,2]. Polymer samples were irradiated for 5 to 180 s by a plasma induced by  
39 electrical discharge, and their resulting luminescence was studied as a function of plasma exposure  
40 time. PIL was later associated with laser spectroscopy and laser-induced plasmas by Gaft *et al.* [3]. In  
41 the context of laser-induced breakdown spectroscopy (LIBS), a pulsed laser of high energy (millijoule  
42 range) is focused at the surface of a sample. The laser fluence is thus sufficient to ablate, vaporize  
43 and excite a small amount of matter, resulting in the formation of a plasma composed of the  
44 chemical elements present in the sample and the ambient gas in neutral and ionized excited states.  
45 When the plasma cools down, radiative relaxation processes occur, producing the atomic and ionic  
46 emission lines that compose the LIBS spectrum, providing access to the elemental composition of the  
47 sample [4]. Practically, the LIBS spectrum varies over the lifetime of the plasma. In the first  $\sim 100$  ns,  
48 the plasma temperature is typically 15,000 K or more, and the electron density is typically  $10^{17} \text{ cm}^{-3}$   
49 or more [5]. This results in an emission spectrum dominated by a continuum due to Bremsstrahlung  
50 and recombination radiation, which is usually considered background of LIBS measurements. Then,  
51 emission from ions typically decays in 100 to 500 ns for the multi-ionized species [6] and several  $\mu\text{s}$   
52 for singly ionized species. Emission lines from neutral atoms can be detected for up to 10  $\mu\text{s}$ , and  
53 finally, molecular emission bands resulting from recombination within the plasma can be observed in  
54 some cases during a few tens of microseconds. Time-resolved LIBS thus gives access to information  
55 of different natures. Indeed, tuning the delay after the laser pulse as well as the gate, namely, the  
56 duration of acquisition, allows somewhat specific observation of either ionic, neutral or molecular  
57 spectral features in LIBS spectra and the extraction of complementary data. The acquisition  
58 parameters (delay and gate) are generally optimized to improve the signal-to-noise ratio and the  
59 contrast between continuum and atomic lines and to reduce spectral broadening effects [7]. Their  
60 control also enables accurate studies of molecular emissions [8,9]. For instance, the detection and  
61 quantification of fluorine in geological samples has been demonstrated through the study of CaF  
62 emission bands [10,11]. Moreover, in several cases, plasma-induced luminescence can also be  
63 detected [3,12], making PIL an additional signal accessible with a time-resolved LIBS experimental  
64 setup simply by tuning the delay and gate parameters of the acquisition. Previous studies have  
65 shown that the observation of PIL, in addition to LIBS information, improves the detection  
66 capabilities for minor elements [13–15]. In some cases, such as for rare earth elements, the detection  
67 capability of PIL may even reach the ppb level [14]. Luminescence relies on emissions from impurities  
68 and defects within the lattice of a material [12,16], and the broad variety of plasma emissions  
69 provides different possible excitation sources for luminescence. PIL thus appears to be a type of  
70 spectroscopy with great potential and a high complementarity with LIBS studies and can be easily  
71 implemented using classic LIBS experimental setups.

72 However, PIL presents several difficulties. First, as with LIBS, it relies upon laser ablation of the  
73 studied material. This results in local damage to the sample: target erosion appears in the form of an  
74 ablation crater [17]. Moreover, Fau *et al.* observed that LIBS laser shots could result in local  
75 amorphization, melting and/or phase transformation in the sample [18]. PIL is therefore a locally  
76 destructive technique, whereas rare or precious samples require fully nondestructive analyses.  
77 Moreover, recording a PIL spectrum with a satisfying signal-to-noise ratio generally requires  
78 accumulation of the signal over a significant number of laser shots (for example, in [14], the PIL signal  
79 is collected over 1000 shots). However, these experimental conditions are not compatible with the  
80 analysis of fragile samples likely to be destroyed during the acquisition of spectra, thus preventing

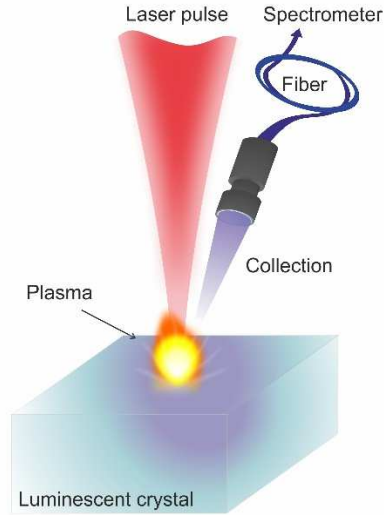
81 one from obtaining a decent PIL spectrum under these conditions. Finally, due to the colocation  
82 (both spatial and spectral) of plasma emission and luminescence, efficient separation of these two  
83 signals relies upon the selection of appropriate time windows [3,14] when luminescence emission  
84 bands exhibit longer decay times than the emission lines related to plasma radiation. Therefore,  
85 luminescence signatures related to short decay times may be hidden by the more intense LIBS  
86 emission lines and hardly observed in the PIL spectra.

87 An alternative setup, called *in-air PIL*, was proposed by Veltri *et al.* [19] and relies on laser-plasma  
88 electron acceleration to perform cathodoluminescence measurements in atmospheric conditions. By  
89 using the interaction of a focused femtosecond laser with air, the authors created an in-air plasma  
90 located a few millimeters from the sample, in which PIL excitation occurred and was observed. In  
91 addition to the advantages mentioned by the authors, this approach also prevents any damage to  
92 the samples, allowing a decent PIL signal to be obtained, even on fragile samples. Even though in-air  
93 laser-induced plasma can be achieved by nanosecond laser interactions [20], the related papers  
94 [19,21] only mention the use of femtosecond lasers for luminescence excitation.

95 Similar to pulsed-laser deposition [22], in which the laser-induced plasma is created on a solid target  
96 located close to the substrate to be treated, we propose for the first time to examine the advantage  
97 of performing PIL spectroscopy with a laser-induced plasma expanding in ambient air after  
98 nanosecond laser pulse interactions occur on a separate ablation target near the luminescent  
99 sample. In this case, the sample probed by PIL is not damaged, and the excitation spectrum can be  
100 tuned by selecting different ablation targets or using optical filters, which is naturally an extension to  
101 the case of in-air plasma discussed above. Furthermore, we demonstrate in the last part of our study  
102 that separating the plasma from the luminescent sample allows additional optical filtering as a  
103 unique solution to separate short decay time luminescence bands from plasma emission lines.  
104 Finally, it is worth pointing out that this paper is not dealing with the advantages of PIL compared to  
105 other luminescence techniques , but claims to describe possible extensions of the PIL technique  
106 itself.

## 107 **2. Standard PIL experiment**

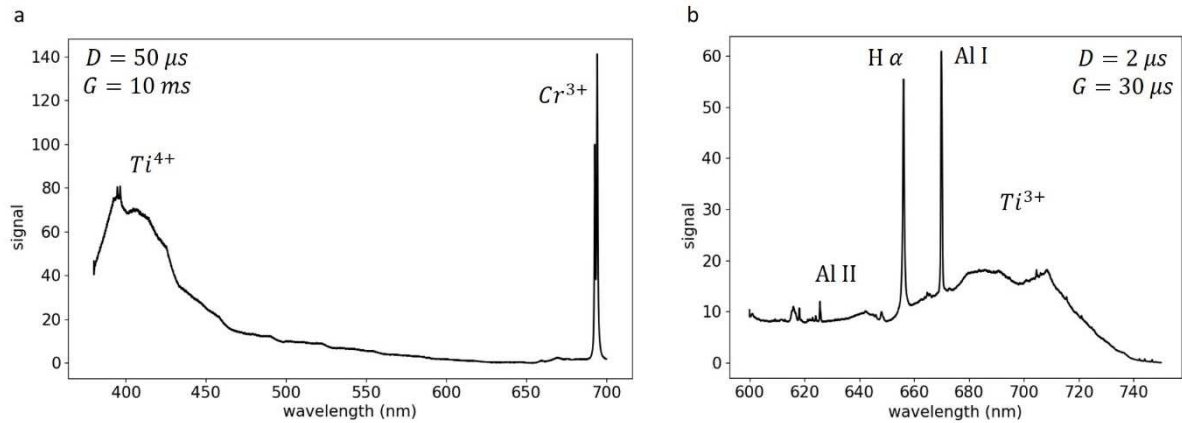
108 We first introduce in this section the standard PIL experimental setup and results that we will  
109 consider as the reference for further discussion. Our experimental setup is schematically displayed in  
110 Fig. 1. It corresponds to a classic LIBS setup. It consists of a diode-pumped pulsed Nd:YAG laser  
111 (Viron, Lumibird) delivering 1064 nm – 6 ns – 10 Hz pulses. The laser fluence onto the sample surface  
112 is approximately 50 J/cm<sup>2</sup>, and the spot diameter is approximately 200 micrometers. The laser beam  
113 is vertically focused through a 10-cm fused silica plano-convex lens onto the surface of the crystal  
114 sample. The PIL radiation is collected and then injected into a circle-to-linear bundle of 19 optical  
115 fibers (each fiber is 2-m long and has a 100- $\mu$ m core diameter) by a 5-cm converging lens and finally  
116 introduced into a Czerny-Turner spectrometer (Kymera 328i, Andor) equipped with a 1200 l/mm  
117 grating blazed at 300 nm. An intensified CCD camera (iStar CCD 340, Andor) enables the tuning of the  
118 delay and gate parameters, as well as the gain, for signal amplification.



119

120 Figure 1 - Scheme of our PIL experimental setup

121 The luminescent sample is a 6x6x12 mm sapphire crystal ( $\text{Al}_2\text{O}_3$ ) doped with titanium, hereafter  
 122 referred to as Ti:Sa. This crystal was selected as a case study since it contains three luminescing ions,  
 123  $\text{Ti}^{3+}$ , and  $\text{Ti}^{4+}$ , as expected, and  $\text{Cr}^{3+}$  as an impurity. These three ions exhibit well known and relatively  
 124 intense emission features with significantly different decay times. More precisely,  $\text{Ti}^{3+}$  exhibits a  
 125 broad emission band between 650 and 900 nm, with a decay time on the microsecond time scale,  
 126 while the luminescence signature of  $\text{Ti}^{4+}$  is a band at approximately 410 nm that lasts several tens of  
 127 microseconds. Finally,  $\text{Cr}^{3+}$  is characterized by a doublet of emission lines at approximately 693 nm  
 128 that decays in several milliseconds [23]. Fig. 2 shows two PIL spectra of this Ti:Sa crystal recorded  
 129 with two different time windows to consider the microsecond and millisecond range decay times.  
 130 More precisely, Fig. 2a corresponds to a delay of 50  $\mu\text{s}$  and a gate of 10 ms, while Fig. 2b displays a  
 131 spectrum recorded with a delay of 2  $\mu\text{s}$  and a gate of 30  $\mu\text{s}$ . Note that these spectra and all the  
 132 spectra presented in this paper are not corrected for the instrument response function; they are only  
 133 corrected for the background signal. The PIL spectrum displayed in Fig. 2a exhibits the emission  
 134 features related to  $\text{Ti}^{4+}$  and  $\text{Cr}^{3+}$ , free from any plasma radiation due to the relatively long delay (i.e.,  
 135 50  $\mu\text{s}$ ). Fig. 2b shows the luminescence band of  $\text{Ti}^{3+}$ , as well as some plasma atomic emission lines.  
 136 According to the NIST database [24], these lines correspond to the Al II line at 624.34 nm, the H- $\alpha$   
 137 line at 656.28 nm and the Al I doublet at 669.61 and 669.87 nm. The lines at approximately 616 and  
 138 618 nm probably correspond to the second order of the Al I doublet at 308.21 and 309.28 nm. Fig. 2b  
 139 illustrates the fact that LIBS and PIL spectral features may overlap when the luminescence decay time  
 140 is relatively short, namely, in the microsecond range or below.



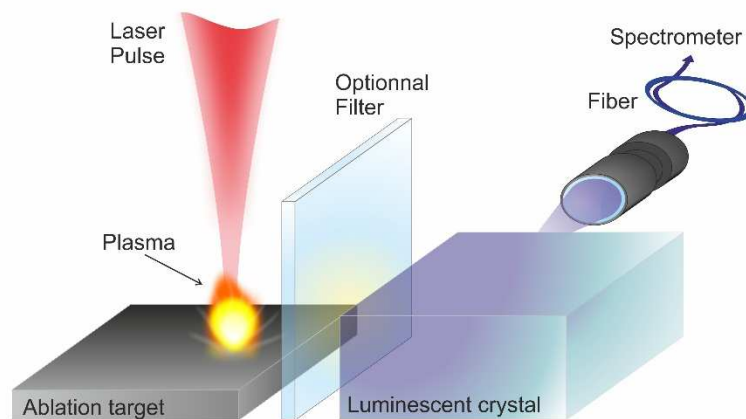
141  
 142 Figure 2 – PIL spectrum of a Ti:Sa crystal: (a)  $Ti^{4+}$  and  $Cr^{3+}$  luminescence signatures acquired with a delay of  $50 \mu s$ , gate of  
 143  $10 ms$ , and gain of 3000 using 500 accumulations (b)  $Ti^{3+}$  luminescence signature and plasma emission lines acquired with  
 144 a delay of  $2 \mu s$ , gate of  $30 \mu s$  and gain of 2000 by using 100 accumulations.

145 Standard PIL is based on laser ablation and plasma creation at the sample surface. In some cases, it  
 146 cannot be implemented, and it is necessary to turn to modified PIL configurations to keep the sample  
 147 safe.

### 148 3. Side PIL configuration

#### 149 3.1. PIL signal excited by an adjacent plasma

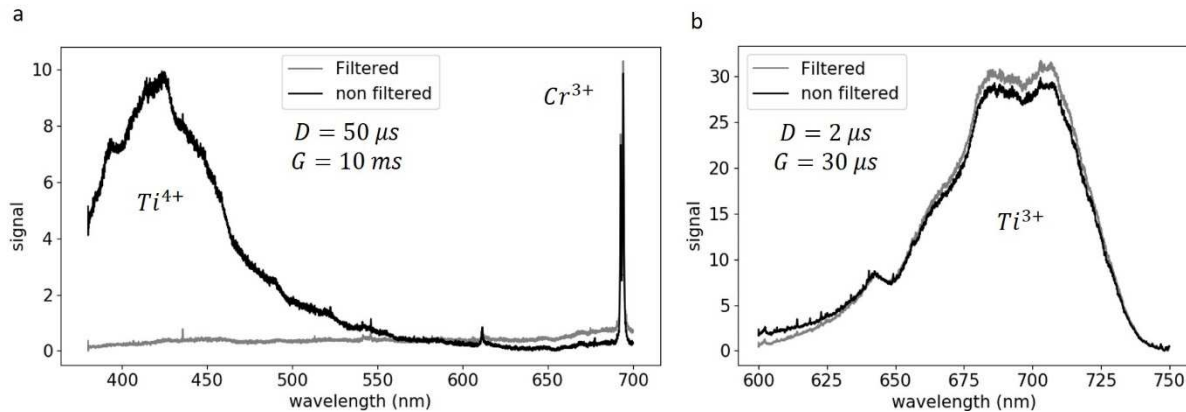
150 We propose a new experimental approach in which laser-induced plasma is not generated at the  
 151 surface of the sample itself but at the surface of a target adjacent to the luminescent crystal, as  
 152 illustrated in Fig. 3. In this way, the sample of interest is not damaged by laser ablation. Moreover,  
 153 the ablation target can be chosen to ensure that a stable plasma can be sustained at its surface, over  
 154 hundreds of laser shots, to provide stable excitation for PIL in the adjacent sample. Third, in this  
 155 configuration, one can insert an optical filter between the plasma and luminescent crystal to select  
 156 the energy range of the plasma photons used for PIL excitation.



157  
 158 Figure 3 – Scheme of a *side-PIL* experiment with an optional optical filter used to filter out part of the excitation spectrum.

159 We conducted a series of *side PIL* experiments on the Ti:Sa crystal already presented in the case of  
 160 standard PIL measurements in Section 2. We use a piece of steel as the ablation target. The distance  
 161 between the plasma and the entrance face of the Ti:Sa crystal is approximately 7 mm, and the  
 162 entrance face is unpolished. We use a longpass filter with an edge at 300 nm. Thus, when the filter is  
 163 inserted in the light path, only excitation photons from the plasma at wavelengths above 300 nm

164 reach the crystal. Fig. 4 shows the PIL spectra obtained in this configuration, with and without the  
165 optical filter. The time parameters are the same as those used in regular PIL in the previous section.



166  
167 Figure 4 – *Side-PIL* spectra (after dark removal) of the Ti:Sa crystal obtained from a steel plasma without (black curves) and  
168 with (gray) an optical filter. In this case, the distance between the plasma and entrance face of the crystal was  
169 approximately 7 mm, and the entrance face of the crystal was unpolished. The optical filter used here transmits only  
170 radiation with wavelengths above 300 nm. (a)  $Ti^{4+}$  and  $Cr^{3+}$  luminescence signatures acquired with a delay of 50  $\mu s$ , gate of  
171 10 ms and gain of 4000 by using 500 accumulations; (b)  $Ti^{3+}$  luminescence signature acquired with a delay of 2  $\mu s$ , gate of  
172 30  $\mu s$  and gain of 4000 by using 500 accumulations.

173 First, we can see in Fig. 4 that without a filter (black curve), the same luminescence signatures are  
174 observed in *side PIL*, as were observed in regular PIL in Fig. 2 (a.  $Ti^{4+}$  and  $Cr^{3+}$  with a long delay, and b.  
175  $Ti^{3+}$  with a short delay). This shows that laser ablation does not have to take place directly on the  
176 luminescent sample for PIL to be observed. Moreover, the  $Cr^{3+}$  and  $Ti^{3+}$  signatures are mostly  
177 unaffected by the addition of the filter between the plasma and Ti:Sa crystal. Based on the filter's  
178 transmission characteristics, these bands are excited by photons above 300 nm. This is consistent  
179 with the fact that Alombert-Goget *et al.* reported that these bands are excited between 350 and 600  
180 nm [23]. The small differences observed in these signatures may be explained by the interaction of  
181 the plasma light with the optical filter itself, namely, the existence of a luminescence signal induced  
182 within the filter in the spectral range from 400 to 750 nm [25,26]. In the case of our experimental  
183 data, this luminescence from the optical filter, which has its own temporal characteristics, may  
184 explain why the intensity observed at wavelengths greater than 600 nm can increase with using the  
185 filter. One can note that atomic emission lines from the laser-induced plasma of Ti:Sa were visible in  
186 Fig. 2b, whereas no atomic emission line is clearly observed in Fig. 4b, despite the time parameters  
187 being similar between the two experiments. This is probably because in *side PIL*, observation is not  
188 directly oriented towards the plasma. However, we also observed during other tests that plasma  
189 emission lines were detected under the experimental conditions corresponding to those of Fig. 4b  
190 when the light from the plasma entered the sample through a polished face (as opposed to what is  
191 obtained for an unpolished face, as shown in Fig. 4b) of the same crystal. The amount of residual  
192 excitation lines in the PIL spectra is probably due to propagation conditions supported by reflection,  
193 refraction and scattering at the entrance face of the crystal, but this is beyond the scope of the  
194 present study, although it may be worth investigating further.

195 Concerning the  $Ti^{4+}$  emission band, however, we can see that the introduction of the filter results in  
196 the complete disappearance of this band, indicating that its excitation source is blocked by the filter.  
197 Since the filter has a transmission close to zero for photons with wavelengths less than 300 nm, this  
198 is consistent with the known excitation band of  $Ti^{4+}$  in photoluminescence, which is between 200 and  
199 270 nm [23].

200 Luminescence excitation observed in *side PIL* is therefore totally consistent with photonic excitation  
201 occurring simultaneously in the UV and visible ranges. Moreover, tuning the spectral range of the

202 plasma radiation reaching the luminescent sample enables us to observe different emission bands  
203 independently and to understand the excitation process responsible for each emission band. This is  
204 the first extension of the classic PIL configuration.

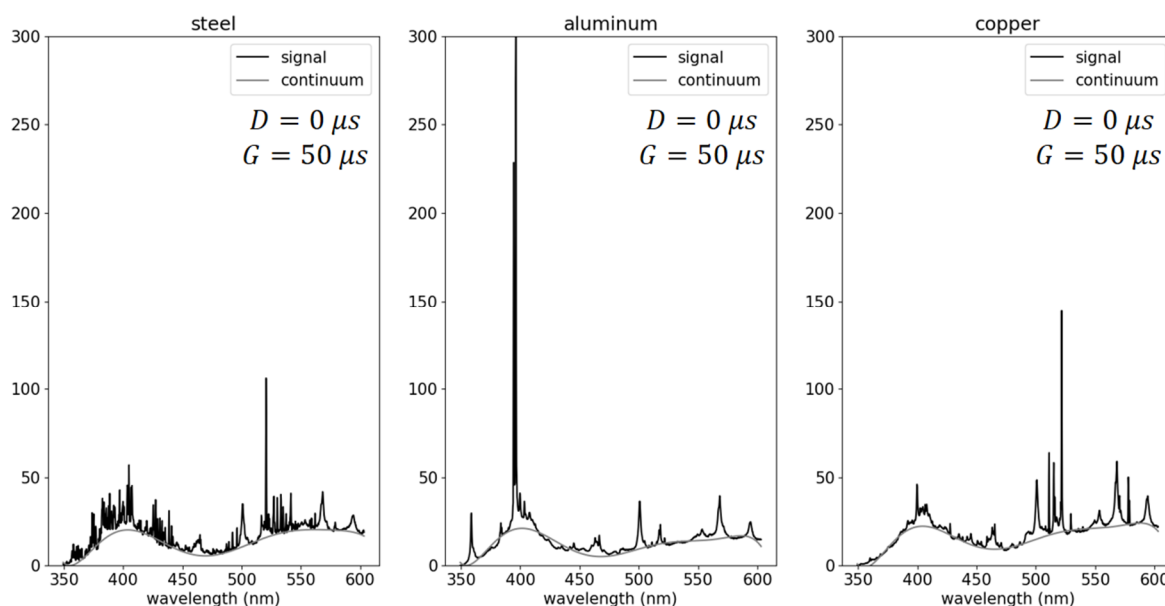
### 205 3.2. Influence of the ablation target on the PIL spectrum

206 *Side PIL* also offers new opportunities to investigate how excitation spectra from different ablation  
207 targets affect the luminescence spectrum of a given sample. This study requires recording i) the  
208 emission spectra of the ablation plasmas obtained on different targets and ii) the PIL spectra  
209 resulting from each plasma. In particular, it allows us to understand how the material-specific  
210 radiation of the plasma, i.e., the atomic, ionic and molecular emission lines observed in LIBS,  
211 contributes to the total radiation emitted by the plasma and, therefore, how it affects the PIL  
212 spectra.

213 Since the excitation of the  $Ti^{3+}$  and  $Cr^{3+}$  bands occur between 350 and 600 nm, as reported in [23], we  
214 decided to record and compare the plasma emission spectra of three ablation targets in this spectral  
215 range, as well as the corresponding *side PIL* spectra.

216 We use the same Ti:Sa crystal used in the tests described in the previous sections. The ablation  
217 targets are pieces of steel (same as that described in Section 3.1), aluminum and copper with flat  
218 surfaces that are large enough for pristine ablation locations to be used for each new round of  
219 measurements. For each metallic target, the laser-induced plasma was kept at the same height and  
220 distance (approximately 7 mm) relative to the entrance face of the Ti:Sa crystal sample. We do not  
221 use a filter here. The LIBS and *side PIL* spectra are shown in Fig. 5.

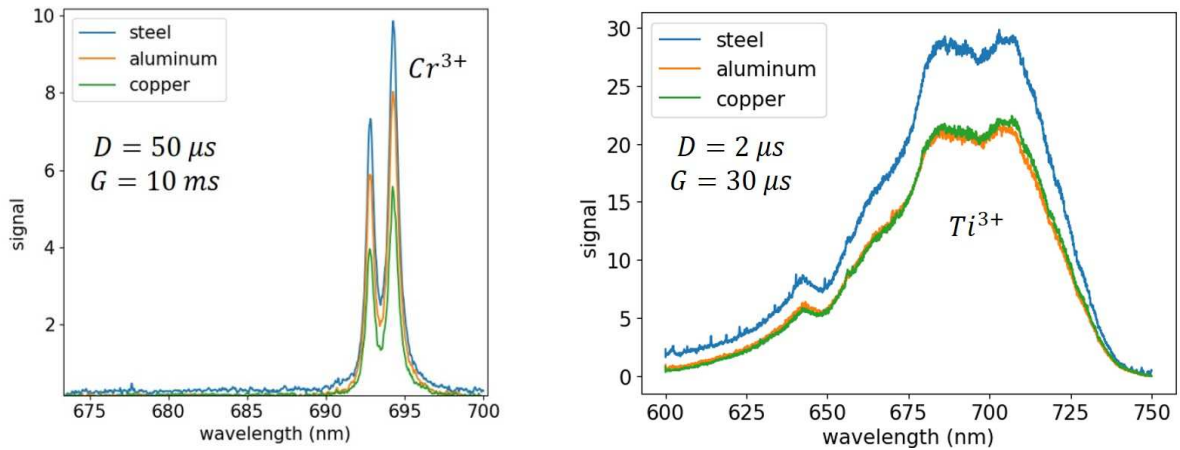
a



b

c



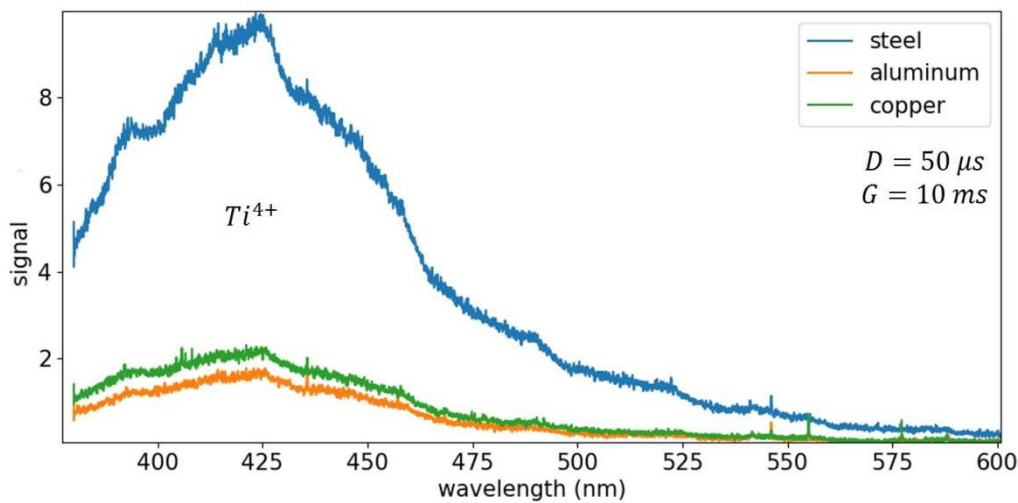


222 Figure 5 – (a) Plasma radiation (time-integrated LIBS) spectra obtained for the three ablation targets (black), steel,  
 223 aluminum, and copper, right after the laser pulse (delay of 0) and with a gate of  $50 \mu\text{s}$ . Polynomial fitting curves (degree of  
 224 7) displayed in gray are given as a rough estimate of the baseline (continuum). (b-c) Close magnified view of the *side PIL*  
 225 spectra of the Ti:Sa crystal excited by the plasma radiation of steel (blue), aluminum (orange) and copper (green), exhibiting  
 226 (b) the  $\text{Cr}^{3+}$  band with a delay of  $50 \mu\text{s}$  and gate of  $10 \text{ms}$  and (c) the  $\text{Ti}^{3+}$  band with a delay of  $2 \mu\text{s}$  and gate of  $30 \mu\text{s}$ , both  
 227 of which were obtained with a gain of 4000 by using 500 accumulations for each ablation target.

228 Let us consider the spectra of the plasma radiation obtained on the three ablation targets, as shown  
 229 in Fig. 5a. We set the delay to 0 and the gate to  $50 \mu\text{s}$  to ensure that the total plasma radiation is  
 230 recorded for each ablation target, including the continuum, atomic emission lines, and molecular  
 231 bands, with varying relative weights as the plasma expands and cools down. The continuum is mainly  
 232 related to the physical conditions of ablation, followed by plasma formation and expansion, whereas  
 233 atomic lines and molecular bands depend on the chemical composition of the ablation target. To  
 234 roughly estimate the relative contribution of the continuum to the total plasma radiation, the  
 235 continuum was fitted with a polynomial function of degree 7. From Fig. 5a, one can directly observe  
 236 that all three polynomial fits (gray curves) are quite similar both in shape and in intensity. On the  
 237 other hand, the atomic, ionic and molecular spectral signatures greatly differ from one spectrum to  
 238 the other. Indeed, the LIBS spectrum of the steel target exhibits a large series of emission lines  
 239 between 350 and 550 nm related to iron, while for the aluminum target, the spectrum is dominated  
 240 by the very intense Al I doublet at 394.40-396.15 nm and then by significantly weaker AlO molecular  
 241 emission bands due to recombination processes occurring in air. For the copper target, several Cu I  
 242 lines can be seen, especially between 500 and 600 nm, as well as molecular bands with much lower  
 243 intensities than the atomic emission lines. We computed the ratio of the area under the fitted curve  
 244 of the continuum to the total area under the LIBS spectrum in the spectral range of 350-600 nm. This  
 245 ratio ranges between 76 and 82% depending on the ablation target. Even if this rough estimate does  
 246 not consider the instrument response function, one can reasonably conclude that between 350 and  
 247 600 nm, the plasma radiation is dominated by continuum emission. We observed in Fig. 5a that the  
 248 continuum emission does not vary much from one plasma to the next. Consequently, the plasma  
 249 radiation, in the visible range, at the origin of the *side PIL* is dominated by the continuum's  
 250 contribution, which is independent of the choice of the ablation target. Finally, note that the plasma  
 251 spectra displayed in Fig. 5a should also be corrected by the absorption probability at each  
 252 wavelength to obtain the actual contribution of each wavelength to luminescence excitation if one  
 253 wants to accurately interpret the differences in intensity observed in the PIL spectra.

254 Considering the *side-PIL* spectra shown in Fig. 5b-c, it appears that the  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$  signatures are  
 255 excited by plasma radiation from the three targets. For the  $\text{Cr}^{3+}$  doublet emission, the largest  
 256 intensity is observed for the steel target, followed by aluminum and copper, and the intensities vary  
 257 by a factor of up to 2. For the  $\text{Ti}^{3+}$  signature, copper and aluminum targets induce very similar  
 258 emission intensities, while the steel target induces a slight increase in intensity (less than 1.5 higher).

259 The other spectral feature we examine is the  $Ti^{4+}$  luminescence band, which is known to be excited  
 260 between 225 and 250 nm [23]. The *side PIL*  $Ti^{4+}$  signatures induced using our three ablation targets  
 261 are shown in Fig. 6. We observe that the signal intensity is five times higher with the steel plasma,  
 262 compared to the other two ablation targets. This indicates a significant difference in intensity  
 263 between the plasma radiations of steel on the one hand, and aluminum and copper on the other  
 264 hand, in the spectral range 225-250 nm. This conclusion is in good agreement with the simulated LIBS  
 265 spectra derived from the NIST database [24], that show a very large number of highly emissive lines  
 266 from the iron contained in steel. Aluminum and copper exhibit far fewer lines in this spectral range.  
 267 This could also be verified by an appropriate experimental setup.



268 Figure 6 – Side PIL spectra of Ti:Sa crystal excited by radiation in the UV range from the plasma created after the laser  
 269 ablation of steel (blue), aluminum (orange) and copper (green). In this case, the distance between the plasma and entrance  
 270 face of the crystal was approximately 7 mm, and the entrance face of the crystal was unpolished. The  $Ti^{4+}$  luminescence  
 271 signature was acquired with a delay of 50  $\mu s$ , gate of 10 ms and gain of 4000 by using 500 accumulations.  
 272

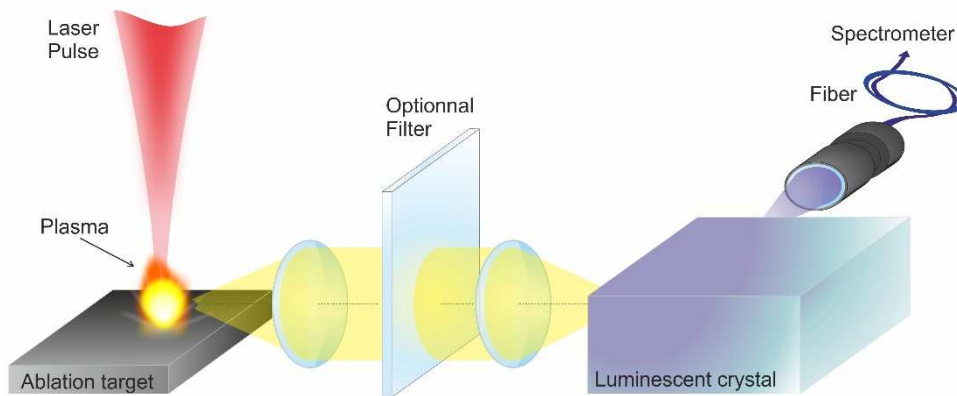
273 We can conclude that in *side PIL*, luminescence excitation occurs due to the photons emitted by the  
 274 ablation plasma over the whole spectral range simultaneously. The use of an optical filter placed  
 275 between the plasma and luminescent sample enables tuning of the spectral range used for PIL  
 276 excitation. We compared the PIL excitation resulting from ablation plasmas obtained on three  
 277 different targets and concluded that in the visible range, the continuum is both predominant and  
 278 similar for all plasmas, resulting in similar PIL emission spectra. For luminescence signatures excited  
 279 in the UV range, the differences observed when changing the ablation target are in good agreement  
 280 with the simulated spectra of plasma emission but were out of the spectral range accessible with our  
 281 experimental setup. Based on this study, we concluded that the choice of the ablation target to  
 282 initiate PIL is not critical, and we decided to use only the plasma induced on the steel ablation target  
 283 for further experiments.

284 Finally, thanks to the *side PIL* configuration proposed here, it is possible to record luminescence  
 285 spectra after excitation by plasma radiation without damaging the sample by laser ablation and using  
 286 only classic LIBS equipment. However, the proximity between the crystal and plasma, which is  
 287 required to optimize the excitation, exposes the crystal to the risk of vapor or particle deposition,  
 288 resulting in a surface coating forming on the crystal, as observed in pulsed laser deposition, which  
 289 may not be acceptable for precious samples or samples that require further analysis.

#### 290 4. Remote PIL configuration

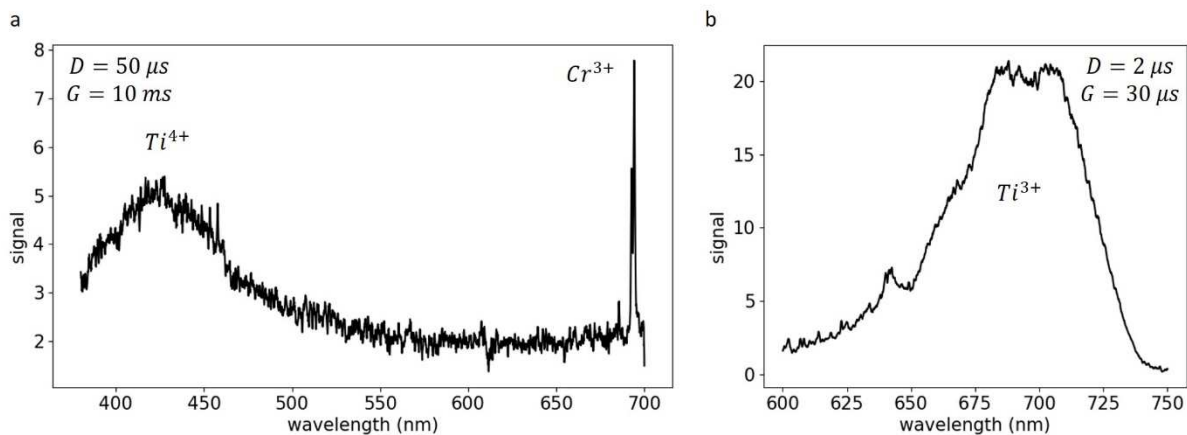
291 **4.1. First demonstration on a Ti:Sa crystal**

292 To protect the sample from coating by plasma ejection, we propose in this section another  
 293 experimental setup, which we call *remote PIL*. In *remote PIL*, the plasma volume is imaged inside the  
 294 luminescent sample thanks to a standard imaging system consisting of two converging lenses, as  
 295 illustrated in Fig. 7. The laser-induced plasma is thus located at the focal point of the first lens, the  
 296 collected light propagates as a collimated beam, and the second lens focuses the beam inside the  
 297 luminescent sample. Under such conditions, any optional optical filter can easily be introduced  
 298 between the two lenses, and the luminescent sample can be placed several tens of centimeters away  
 299 from the plasma, which prevents any risk of deposition. In our case, the focal distance of the two UV-  
 300 fused silica plano-convex converging lenses was 5 cm, and the plasma-sample distance was close to  
 301 20 cm. The choice of the material used for the converging lenses is critical since its UV cutoff  
 302 determines the highest energy of the photons eventually available for luminescence excitation in  
 303 *remote PIL*, and, therefore, the emission bands that can be observed.



304  
 305 Figure 7 – Scheme of the experimental setup used for *remote PIL*

306 To demonstrate the ability of this new experimental setup to perform PIL measurements, we  
 307 implemented the experimental setup of *remote PIL* described in Fig. 7 for the case of using a steel  
 308 sample as the ablation target and Ti:Sa crystal as the luminescent sample. The PIL spectrum of Ti:Sa  
 309 recorded in this configuration, with the same acquisition parameters as those selected to obtain the  
 310 *side PIL* spectra presented in Fig. 4, is displayed in Fig. 8. However, smoothing (with a moving average  
 311 over 21 pixels) was applied to these spectra to reduce noise since the intensity of the *remote PIL*  
 312 signal recorded under these experimental conditions was quite low.



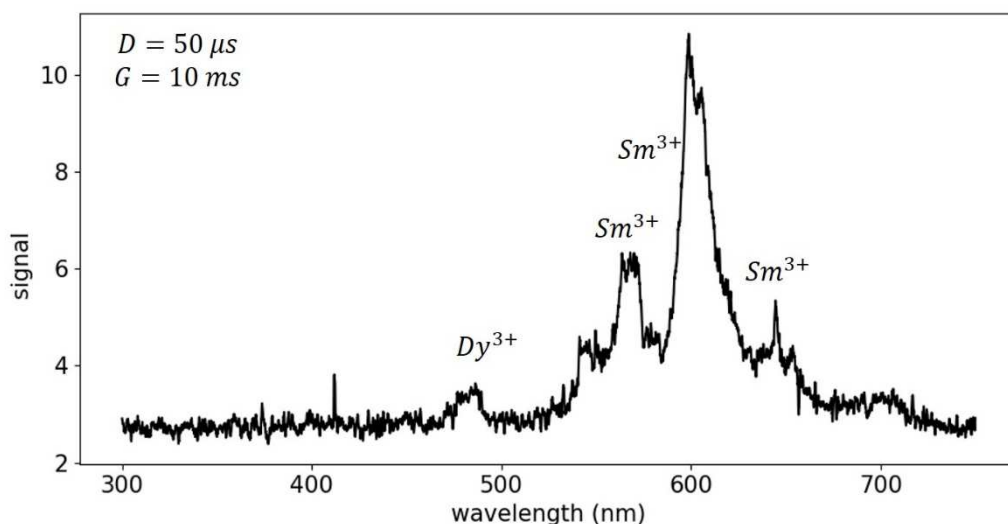
313  
 314 Figure 8 – *Remote PIL* spectrum of the Ti:Sa crystal obtained after laser ablation of a steel target; (a)  $Ti^{4+}$  and  $Cr^{3+}$   
 315 luminescence signatures acquired with a delay of  $50 \mu s$ , gate of  $10 ms$  and gain of 4000 by using 500 accumulations; (b)

316  $Ti^{3+}$  luminescence signature acquired with a delay of  $2 \mu s$ , gate of  $30 \mu s$  and gain of 4000 by using 500 accumulations. The  
317 spectra were processed in the following way: the dark spectrum was subtracted, and a moving average over 21 pixels was  
318 applied.

319 From Fig. 8, one can conclude that *remote PIL* has been successfully demonstrated in the case of the  
320 selected Ti:Sa sample located more than 20 cm away from the plasma to avoid any risk of damage.

## 321 4.2. Application to a natural crystal of apatite

322 Subsequently, to demonstrate that *remote PIL* is not limited to the characterization of highly  
323 luminescent synthesized crystals, we replaced the Ti:Sa crystal with a natural sample of Durango  
324 apatite ( $Ca_5(PO_4)_3(OH,Cl,F)$ ). This sample is well known for its enrichment in rare earth elements,  
325 which exhibit well-known luminescence bands [12]. In this practical case, we failed to acquire a  
326 satisfying PIL spectrum under the standard PIL conditions, namely, by forming the plasma on the  
327 surface of the sample itself. In fact, this sample is too fragile to sustain several hundred laser shots at  
328 a given location, the material is ablated very quickly, and the plasma is not stable enough to enable  
329 luminescence observation with a sufficiently good signal-to-noise ratio. The *remote PIL* spectrum of  
330 this sample is displayed in Fig. 9.



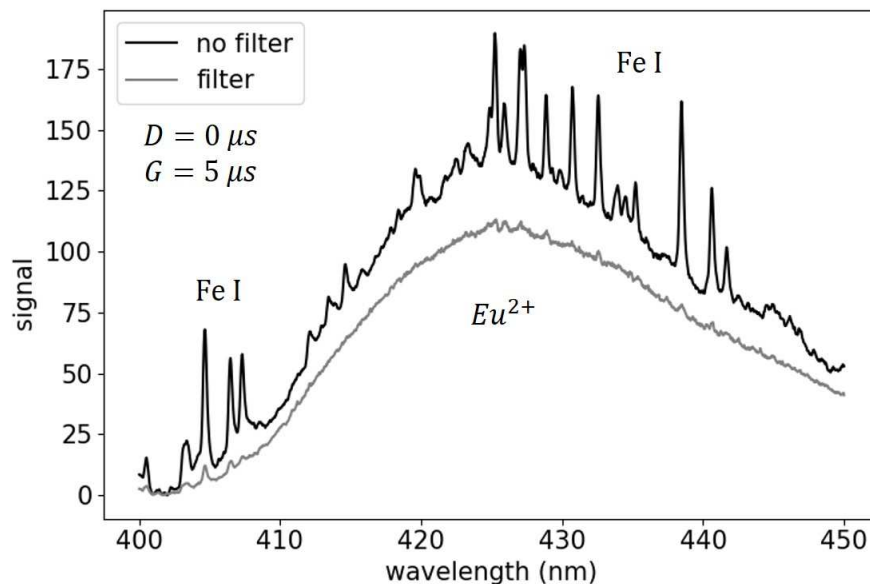
331  
332 Figure 9 – *Remote PIL* spectrum of Durango apatite obtained with a delay of  $50 \mu s$ , a gate of  $10 ms$ , a gain of 4000 and 500  
333 accumulations.  $Sm^{3+}$  signatures are visible at approximately 570, 600 and 645 nm.  $Dy^{3+}$  is observed at 480 nm. The  
334 spectrum was processed in the following way: the dark spectrum was subtracted, and a moving average over 21 pixels was  
335 applied.

336 From Fig. 9, several spectral signatures related to rare-earth elements present in this apatite sample  
337 can be easily identified, and more precisely, some lines/bands related to  $Sm^{3+}$  and  $Dy^{3+}$  are observed  
338 [12]. This result demonstrates that the new setup we have proposed to record PIL spectra remotely  
339 can also be applied to the characterization of natural samples and emphasizes the advantage of this  
340 nondestructive method in the case of fragile samples.

## 341 4.3. Application to short-lived luminescence

342 The other advantage of *remote PIL* is that it provides the ability to perform optical filtering of  
343 excitation light. In the standard PIL configuration, the time delay and gate are specifically adjusted to  
344 filter out the atomic emission lines and molecular recombination bands from the plasma and record  
345 the luminescence spectral features in the best conditions of the signal-to-noise ratio. However, in  
346 some cases, there are luminescence features that exhibit fast decay times, namely, less than  $1 \mu s$ ,

347 and thus, the temporal filtering commonly applied in PIL is not sufficient in such cases to separate  
 348 the sample luminescence and the plasma emission lines, which exhibit the same decay time. This is  
 349 still the case for *remote PIL* but we demonstrate that additional optical filtering makes it possible to  
 350 overcome this problem. To this end, we selected an artificial fluorite crystal activated by  $\text{Eu}^{2+}$ . The  
 351 emission band of  $\text{Eu}^{2+}$ , peaking at approximately 425 nm, is known to decay in less than  $1 \mu\text{s}$  [27].  
 352 The *remote PIL* spectrum of this sample recorded with a delay of 0 and a gate of  $5 \mu\text{s}$  is displayed in  
 353 Fig. 10.



354  
 355 Figure 10 – *Remote PIL* spectrum of  $\text{Eu}^{2+}:\text{CaF}_2$  obtained immediately after the laser pulse (delay of 0) with a gate of  $5 \mu\text{s}$  and  
 356 without an optical filter (black line), showing LIBS emission lines from light transmitted into the crystal, and that with an  
 357 optical filter (gray line) after correction by the transmittance value of the filter, in which only  $\text{Eu}^{2+}$  luminescence remains.

358 Fig. 10 shows a *remote PIL* spectrum of  $\text{Eu}^{2+}:\text{CaF}_2$  composed of  $\text{Eu}^{2+}$  luminescence band (400-450 nm)  
 359 and the atomic emission lines (from iron in this case) from the ablation target (steel in this case). We  
 360 now introduce an optical filter into the light path of the excitation radiation coming from the plasma.  
 361 The filter is characterized by a transmittance value close to 50% in the 300-360 nm range and close to  
 362 0% in the 400-650 nm range. With this filter (gray curve), the plasma emission is drastically  
 363 attenuated in the spectral range presented in Fig. 10, making it possible to retrieve from the PIL  
 364 spectrum only luminescence signatures, without any additional contribution. Note that the spectra  
 365 presented in Fig. 10 could also have been recorded under the *side PIL* conditions. However, the  
 366 optical filter would have been potentially damaged due to its proximity to the laser-induced plasma.  
 367 Finally, this example of a fluorite sample emphasizes the advantage of the *remote PIL* configuration  
 368 to analyze fast decaying emission bands that the temporal resolution cannot separate from the  
 369 plasma emission lines.

370 More generally, the selection of optional optical filters, which one can introduce in the light path of  
 371 the *remote PIL* setup, could allow us to significantly extend the potential of PIL. Indeed, while the  
 372 luminescence excited without a filter is the result of excitation by a broadband plasma radiation  
 373 spectrum, optical filters could allow us to tailor this spectrum to specifically excite selected  
 374 transitions. Thus, *remote PIL* may offer new opportunities for luminescence excitation, midway  
 375 between classical PIL, in which all wavelengths simultaneously contribute to excitation, and classic  
 376 photoluminescence, in which a single selected wavelength induces luminescence excitation at one  
 377 time.

## 378 Conclusion

379 We describe two new experimental setups easily made with classic LIBS equipment, and we discuss  
380 their ability to achieve PIL measurements. For these two configurations, the plasma is not created on  
381 the sample surface but is instead made at the surface of a target dedicated to laser ablation and  
382 plasma formation. The *side PIL* configuration was first implemented to demonstrate that separating  
383 plasma formation from luminescence was viable for spectroscopy. This setup also allowed us to  
384 demonstrate that plasma photons over the whole spectral range contribute to PIL excitation. The  
385 demonstration was achieved by using a Ti:Sa crystal as the luminescent sample and three different  
386 ablation targets, namely, steel, aluminum and copper. The comparison of the PIL spectra obtained  
387 with the three plasmas, as well as the study of the plasma emissions detected over the first 50  $\mu\text{s}$   
388 after the laser pulse, shows that PIL excitation in the visible range is dominated by the continuum of  
389 the plasma emission. The result of UV excitation on PIL was consistent with the simulated LIBS  
390 spectra but was not experimentally verified. In the second experimental setup, *remote PIL*, the  
391 plasma is created on the ablation target and is directed into the luminescent crystal, located several  
392 tens of centimeters away. This setup allowed us to insert an optical filter between the imaging lenses  
393 and thus filter out the atomic emission lines from plasma radiation that overlap with the short decay  
394 time luminescence emission bands. We validated this setup by using Ti:Sa again, as well as a natural  
395 Durango apatite sample and an artificial crystal of fluorite enriched in  $\text{Eu}^{2+}$ , which is known to decay  
396 in less than 1  $\mu\text{s}$ . We believe this new approach may enable various new laboratory studies on  
397 plasma-induced luminescence.

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401 used to observe the  $\text{Eu}^{2+}$  signature in fluorite with *remote PIL*.

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## Laser-Induced Plasma

## Luminescence

