

New approach to investigate irradiated calcite crystals – UV Raman and Photoluminescence with UV excitation *

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In the past, calcite (CaCO_3) turned out as a sensitive natural detector for ion defects. Additional experiments shall now reveal, if there are more useful properties of this very common mineral.

During a test experiment at the SIS, a trigonal calcite crystal of $6 \times 6.5 \times 4 \text{ mm}^3$ in size was irradiated with 192 MeV/u ^{238}U ions of fluence $1 \times 10^{11} \text{ cm}^{-2}$ (subsequently denoted as SIS-calcite). We observed a pronounced ionoluminescence and unexpected long phosphorescence for about 20 min, which was not reported so far.

Crystals from the calcite family are known to luminescent under UV excitation [1]. We thus exposed the SIS-calcite offline with UV light of wavelengths $\lambda_L = 366 \text{ nm}$ (“long UV”) and $\lambda_S = 254 \text{ nm}$ (“short UV”) to investigate whether the increase of defect concentration through ion irradiation changed the properties of the SIS-calcite.

No luminescence was detected for the “long UV”-excitation, whereas under the “short UV” excitation the SIS-calcite showed a thin line of greenish to yellowish luminescence localized around to the range where the electronic energy loss of the ions is maximum. The rest of the crystal did not contribute to luminescence.

Trigonal calcite crystals irradiated at the UNILAC with 11.1 MeV/u ^{197}Au -ions showed the same greenish to yellowish luminescence when stimulated with “short UV”. The luminescence starts to become visible at a fluence of $1 \times 10^9 \text{ ions/cm}^2$. Subsequently, experiments with UV-stimulated Raman spectroscopy and photoluminescence (PL) were performed to test the luminescence response to UV stimulation. The work is motivated by the expectation that a UV-stimulated change in the luminescence pattern may be a suitable non-destructive analytical technique to quantify defect concentrations in calcite crystals produced by bombardment with heavy ions in the low fluence regime ($< 1 \times 10^9 \text{ Au-ions/cm}^2$).

The experiments were performed with the UV-Raman and photoluminescence spectrometer (UV-laser: 244 nm) of Jobin Yvon Horiba. Calcite irradiated with $1 \times 10^6 \text{ Au-ions/cm}^2$ (11.1 MeV/u) show distinct photoluminescence with bands at about 520 and 545 nm (Fig. 1), which matches the greenish, yellowish color of the luminescence light whereas unirradiated calcite crystals show only a minor peak at 545 nm. When increasing the fluence to $1 \times 10^8 \text{ Au-ions/cm}^2$, the amplitude of both peaks increases (Fig. 1). All spectra are taken with the following parameters: grate 300, objective 40 \times , accumulation 2 \times , hole 50.

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Excitation (UV-laser: 244 nm) of the SIS-calcite also indicated the already known two bands with high amplitude (Fig. 2). In addition, a new peak at about 575 nm is observed.

Summarizing the first results, UV-excitation combined with photoluminescence spectroscopy is sensitive enough to detect crystal defects created by heavy ions (11.1 MeV/u ^{197}Au) at a fluence as low as $1 \times 10^6 \text{ ions/cm}^2$.

So far Raman spectroscopy and detection with the UV-excitation (Laser: 244 nm) did not lead to any fluence-related change of the Raman bands.

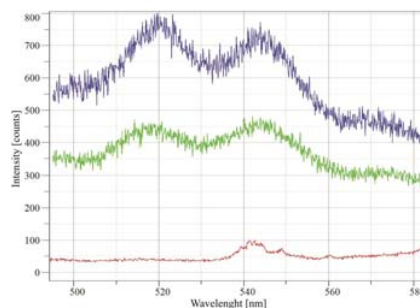


Figure 1: PL-Spectra of calcite crystals irradiated with 1×10^6 and $1 \times 10^8 \text{ Au-ions/cm}^2$ (11.1 MeV/u). Spectra are not shifted, (detection time 20 s irradiated, 1 s non-irradiated).

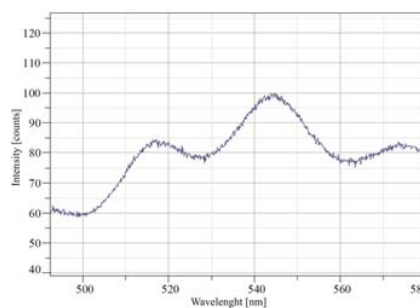


Figure 2: PL-Spectra of SIS-calcite crystal irradiated with $1 \times 10^{11} \text{ U-ions/cm}^2$ (192 MeV/u). Strong luminescence due to good noise/signal ratio (detection time 5 s).

References

- [1] M. Gaft, L. Nagli, G. Panczer, G. Waychunas and N. Porat. “The Nature of Unusual Luminescence in Natural Calcite CaCO_3 .” *American Mineralogist* 93, no. 1 (2008): 158-167.