



## Differentiation of polymorphs by Ionoluminescence.

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### ABSTRACT

Polymorph minerals are natural materials that share the same composition but have a different structure. Traditionally, the characterization of polymorphs has been done using different techniques of microscopy, X-ray diffraction Raman or IR Spectroscopy for instance.

In this work we propose the use of a new technique as an alternative to characterise polymorphs: Ion Beam Induced Luminescence (IBIL). As an advantage to the other techniques, IBIL can be carried out simultaneously with the PIXE technique or other Ion Beam Analysis techniques and the combination will yield results on elemental composition and luminescence properties at the same time.

Different minerals have been analysed with IBIL as an example of application to the characterization of polymorphs and its correspondent spectra are explained in this paper.

### INTRODUCTION

Polymorphism is the phenomenon that describes multiple possible states for one same material, meaning that a material with a given composition can exhibit different crystalline structure or conformational arrangement depending on the conditions of growth or the processes it undergoes (temperature, pressure changes, etc). Polymorph minerals share the same chemical composition but due to their structural diversity show discrepancies in their physical and/or chemical properties; this makes them very interesting materials for refractory ceramics [1], high-efficiency solar cell materials [2], sensors [3] and photo-chromic devices [4]. The characterization of polymorph materials usually relies on techniques such as Optical

Microscopy and X-Ray Diffraction [5,6,7], Raman Spectrometry [8,9], Infrared Spectroscopy and Electronic Spin Resonance [10], Neutron Diffraction [11] or calorimetric methods [12]. Recently, Ion Beam Induced Luminescence (IBIL) studies have shown this technique's potential in matter of polymorph differentiation for calcite – aragonite minerals [13].

In this paper we present new results that confirm IBIL as an alternative to the usual techniques for polymorph differentiation in minerals. More information of the application of this technique in minerals can be found in [13]. Examples of natural samples of diamond – graphite, andalusite – kyanite – sillimanite and low quartz – trydimite are shown. An extrapolation of this can be made to their synthetic analogues, some of which present very interesting properties, such as synthetic diamonds (CVD diamonds, for instance).

**Table 1.** Samples analysed with IBIL.

Sample	Formula	Cation coordination N	Site cation symmetry	Number of Al <sup>3+</sup> sites	IL feature
Diamond	C	4			N-impurities
Grafite		3			
Andalucite	Al <sub>2</sub> SiO <sub>5</sub>	6, 5	2, m	2	--- Cr <sup>3+</sup> Cr <sup>3+</sup>
Kyanite		6	1	4	
Sillimanite		6,4	-1, m	2	
Quartz – low	SiO <sub>2</sub>	4	2	2	Lattice
Tridymite		4	1	12	

## EXPERIMENTAL

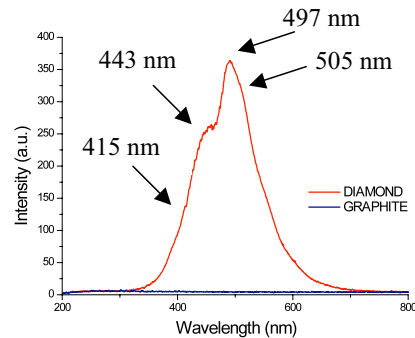
Natural mineral samples [table 1] were subjected to IBIL measurements at the CEA-IPNAS cyclotron at the University of Liege in Belgium. Measurements were carried out in the archaeometry in-air beamline of the particle accelerator. Samples were placed approximately at 0.4cm from the beam extraction nozzle to the atmosphere and subjected to proton beam irradiation of 3 MeV with variable current intensity depending on the sample's sensitivity towards the luminescent process (5-15nA). Light emission induced by the proton beam in the samples was collected through an optic fibber of 1 mm diameter placed 45° to the beam direction at 0.5 cm approximately from the sample. Light was analysed with OceanOptics HR2000 spectrometer that covers the UV-visible range from 200 – 1100nm and has 1nm resolution in wavelength. OOI32Base software was used to acquire the spectra and each measurement took 2 seconds.

## RESULTS AND DISCUSSION

### Carbon: Diamond & Graphite

Carbon presents itself in nature at least as two polymorph structures; the most appreciated diamond (high pressure high temperature carbon) and the low pressure low temperature, graphite. Ion Beam Induced Luminescence of diamond before studied [14,15,16] has been related to the presence of nitrogen centres in its structure. Figure 1 shows the IBIL spectra for samples of diamond and graphite. In our diamond spectrum the band at 415nm is related to N<sub>3</sub> centers, the 442nm band corresponds to dislocations, at 497nm and

505nm the bands correspond to H<sub>4</sub> and H<sub>3</sub> centers respectively. As for the graphite sample no emission bands were registered in the wavelength range studied.



**Figure 1.** Natural Diamond from the Gemmology School of the Universidad Autonoma de Madrid.

### Silicates Al<sub>2</sub>SiO<sub>5</sub>.

There are three polymorphs for the Al<sub>2</sub>SiO<sub>5</sub> silicate: Andalusite (orthorhombic, Pmmm), kyanite (triclinic, p-1) and sillimanite (orthorhombic, Pmmm). Their mineral structures are in the three cases controlled by AlO<sub>6</sub> octahedron units forming chains that run parallel to the z crystallographic axis. These chains are cross-linked by SiO<sub>4</sub> tetrahedra and additional Al coordination polyhedra (where ion substitutions presumably take place); octahedra for kyanite, tetrahedra and octahedra for sillimanite and 5- 6 -fold coordination for andalusite. One peculiarity in the structure of kyanite is the non-equivalency of its octahedral sites that may lead to different

emissions from the same cation impurity [18].

Table 2 .- Comparison of data previously reported for kyanite and sillimanite samples obtained

Sample	Cation Site	bands Emissions	Wojtowicz 26 K Low temperature (λ en nm)	Wojtowicz RT (λ en nm)	This work IL emission bands. (λ en nm)
Kyanite	A	P R	705,2	688,5	682 710
	B	Q	703,7	705 (Q+R)	690 (R lines?)
	C	T	720		720
	D	T	800	800	800
Sillimanite	A	No emission		790	790

by Wojtowicz were obtained with 514,5 nm laser Argon line.

Previous work corresponding to kyanite's luminescence [18,19] shows the existence of the doublet P band at 688,5nm made in fact of Q and R bands that would overlap to give an emission around 705nm. Another composed broad band in the area of 800nm (S band at 720nm and T band at 800nm) has been described. All of them have been attributed to the presence of Cr<sup>3+</sup> or Fe<sup>3+</sup> in high crystalline field (10 Dq) localized in the octahedral non equivalent sites A, B and C of the kyanite's structure.

The IBIL spectra corresponding to our kyanite sample is shown in figure 2. Main features are three sharp dominant bands placed at 682, 690 and 710nm plus a complex structured band with maximum at 720nm that extends almost to 900nm. The spectra obtained in this case are very similar as the previously reported [18] where signals at 682 and 710nm correspond to the Q and R band respectively; the 690nm one, is near to the well-known sharp band of Cr<sup>3+</sup> transition <sup>2</sup>E - <sup>4</sup>A<sub>2</sub> that can be found for instance in ruby. The broad band at 720nm band corresponds to the S and T transitions in the 800nm range. A comparison between the results in this work and the data given by Wojtowicz et al. (18) can be found in table 2.

Sillimanite's spectrum also present in figure 2 features a band with a maximum in 790nm related to the presence of Cr<sup>3+</sup> in octahedral sites in a weak crystalline field [20].

No emission was detected for andalusite samples.

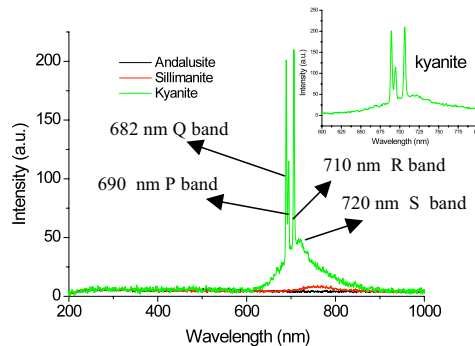


Figure 2. IL spectra of Al<sub>2</sub>SiO<sub>5</sub> polymorphs: green for kyanite, red for sillimanite and black for andalusite.

### Silicates SiO<sub>2</sub>

The structure of SiO<sub>2</sub> can be described as chains of SiO<sub>4</sub> tetrahedron spiralling up the z- axis; the outer apices of the tetrahedron being shared with adjacent chains. SiO<sub>2</sub> has six polymorphs depending of the pressure and temperature; the most abundant are alpha-quartz (trigonal p32), tridimite (monoclinic Cc) and cristobalite (tetragonal p422). All of the polymorph varieties are interconnected by means of reconstructive displazative transformations where the Si-O bonds never break but accommodate the new pressure-temperature conditions. Alpha-quartz, tridimite and cristobalite are stable at RT

and thus the three of them can be found in nature.

Literature reports agree on the attribution of quartz's broad and complex emissions in the area of 400nm (also called green band) to intrinsic defects: oxygen vacancies [21] or radiation induced self trapped excitons (STE) [22]. The IBIL spectra obtained for samples of quartz and tridimite in figure 3 show quartz bands similar to Cathodoluminescence results obtained for this material [23]. We can thus attribute the bands observed with IBIL to the before mentioned intrinsic defects.

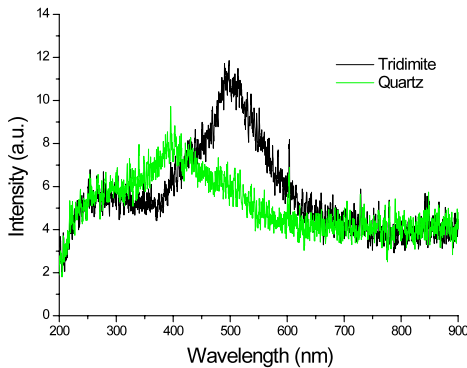


Figure 3. IL spectra for quartz and tridimite.

Tridimite IBIL spectrum has never been published before. Our spectrum in figure 3 shows a broad and complex band with a shoulder at 420nm and peak at 500nm. The similarities between the quartz spectrum and the tridimite are evident in the figure, though there is a shift of around 100nm between both curves from the UV (400nm) to the visible part (500nm) of the electromagnetic spectrum. We believe that the origin of this band is basically the same that has been suggested for quartz; this is, that the emission is due to intrinsic defects. The shift towards higher wavelengths would be related to the structural variations of the tridimite in relation to quartz. In this sense, the local symmetry corresponding to  $Al^{3+}$  sites and bonding angles that make the quartz a much more opened structure than tridimite, would bring as a consequence the variation of the crystalline field and thus the emission wavelength. The 100nm variation observed indicates that the local field in tridimite is weaker than in alpha quartz.

## CONCLUSIONS

Polymorph minerals are natural materials that share the same chemical composition whilst presenting different structure. Because of this dissimilarity, polymorphs should show sensitive differences in their luminescent spectra. No previous studies have been done in these materials with the IBIL technique. In this work we have presented some IBIL spectra of polymorphs that confirm this fact and set the first steps towards using this technique for polymorph differentiation.

In the range of the electromagnetic spectrum studied (200-1100nm), diamond showed luminescence due to the presence of nitrogen-related defects while graphite did not present any luminescent feature in this region.

As for the  $Al_2SiO_5$  polymorphs, kyanite featured IBIL bands due to the presence of  $Cr^{3+}$  in diverse non-equivalent octahedral sites whereas sillimanite only presented a broad band in the 770nm region and andalusite did not yield luminescence in the area of the electromagnetic spectrum studied.

Quartz and tridimite have shown similar IBIL bands in their spectra if only shifted some 100nm towards the IR region. This is attributed to the change of symmetry of the cationic site due to the variation in the angle of the Si-O bond that consequently results in a change of the crystalline field.

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