Ionoluminescence and minerals: the state of the art

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Until now, Ionoluminescence (IL) has been mainly exploited to detect impurities or defects inside materials, most of which, synthetic. This paper gives a summary on new applications of IL, going one step further by applying the technique to minerals, simulants and synthetic analogues. A new IL model is discussed.

Keywords: Ionoluminescence; mineral; defects; impurities; mechanism.

Hasta el presente, la Ionoluminiscencia (IL) ha venido siendo utilizada principalmente para detectar la presencia de defectos en materiales, la mayoría de los cuales son sintéticos. En este trabajo se presenta un breve sumario de nuevas aplicaciones de la IL, yendo unos pasos más allá en la aplicación de la tecnica a minerales, análogos y sintéticos. Se presenta, también, un nuevo modelo de IL para explicar los resultados obtenidos.

Descriptores: Ionoluminiscencia; mineral; defectos; impurezas; mecanismo.

1. Introduction

The mineral world not only surrounds us creating breathtaking landscapes of incomparable beauty; though part of our everyday surrounding, minerals are considered too symbols of wealth since Antiquity in different grounds. The possession of these materials has evidenced the economic personal status of a household whether in the form of riches found in the building materials and ornaments of their properties –think about the roman mosaics for instance, or the *stucchi* or *affreschi*-, or in the possession of jewels such as the Garnet collections found in Merovingian tombs, the Visigoth or the more known Egyptian treasures. From the personal status of one single person or family to the important retribution for economy by means of their exploitation, mineral resources have always been associated to incoming assets for the people or countries that posses them. Even now, the industrial mineral market still sustains a considerable part of the economy in many countries.

Minerals have been too an inspirational material in science and technology. Technology has been mainly based for centuries in mineral knowledge and mineral proprieties. Perhaps, one of the most interesting aspects of minerals nowadays in this field, is the fact that based on this mineral knowledge the scientific community has been able to propose and develop new materials adapted to solving a great variety of problems. From the well-known ruby gemstone turned to ruby laser in the '50s to the latter developments in the use of diamond as a body compatible biologic dosimeter (1), minerals remain a constant source of progress.

Progress achieved based on the knowledge of minerals has been running parallel to the development of new interesting techniques bearing great social and economic impact. Fundamentally, new techniques based on the interaction of radiation with matter have been feeding back and expanding the knowledge of the materials and vice versa. Datation methods of geological and archaeological materials by luminescent methods [2,3], retrospective dosimetry of natural or industrial accidents [4], detection of irradiated materials [5,6] and characterization by means of non destructive methods (PIXE, RBS, Raman, XRF) of antique materials [7,8] are only some examples of the contribution of this fact to various scientific areas.

One of the most recently techniques developed based on radiation-matter interaction is Ionoluminescence (IL). This technique had not been applied to mineral samples, but was basically employed for new synthetic materials' characterization before [9-20]. Latest works prove that IL can be too an interesting tool to characterise minerals [21,22].

Ionoluminescence (IL) can be defined as a non-thermal light emission phenomenon induced by bombardment of high energetic accelerated particles or ion beams. Though this phenomenon has been known for quite a long time, there has not been until recently any study or model capable of explaining it. Some basic notions related to the IL phenomenon have been however reported by diverse authors [11,12,21,22].

IL is just a form of luminescence that uses an accelerated ion beam as excitation source. The luminescent signals achieved with IL are related to the emitting atoms, concretely to the energy levels of their external valence electrons. In this regard, IL is very sensitive towards the chemical state (valence), and the local symmetry of the emitting atom, as well as to the covalence character of the bonds it forms inside the material and the spatial symmetry of the crystalline lattice in which that atom is located. IL is especially sensitive towards the presence of certain elements, such as d-transition metal ions and rare earths.
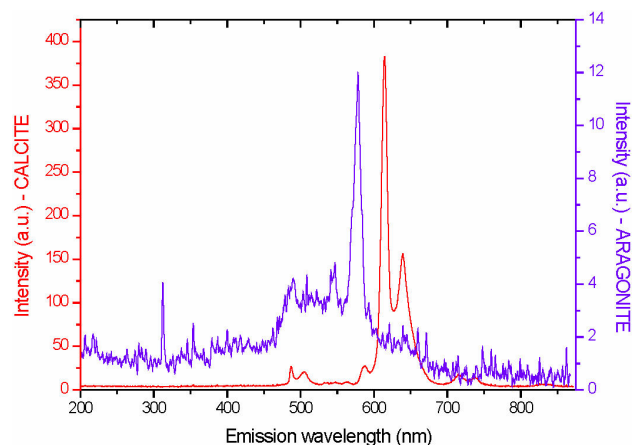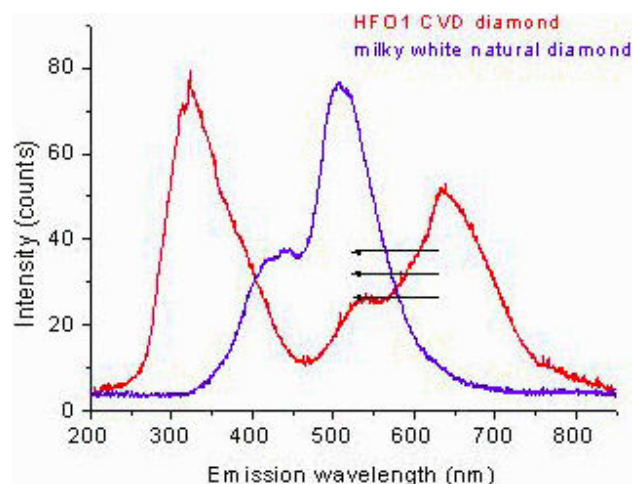
FIGURE 1. Calcite and Aragonite IL spectra.

FIGURE 2. IL spectra of natural and synthetic diamond. Nitrogen bands are in the orange region of the spectrum for CVD while for natural samples they appear shifted towards smaller wavelength [24].
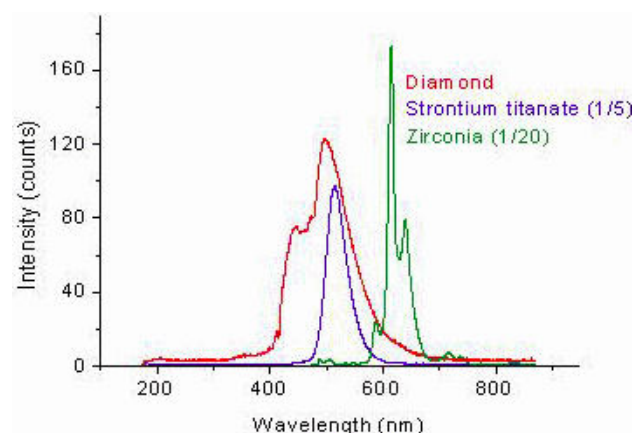

FIGURE 3. IL spectra of diamond, strontium titanate and zirconia [24,25].
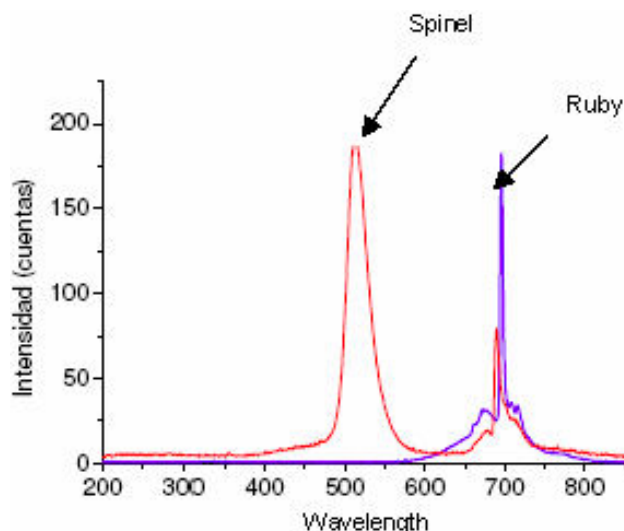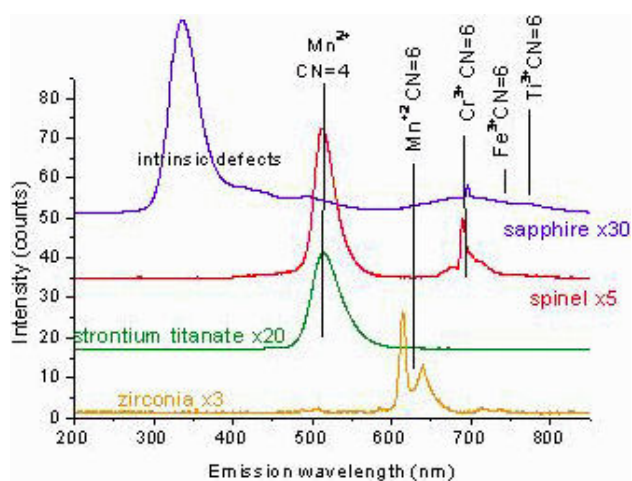

FIGURE 4. IL spectra of Ruby and synthetic spinel.

FIGURE 5. IL spectra of some diamond synthetic simulants: sapphire (blue line), spinel (red line), strontium titanate (green line) and zirconia (orange line). They all feature d-transition metals: Mn^{2+} and/or Cr^{3+}. Synthetic sapphire also shows intrinsic defects and Fe^{3+} and Ti^{3+} ion emissions [22].

As any other luminescent techniques, IL is suitable for studying radiation-matter interaction processes. Its performance has been mostly compared to that of Cathodoluminescence (CL), and it has been found that IL furnishes more representative information than CL due to a higher penetration range of the accelerated ion beam inside the material when compared to that of an electron beam.

Because IL uses a higher energy beam (MeV range), it is also in grade of exciting higher electronic levels that cannot be reached with CL (keV range), plus, there is a possibility of doing non invasive analysis in air that better suites the requirements for archaeological and artistic samples.
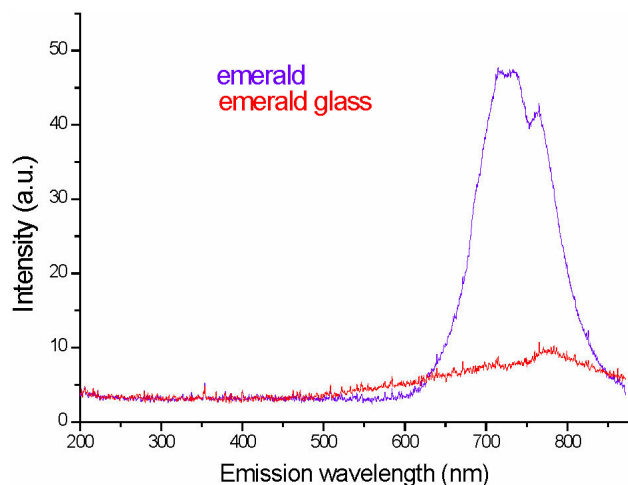
FIGURE 6. IL spectra of an emerald glass and a natural emerald mineral sample. Note that the beam current intensity applied for the obtention of the emerald glass signal was approximately two times higher than in the emerald crystal, and that in spite of this IL intensity is near five times less [22].
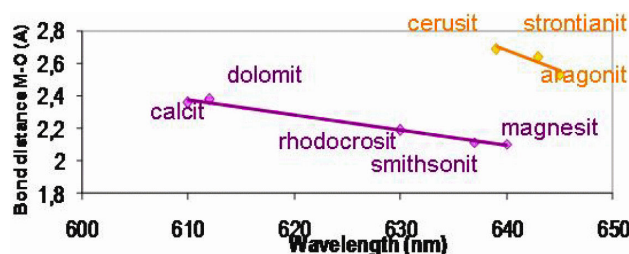

FIGURE 7. Rhombohedral and Orthorhombic series of carbonates. Each point represents Metal-Oxygen of polyhedron coordination distance vs characteristic IL emission of Mn^{2+} ion.
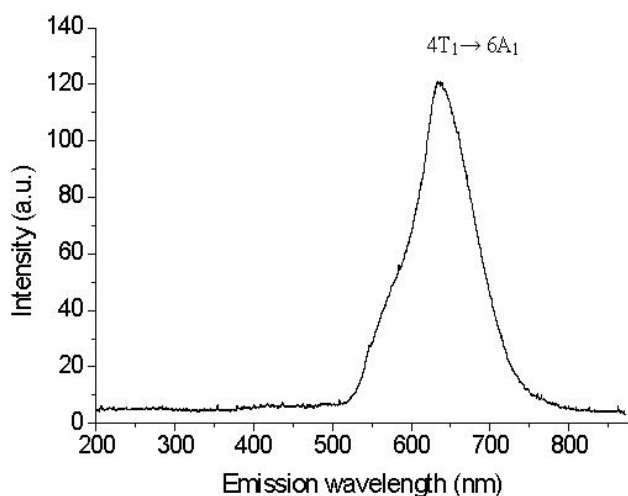

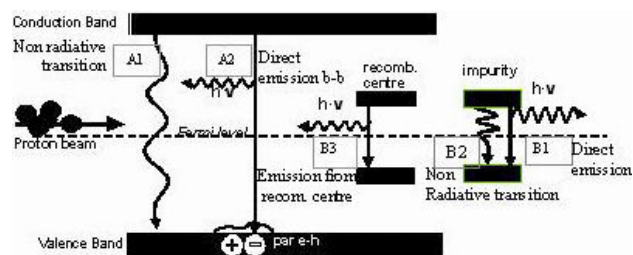FIGURE 8. Dolomite IL spectrum.

FIGURE 9. IL mechanism as inferred from the mineral experience and based on Agulló *et al.* mechanism [26].
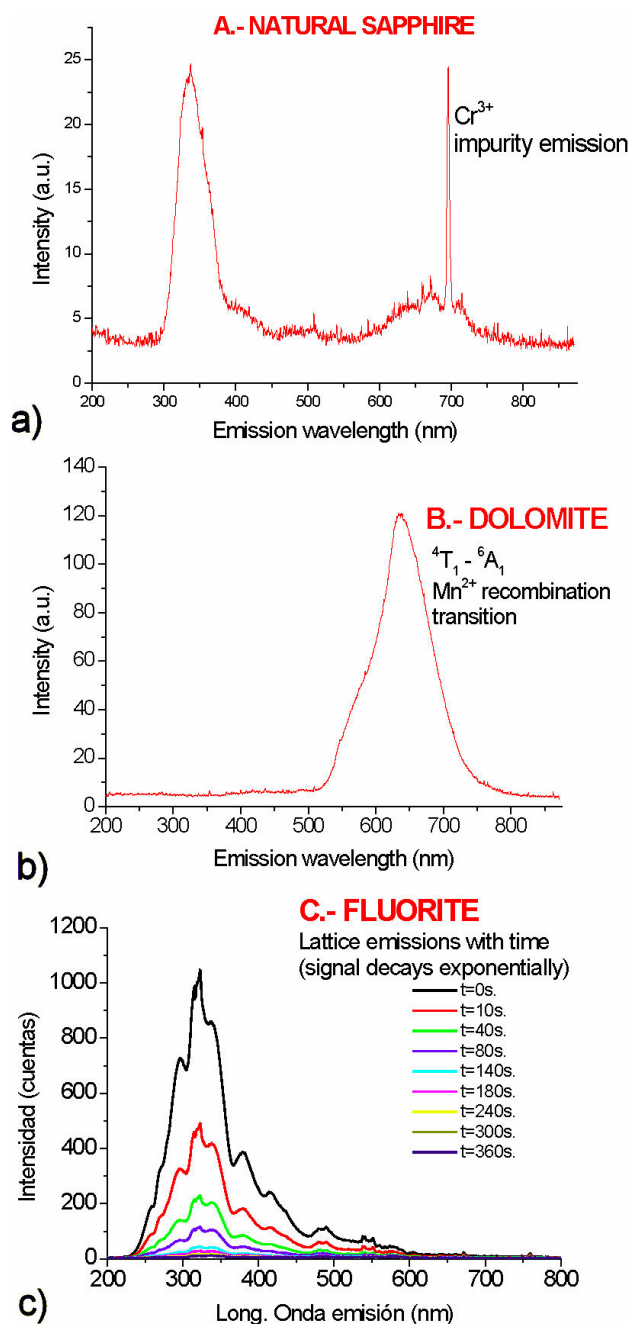

FIGURE 10. IL spectra of different minerals. A) Cr^{3+} emission impurity in corundum. B) Mn^{2+} emission from recombination centre in dolomite. C) Lattice emission band in fluorite crystals.

TABLE I. Carbonates, their M-O bonding distance and $^4T_1 \rightarrow {}^6A_1$ transition assigned to Mn^{2+} ion.

Crystalline System and Metal number coordination (CN)	Mineral	Formula	Average $M-O$ distance(Å)	$\lambda emission(nm) \pm 0,9nm$
	Calcite	$CaCO_3$	2,3598	610
	Magnesite	$MgCO_3$	2,1018	640
Rhombohedral (CN=6)	Rhodocrosite	$MnCO_3$	2,19	630
	Smithsonite	$ZnCO_3$	2,1107	637
	Dolomite	$CaMg(CO_3)_2$	2,38(A site) 2,084(B site)	612 642*
Orthorhombic (CN=9)	Aragonite	$CaCO_3$	2.53	645

IL can be used not only for characterising materials; it can be applied during material modification with ion beams in order to follow the creation of intrinsic defects or even the change of the energy of the bombarded ion inside its lattice or the change of the ion species [22]. One great advantage is that it can be run altogether with any other IBA techniques.

The present work gives a general overview on the state of the art of the application of IL generated by minerals. Examples that enhance different features will be here illustrated in order to show the technique's potential. Differentiation of polymorphous, discarding of simulates, crystal field studies, examples will be set, to have an overview on its possibilities. Finally an IL mechanism is considered in order to explain our experimental results.

2. Experimental

Measurements were carried out inside a vacuum chamber at the Pelletron Accelerator of the Instituto de Física (Universidad Nacional Autónoma de México). The set-up has been described elsewhere [21]. A 1.9 MeV proton beam of variable intensity (250 nA - 3μA) depending on the sample's sensitivity towards the IL process was used as excitation source. Measurements took just some seconds for each sample.

3. Results and discussion

1) Differentiation de polymorphous : IL calcite- aragonite ($CaCO_3$)

Polymorphs are minerals appertaining to the same specie that bear the same crystal chemical composition but have different crystalline structure. There are several examples of polymorphic mineral composition; e.g. calcite and aragonite for $CaCO_3$; anatase-brookite and rutile for TiO_2; andalucite - kyanite and sillimanite for Al_2SiO_5; graphite – diamond for C.

It has been suggested that IL can be used for distinguishing polymorphs as the different space group of symmetry imposes great variations in energy levels of luminescence impurity and as consequence the variation of emission spectrum. An example is given in Fig. 1 for calcite – aragonite polymorphous.

The main emission observed for $CaCO_3$ polymorphous, linked to $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} ion transition, have been placed in Table I for comparison between these polymorphs. The wavelength observed for this transition is linked to the variation of the lattice space group, local hole symmetry, polyhedron coordination, crystal field and mean Metal - Oxygen distance [23]. It is expected similar variation from above examples given; that is, diamond- graphite, or andalucite-kyanite- sillimanite.

2) Applications in gemstones.

Most of the principal applications that are described in this work are related to minerals that are part of historic-artistic artefacts, for this has been for many years our main expertise field. In this regard we would like to point out some particular IL accomplishments.

a) Differentiation of natural diamond (C) from its synthetic analogous (C).

The presence of diamonds in historic objects is relatively new. However our interest in differentiating diamonds from its synthetic analogous looks more into the future rather than the past. It is a well-known fact that there is an overgrowing presence of synthetic diamonds in the market so that discrimination methods are being increasingly demanded in the jewellery field.

Previous IL studies [22,24] have allowed to establish some future bases of encouraging studies that will serve to the differentiation of natural diamond from its synthetic analogue (Fig. 2).

By comparing IL spectra of both diamond and CVD synthetic diamond (Fig. 2) it becomes clear that nitrogen bands for the synthetic CVD diamond are in the orange region of the spectrum for CVD while for natural samples they appear shifted towards smaller wavelength.

This research line has important potential applications facing the future in order to differentiate minerals from their respective synthetic analogous.

b) Differentiation of diamond from its imitations (simulants) (Strontium titanate- $SrTiO_3$ and zirconia ZrO_2).

Since the '40s decade, the world of diamond jewellery has been in direct competence with synthetic compounds that are always economic and with better optic qualities. IL can be used to discriminate these materials as can be seen from the (Fig.3).

In (Fig.3) the IL spectrum of a natural diamond simple can be seen together with two of its most used synthetic analogous; strontium titanate and zircon. While diamond spectrum shows bands centred in the visible region (400-600nm) related to the presence of nitrogen centres, strontium titanate and yellow zircon show bands related to Mn^{2+} in Td and Oh coordination respectively.

c) Diferentiation of ruby (Al_2O_3 :Cr^{3+}) and red spinel (XY_2O_4; X=Mg, Fe, Zn, Mn, Y= Al, Mg, Fe, Ca, Ti).

Due to its extraordinary resemblance, spinel and ruby have been used indiscriminately to some extent through history, though not always in a conscientious way. There are some well-known examples of this fact, such as the Black Prince Ruby (an spinel) in the English crown.

It's discrimination does not seem quite a problem in the scientific world. The only problem that arises for gemstone characterisation is often the need to extract the gemstone from the artefact where it is located. Here is where techniques such as Raman, IR or more recently PIXE or IL can be of use.

To interpret correctly the IL results, there are some considerations that need to be taken regarding the structure of the compounds that are to be differentiated: Ruby and Spinel, in this case.

It is a well-known fact that ruby (Al_2O_3:Cr^{3+}) is the deep red variety of corundum (Al_2O_3). From a structural point of view ruby presents almost an hexagonal oxygen packing, with 1/3 oh the Oh sites left by this arrangement occupied by Al^{3+} ions. In the ruby variety of corundum, some of those Al^{3+} would be substituted by Cr^{3+}.

On the contrary, in the spinel series, the oxygen atoms are arranged in a cubic close-packing with Td and On interstices. There are two types of cations X^{2+} (Td sites) and Y^{3+} (Oh sites) for normal spinels.

The IL spectrum obtained for a ruby sample and a spinel is shown in (Fig.4). The emissions obtained round 700nm correspond to the $^4T_2 \rightarrow ^4A_2$ chromium (III) transitions that occupy the Oh sites in the structure. The 520nm emission on the contrary is consistent with the ^4G—^6S transition of Mn^{2+} in Oh coordination.

The strong differences existing between both spectra allow the discrimination of these two gemstones without dismounting the jewellery piece. The knowledge of the role that impurities play in the lattice and their possible situation inside it (coordination) is crucial for the scope of differentiating gemstones and synthetic analogous as (Fig.5) shows.

In [Fig.5] synthetic sapphire features Cr^{3+} transitions and intrinsic defects [20]. Fe^{3+} and Ti^{3+} [16] are too present. Spinel's bands consist of identical Cr^{3+} transitions in the same wavelength range, but show Mn^{2+} impurities (513nm) as well [21].

Emission spectra of strontium titanate (514nm) and cubic zirconia (487, 505, 587, 613, 639, 715 and 738 nm) also in (Fig.5) have been too related to Mn^{2+} transitions [21,22].

3) Crystalline and vitreous material

Due to the non existing long-distance symmetry in vitreous materials, emitting atoms are not placed in equivalent sites inside the vitreous matrix. This makes the signal less intense and broader when compared to a crystalline material.

An example of this fact can be seen in an emerald crystal when compared to an emerald glass that bears the same composition of the former one. Emissions in both cases are due to the presence of Cr^{3+}.

4) Crystal field studies

The principal idea of performing crystal field IL studies is that of searching a model that might explain the luminescent behaviour of crystalline solids. As an example we provide two of these applications.

a) Process modelization.

According to Fonda's theory (23), and provided by a sort of minerals appertaining to the similar structural minerals of two series such as carbonates, it is possible to prove that for oxygen bearing compounds the variation of the

IL emission wavelength is a function to the distance metal to oxygen in those compounds (Fig.7). This function constitutes and indirect measure of the crystal field.

b) Site differentiation.

The data plotted in (Fig. 7) are in agreement with the pattern predicted by crystal field theory (23); that is, in oxygen containing compounds of the same structure, the luminescence emission shifts to longer wavelengths as the bond spacing decreases. The manganese ions are thus very sensitive to their immediate environment, and so changes in the metal to oxygen distance results in wavelength shifts. The importance of this dependence on the bond length can immediately resolve some problems on the assignments of ions in structure; for example, the problem on the assignment of Mn^{2+} to the A or B lattice sites of dolomite [25].

The observed signal at 642 nm (Fig.7), assigned to $^4T_1 \rightarrow {}^6A_1$ can throw some light to this question. This Mn^{2+} site in dolomite fits the pattern of all other rhombohedral carbonates, which means that the majority of the Mn^{2+} ions occupy the B site inside its structure (with a metal-oxygen distance of 2,084 Å). IL shows other emission features, and in particular there is a luminescence shoulder near 600 nm. This would match in wavelength terms to Mn^{2+} hosted in A site geometry (2,38 Å). Taking in account relative intensity of 642 nm and 600 nm emission bands should give an estimation of 60 % of Mn^{2+} in B site and 40% of Mn^{2+} in A site.

5) IL mechanism

For the moment being, there is no thing such a well established IL mechanism that may satisfactory explain all the aspects involved in the IL phenomenon. However, we have made some adjustments to the one suggested by Agulló *et al.* [26] following the Band Theory in order to explain some of the results obtained in our IL mineral studies.

When the proton beam strikes the lattice of the mineral, most of its energy is employed for the creation of an excited electron cloud. The excited material then stabilises by emitting energy in different forms. There are two main de-excitation paths: A and B (Fig.9) that can be pictured as follows.

A: Lattice relaxation. This path can be achieved through different processes: A_1 and A_2.

A_1.- Non radiative emisión of phonons from the lattice.

This would be the most probable process occurring. The de-excitation process would take by means of the non emitting lattice relaxation (phonon creation).

This process would increase the temperature in the crystal (if the irradiation is continuous and the ion flux remains constant) and would lead to amorphousization of the crystalline area involved. This mechanism is known as Thermal Spike Model.

A_2.- Lattice characteristic light emission.

By characteristic light emission of the lattice we mean the emission coming from the Band system in the crystal; CB and VB, as has been observed for the silicon-oxygen tetrahedra in silicates or pure SBN).

After ionization takes place, there would be some emission coming from the correspondent excited state (CB) to the fundamental level (VB). The results lately obtained in IL of pure compounds seem to place this emission in the UV region between 250-400nm [27].

B: Relaxation through excited levels of an impurity present in the lattice. Here again there are three different possible paths.

B_1.- Radiative emission of an impurity located in the crystal.

The radiative emission of an impurity located in the matrix of the crystal takes place from their excited level to their ground level. This emission is very sensitive towards the valence state, coordination and distance from the emitting atom to the element to which is coordinated. The light emission generated in this way fades with the ion beam dose and an increment in temperature is observed. The velocity in which this occurs is particular of each defect; different centres or defects have different light fading rates. This behaviour can be fitted to exponential curves (such as those for diamond and fluorite).

B_2.- Non radiative decay of localizad excitons (phonons).

This process can occur either in a spontaneous way (in which case it would favour the A_1 path) or require overcoming a potential energy barrier.

B_3.- Energy transfer from the impurity to recombination centres.

This possibility widely discussed in other luminescent phenomenon (CL, TL) has been evidenced too for IL in mineral carbonates.

The A and B mechanisms would serve to explain the different types of IL spectra obtained for minerals found until now and represented in Fig.10. This is:

1. Emission coming from an impurity.

2. Emission coming from recombination centres.

3. Emission from the lattice.

4. Conclusions

We are aware that there is a large path ahead to master some of the aspects concerning IL in materials, results obtained in this work lead to some conclusions:

a) IL, both in natural minerals and synthetic crystals, is a technique with great prospective in future application field that remain still unexplored such as the differentiation of polymorphs, the discrimination of minerals from its synthetic analogues, the study of the geometry of sites inside crystalline lattices or the degradation of crystalline materials for instance.

b) In a rough schematic way, the IL phenomenon can be explained by a very simple model:

$$\text{Proton beam} \rightarrow \text{crystalline material (lattice + impurities)} \rightarrow \text{LATTICE* + IMP*}$$

$$\rightarrow \text{fonons (heat)} + h\nu_{\text{LATTICE}} + h\nu_{\text{IMP}} \tag{1}$$

A proton beam colliding in a crystalline material (an ensemble of lattice plus impurities) generates some electron cloud that appears localized in the lattice and the impurities, thus having an excited lattice and excited impurities. Some different relaxing mechanisms are available for the material to return to its ground state, namely non-radiative and radiative emissions coming either from the lattice or from the impurities. This various mechanisms are dependent on irradiation time (proton dose). The final effect is that of the heating of the lattice that thermally quenches all the other forms of emission.

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