

Luminescence Property of Perovskite Structure

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Abstract — The photoluminescence property (PL) is a desired property for materials and the luminescence of perovskite type compounds have been known for a long time. This property was first identified to crystalline perovskite and it has only been recently identified in structurally disordered perovskite. In this work, we present a study about photoluminescence of structural disordered perovskite-structured compounds. There will be a special focus on the PL emission of titanates and zirconates: the main representants of these materials class. It will be discussed the origin of PL emission in these compounds. In addition, it will be related rare earth ion-doped structural disordered perovskite and PL emission.

Index Terms — Luminescence, perovskite, order-disorder, rare earth.

I. INTRODUCTION

In recent years, photoluminescent properties (PL) has been attracted great interest in the development of new ceramic materials with optical properties of high efficiency allowing advances of great importance for modern society.

Some factors to photoluminescent materials such as, structural defects, reaction kinetics and processing temperature are decisive to the properties and performance of these materials for possible applications in electro-optical device. From the technological point of view, the possible applications of these material are in economic fluorescents lamps, medical imaging X-ray, LED, computerized tomography and solid-state lasers.[1-6]

Luminescence is defined broadly as the generation of light in excess of that radiated thermally. The exciting radiation is absorbed by the activator, raising it to an excited state. The excited state returns to the ground state by emission of radiation. The radiative emission process competes the nonradiative return to the ground state. The electromagnetic radiation emitted by a luminescent material is usually in the visible region, but it can occur in other regions of the spectrum. [7-12]

The photoluminescence emission were observed in several ceramic materials, which are intensely studied in the literature, such as zirconates (PbZrO_3 , SrZrO_3), molibdates (SrMoO_4 , BaMoO_4 , PbMoO_4), tungstates (SrWO_4 , CaWO_4 , SrWO_4) and specially in titanates (BaTiO_3 , PbTiO_3 , SrTiO_3).

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II. LUMINESCENT EMISSION TO PEROVSKITES

The ABO_3 (A and B are cations and O is the oxygen anion) type perovskites constitute one of the most important classes of materials and they has received special attention in recent years due to its applications in several electronic technology.[13-18]

According to the classic theory, metal oxides can be classified as network formers (W, Zr, Mo, Ti) and network modifiers (Ca, Sr, Ba, Pb). Network forming oxides have a basically covalent nature and can form random three-dimensional oxianion networks.. The network formers must be based on metals whose chemistry preferentially forms oxianion complexes with sixfold metal–oxygen coordination (octahedral coordination with Oh symmetry). Oxianions formed of Nb, Zr, V, Mo and W, for instance, are good candidates. Metals that preferentially form cations, such as Na, Li, Ca, Ba, Sr and Pb, can be used as network modifiers. [19-21]

Over the last 25 years, various hypotheses were proposed to explain the PL phenomenon in crystalline or disordered titanate compounds. There is a consensus on the fact that PL emission is the result of a radiative decay of the excited electrons to the ground state. In the case of a nonradiative return to the ground states, the energy of the excited states is used to excite the vibrations of the host lattice, that is, to heat the host lattice. On the other hand, different research attempt to explain how the radiative decay happens through new theories, such as self trapped excitons (STE), and semiempirical quantum chemical calculations, that the origin of the intrinsic excitonic luminescence of ABO_3 perovskites at low temperature is linked to the recombination of electrons and hole polarons forming a charge-transfer vibronic exciton.[9, 22-28]

III. SYNTHESIS OF DISORDERED PEROVSKITES

The solid-state reaction route is the most widely used method for the preparation of polycrystalline oxides. The perovskites are traditionally prepared using powders precursors containing each metal, such as carbonates, acetates or nitrates and fired at temperatures often in excess of 1000 °C for periods of days, or even weeks, with intermittent regrinding of the mixture to ensure homogeneity. The products formed by this synthesis are highly crystalline but there is little scope for control of crystal form, and only the most thermodynamically stable phases are produced. For instance, the perovskite structured CT crystal was initially prepared by conventional solid-state reaction using a

stoichiometric ratio of TiO_2 and CaCO_3 at temperature of 1350°C . [29]

Although the crystal chemistry (i.e., composition and atomic structure) of an oxide phase is vital in dictating its underlying properties, in terms of practical applications control of crystal form and crystallinity (morphology, particle size and shape, textural properties, or porosity) is also vital for allowing the fabrication of useful devices based on any material. [30, 31]

The development of new techniques to produce covalent solids based on soft synthesis at low temperatures created new prospects in this area, mainly thanks to the possibility of producing periodically disordered structures with preferentially oriented atoms, creating controlled systems in templates, zeolites, oxalates, polymers or complexes environments for metallic ions, resulting in new oxides with new morphologies and surprising properties.

The synthesis and properties of new compounds are closely linked to the identification of their crystal structures. The undistorted perovskite structure is cubic, and it can be described as a framework of corner-shared BO_6 octahedra that contains A cations in 12-coordinate sites. This is a fully ordered structure. [19-21, 32]

The existence of imperfections or defects leads to disordered structures. A structurally disordered solid is a solid in which there is no some complete order of the positions of the atoms. Structural disordered can be assigned to oxygen vacancies, lattice defects, impurities and/or local bond distortion. Any of these defects provokes distortions from the ideal perovskite structure and it can significantly impact the physical properties. Cation substitutions, which can take on either ordered or random arrangements, have been used with much success to provoke structural disorder. For instance, Qin et al. [33, 34] studied the local distortions associated with substituting Sr for Ca are expected to impact on the phase transitions of $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ which can be explained in terms of octahedral tilting. Zhang et al. [35] investigated the structures and phase diagram for the system $\text{CaTiO}_3\text{-La}_{2/3}\text{TiO}_3$. They observed a tetragonal or orthorhombic distortion accompanying cation ordering and/or octahedral tilting in role of La substitution.

Perovskite oxides can be prepared in a disordered form using an appropriate synthetic method. Chemical preparation methods, especially co-precipitation, sol-gel synthesis and polymeric routes, offer advantages over traditional physical reactions of component oxides in terms of higher purity and greater homogeneity, as well as the possibility of producing oxide systems at various self-organization levels by controlling the heat treatment of an initial precursor. Therefore, it is important to understand the influence of different processing methods on the structural organization degree and optical properties of these materials.

In this context, two synthetic routes draw attention: (i) the Polymeric Precursor Method (PPM) and (ii)

Microwave-Assisted Hydrothermal Method (HTMW). These methods are able to synthesized perovskites with different structural disorder degree.

The PPM method is based on the chelation of cations by a carboxylic acid, such as citric acid, in an aqueous solution. The polycondensation reaction of this method materials results in an amorphous phase or a low degree of crystallinity. Thus, it is necessary to perform a crystallization procedure, e.g. usually using heat treatment. Two kinds of powder can be obtained: the first, a structurally disordered powder, which was heat treated below the crystallization temperature, and the second, a structurally ordered powder, which reached crystallization. Moreover, it is possible to control the order-disorder degree in desired material by control of the heat treatment temperature. [36-38]

The HTMW method is a genuine low temperature procedure that allows high heating rates and short annealing times, since it is observed the interaction of the microwave radiation with the matter. So, HTMW process allows a rapid and homogeneous microwave heating during the hydrothermal method, accelerating like this the crystallization process of the synthesized products through the increase of the nucleation rate. However, the powders obtained present a lower amount defects, i.e., structural disorder. [32, 39, 40]

The Figure 1 illustrates the two possibilities to obtained disorders structures.

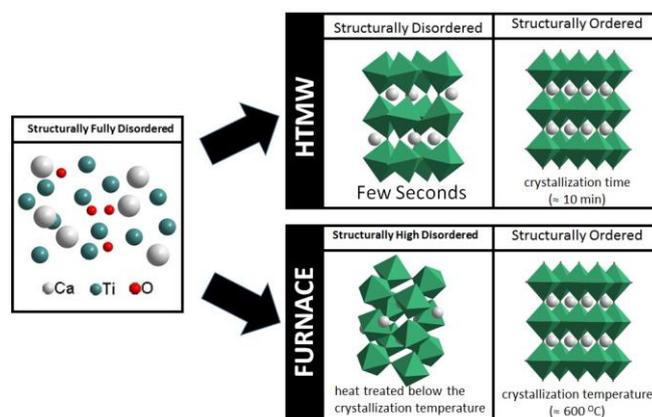


Figure 1: Disorders structures obtained by PPM and HTMW methods.

IV. LUMINESCENCE OF ORDERED PEROVSKITES

Photoluminescence in crystalline titanates has already been well established. As explained by Blasse [9], the PL arises from a radiative return to the ground state, phenomenon that is in concurrence with the non-radiative return to the ground state where the energy of the excited state is used to excite the vibrations of the host lattice, i.e., to heat the lattice. The radiative emission process occurs more easily if exist in the structure trapped holes or trapped electrons. [19, 26-28]

In addition, luminescence of rare-earth ions doped in

perovskites type oxides was actively investigated in 1960s and 1970s. There is ample experimental evidence that in the rare-earth rich perovskites vacancies do indeed accumulate onto alternate A-site planes, that is there is a layered ordering involving the alternation of cation-rich and cation-poor planes.[20, 41-43] The luminescence spectra of rare earth ions in crystal are composed of sharp lines ascribed to electronic transitions within 4f shell.

Yamamoto and co-authors [42] investigated the existence of a correlation between the emission shape and the site symmetry of rare earth ions using various perovskites with different crystal structures as host materials. They observed different emission to Eu^{3+} ions in SrTiO_3 and BaTiO_3 due to site symmetry occupied by Eu^{3+} .

The Figure 2 presents spectra emission to different rare-earth ions doped CaTiO_3 . It can be observed only rare earth ions emission due to part of the charge transfer band (CTB) of $\text{RE}^{3+}-\text{O}^{2-}$ bond, and by the f-f transitions within electron configuration.

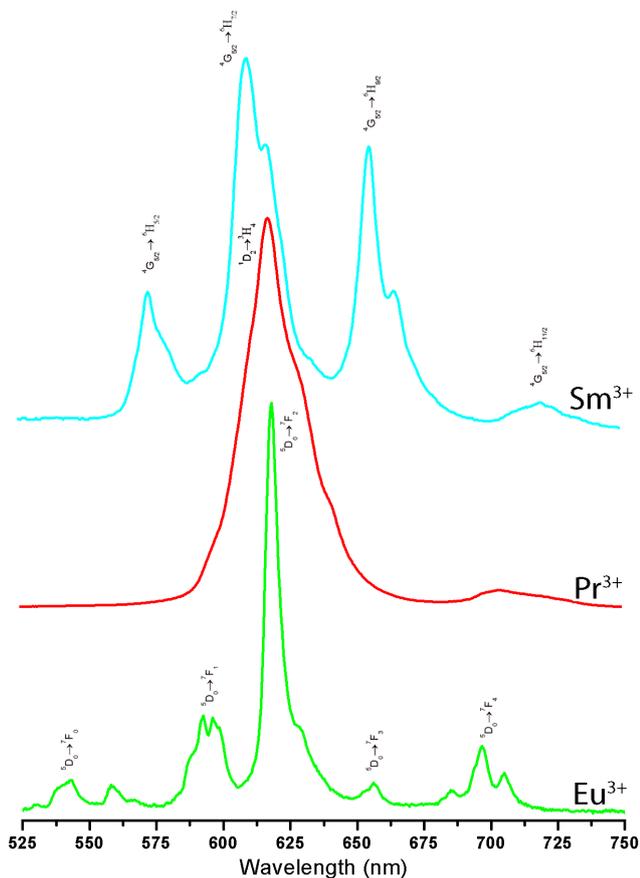


FIGURE 2: PL spectra of rare-earth doped CaTiO_3 obtained with excitation wavelength the 350.7 nm.

Special attention has been given to praseodymium-doped perovskite. Pr^{3+} doped ATiO_3 ($A = \text{Ca}, \text{Sr}, \text{and Ba}$) systems are attractive candidates for red phosphor applications with close to “ideal red” emission and high chemical stability, e.g., $\text{CaTiO}_3:\text{Pr}^{3+}$ exhibit intense sharp emission at 612 nm. One major research focus involves understanding the influence of charge compensation at the Pr^{3+} defect centers on the efficiency of the PL. The emission is attributed to the

characteristic $1D_2 \rightarrow 3H_4$ transition of Pr^{3+} .[44] In order to enhance the luminous properties, many researchers have studied these phosphors by varying the concentration of praseodymium, different charge compensators, and different synthesis methods.[45-51]

An interesting study was conducted by Pinel and co-authors [52]. They reported different luminescence properties to Pr^{3+} in CaTiO_3 and CaZrO_3 . This authors believe that the relative high stability of the 4+ valence state of zirconium is not in favour of low-lying intervalence charge transfer state, allows to explain the difference of optical behaviour between $\text{CaTiO}_3:\text{Pr}^{3+}$ and $\text{CaZrO}_3:\text{Pr}^{3+}$.

Upconversion is an anti-Stokes emission process that converts long-wavelength pump sources into short-wavelength emission.[53] There have been many reports on various host matrix for UC luminescence, such as oxides, fluorides, phosphates, and, evident, perovskites.[54-59] Due to the abundant energy levels and narrow emission spectral lines, the Er^{3+} ion, which is the first and the most popular ion showing green and red UC emissions. Paired, Yb^{3+} ion is a well-known sensitizer that will conspicuously increase the optical pump efficiency due to the high absorptin cross-section of Yb^{3+} ion around 980 nm and the efficient energy transfer from Yb^{3+} ion to Er^{3+} . Efficient infrared-to-visible up-conversion is reported in the doped perovskites: Er [60], Er and Yb [61, 62], Tm and Yb [63], Er,Tm and Yb [64], etc.

The Figure 3 presents spectra emission to erbium and ytterbium ions doped CaTiO_3 and CaZrO_3 . In both, it is observed efficient infrared-to-green up-conversion emission.

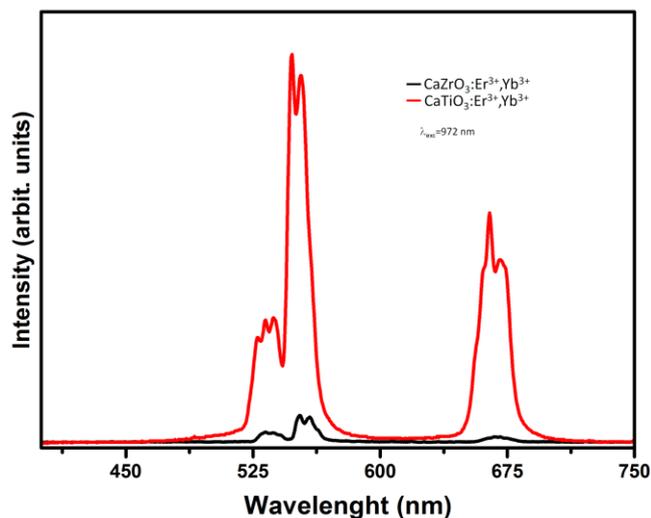


FIGURE 3: PL spectra of CaTiO_3 and CaZrO_3 obtained with excitation wavelength the 972 nm.

V. LUMINESCENCE OF DISORDERED PEROVSKITES

The structural defects modify the electronic band structure of perovskites, affecting its PL properties. The luminescent emission to disordered perovskites have been target of many investigations.[65-71] Although the origins of photoluminescence (PL) are not yet entirely understood in defect-related materials, there is mounting evidence that emission arises from the structural defects, such as: vacancies, impurities, radical impurities, donor-acceptor

pairs, etc.

For instance, there are in the literature a series of disordered (amorphous) titanates, zirconates, niobates perovskites prepared by a PPM method. A visible emission band was observed in the disordered samples under an excitation with energy lower than the band gap at room temperature. [65-71] It believes that the visible emission cannot be attributed to a band-to-band transition of titanates, because the energy of the excitation line used in these experiments is much lower than the band gap of ordered perovskites, and consequently it is impossible to excite an electron directly from the valence bands to the conduction bands.

The origin of this emission has been amply discussed in the literature. For instance, structurally ordered SrZrO₃ presents [ZrO₆] clusters environments and [SrO₁₂] clusters environments, i. e., the coordination shell around Zr atoms is composed by six oxygen atoms and coordination shell around Sr atoms is composed by 12 oxygen atoms. On the other hand, structurally disordered SrZrO₃ presents two types of environments for zirconium and two types of environments for strontium: [ZrO₅], [ZrO₆], [SrO₁₁], and [SrO₁₂]. The presence of different complex clusters is responsible for introducing delocalized electronic levels inside the band gap.[28] To clarify these concepts, the ordered and disordered clusters can be illustrated on following simple example to zirconates (Figure 4).

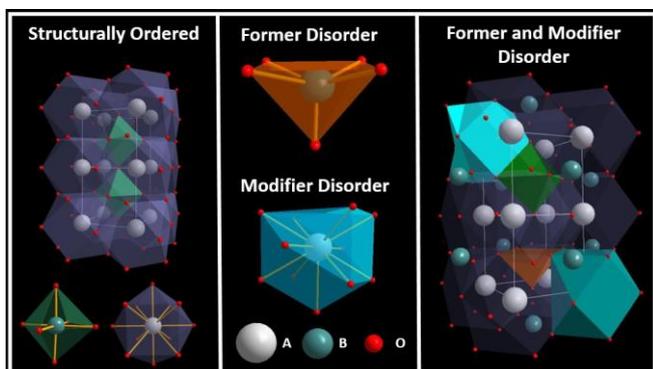


FIGURE 4: Structural models for the CZ: (a) ordered and (b) disordered.

The first one is a crystalline or ordered structure composed of the ideal [ZrO₅-O-ZrO₅] and [SrO₁₁-O-SrO₁₁] cluster networks, where the general form of ABO₃ of perovskite it is used. The second type consists of a disordered structure associated with the presence of tilted octahedral cluster containing networks of [ZrO₅-O...ZrO₅] and [SrO₁₁-O-SrO₁₁] clusters. Another possibility is not shown, but it would have the presence of networks of randomly mixed [ZrO₅-O...ZrO₅] and [SrO₁₁-O...SrO₁₁] clusters.

Experimental results of XANES spectroscopy were decisive to pointed different coordination modes to A and B sites to the disordered perovskites.[66, 67, 72-74] Figure 5 presents Ti K-edge XANES spectra of Ba_{0.95}Ca_{0.05}TiO₃

obtained by MPP method and heat annealed at 500 °C (structurally disordered) and 600 °C (structurally ordered). These spectra allow differentiate between structural ordered materials and structural disordered materials.

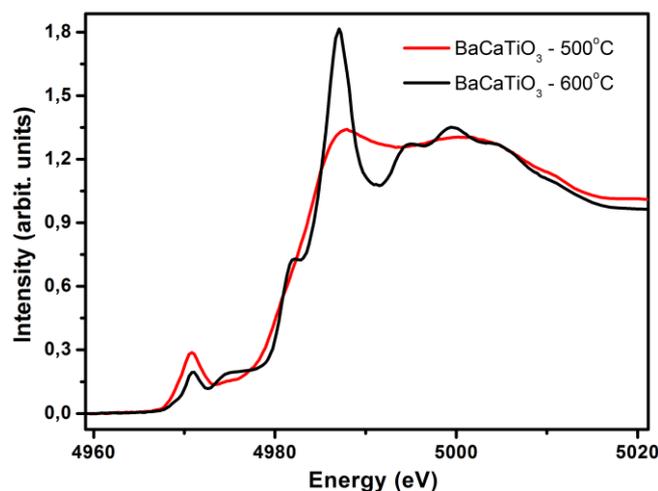


FIGURE 5: XANES spectra to Ba_{0.95}Ca_{0.05}TiO₃ heat treated at 500 and 600 oC.

The XANES spectrum of Ba_{0.95}Ca_{0.05}TiO₃ annealed at 600 oC revealed that the local structure around titanium atoms was characteristic of the titanate crystalline compound with only hexacoordinated TiO₆. On the other hand, the XANES spectrum of the Ba_{0.95}Ca_{0.05}TiO₃ annealed at 500 °C showed a characteristic mixed local structure containing sixfold and fivefold titanium coordination, with TiO₅ units and TiO₆ units.

The physical origin of the preedge feature is the transition of the metallic 1s electron to an unfilled d state. This forbidden electronic transition dipole is normally allowed by the mixture of p states from surrounding oxygen atoms into the unfilled d states of titanium atoms. [75-77] The observation of a large peak after the edge on these samples when compared to crystalline ones could also be interpreted as the existence of a certain degree of disorder at the medium-range environment around titanium atoms.[66, 67, 72-74]

Optical properties such as PL depend on both structural and electronic properties, including compositional ordering and the presence of impurities and defects. The strength of the electron-phonon interaction can be ascribed to the difference between the excitation and the maximum emission (Stokes shift).

The Figure 6 illustrates typical PL spectra to ordered and disordered CaTiO₃ obtained by PPM method. In this synthesis method, CaTiO₃ heat treated at 600 °C presents fully structural order, while CaTiO₃ heat treated below 600 °C, i.e., 500 °C, presenting a certain order-disorder degree.

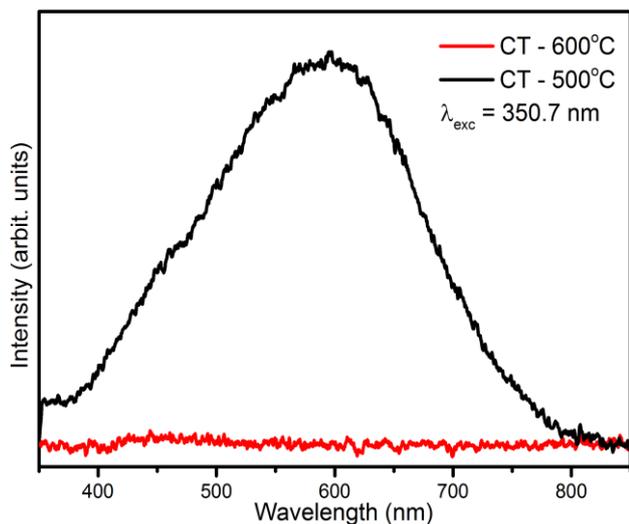


FIGURE 6: PL spectra to CaTiO₃ heat treated at 500 (structural disordered) and 600 °C (structural ordered).

In disordered perovskites, the PL behavior observed at room temperature is a broad band emission spectrum in the visible region. The emission shape is typical of the multiphonon process, i.e., it has several relaxation channels indicative of a broad energy band gap.[28, 38, 65, 67, 78, 79] Although these are disordered materials, it is also a well known fact that the details of band structure in solids are mainly determined by the potential within the unit cell rather than by long range periodicity.

The broad band visible PL emission of CaTiO₃ is associated with structural order–disorder. In association with XANES experiments, it was possible to relate the coexistence of two types of coordination for titanium with PL emission.[38, 66, 69, 80-82] The presence of different complex clusters is responsible for introducing delocalized electronic levels inside the band gap. In particular, to disordered perovskites many electron–hole recombination are allows. Thus, the broad band PL emission is consisted the sum of emission individuals. All the transitions for disordered perovskites, at room temperature, occur at energies far less than the band gap of these materials (~3-4 eV).

In a similar way, PL emission to perovskites obtained by HTMW method is linked to structural disorder. These materials are crystalline with structural disorder, and that this disorder is responsible for the intermediate energy states within the band gap. These intermediate energy states are the ones mainly responsible for PL emission in CaTiO₃ obtained by this method.[39, 72] The Figure 7 illustrates typical PL spectrum to CaTiO₃ obtained by HTMW method.

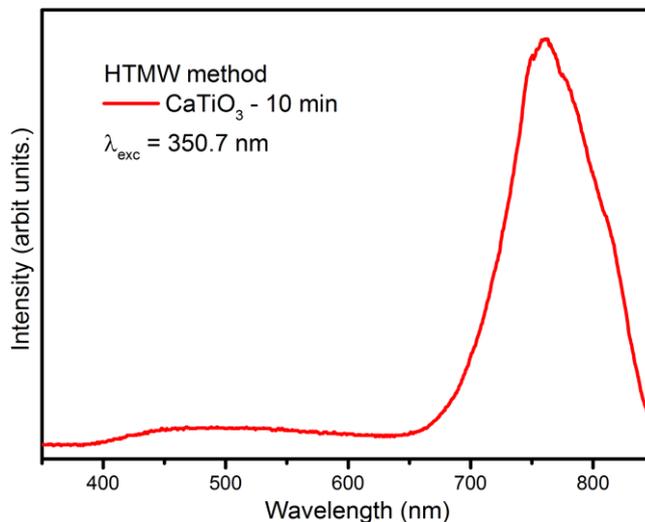


FIGURE 7: PL spectrum to CaTiO₃ obtained by HTMW method synthesized at 140 °C for 10 min.

The PL spectrum of CaTiO₃ contains two broad asymmetrical luminescence bands centered at 475 nm and 761 nm, which are distributed in the range of 395–600 nm and 675–850 nm, respectively. These transitions can be associated with intrinsic defects that yield in the band gap.

In order to compare among PL spectra of CaTiO₃ obtained by PPM and HTMW methods, we used a colour-difference formula designed to give a quantitative value of the perceived colour difference among PL spectra of samples in specific experimental conditions.[83, 84] The Figure 8 shows the CIE (Commission Internationale de l'Eclairage) diagram for CaTiO₃ synthesized by PPM and HTMW methods. The CIE chromaticity coordinates [x-axis, y-axis] for the samples are [x = 0.3854, y = 0.3970] to material obtained by PPM and [x = 0.3087, y = 0.3413] to material obtained by HTMW.

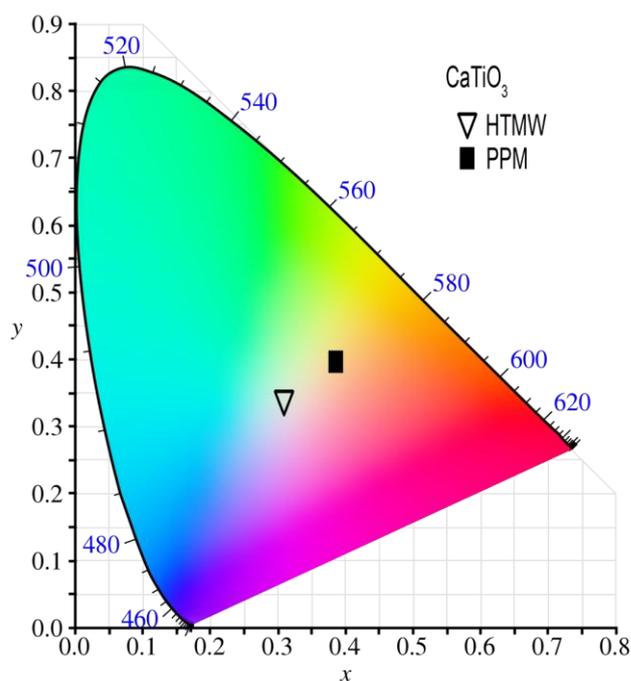


Figure 8: Colorimetric data for CaTiO₃ synthesized by PPM and HTMW methods.

The differences on the CIE chromaticity coordinates are related to different structural order present in the powders. The origin of PL emission in perovskites synthesized by PPM and HTMW methods are closely linked to structural disorder. However, there are differences in atomic scale to materials obtained by these methods. So, not only the profile of PL emission is related to used synthesis method but also the observed emissions.

VI. CONCLUSION

In this work, we presented a study about photoluminescence of structural disordered perovskite-structured compounds. A special focus was given to the PL emission of titanates and zirconates: the main representants of these materials class. It was discussed the origin of PL emission in these compounds. The hole of structural order was discussed. At this point, we can conclude that the luminescent emission in perovskite like material are linked to structural order.

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