

Maser-rays Based on Synchrotron Radiation-Total Reflection X-ray Fluorescence (SR-TXRF)

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To cite this article:

Orlando Elguera Ysnaga. Maser-rays Based on Synchrotron Radiation-Total Reflection X-ray Fluorescence (SR-TXRF). *Engineering Physics*. Vol. 5, No. 2, 2021, pp. 40-53. doi: 10.11648/j.ep.20210502.13

Received: October 4, 2021; **Accepted:** December 2, 2021; **Published:** December 9, 2021

Abstract: In 2012, during the experiments performed at LNLS (Brazilian Synchrotron Light Laboratory) based on SR-TXRF measurements of Ormosil films containing phosphotungstates ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) was observed an image that could be interpreted as the result of the transition from the incident X-ray beam (packets of photons) to a continuous light beam (set of continuous waves). A hypothesis could be based on a summation of small local crystalline domains, which respond differently to the incident beam, resulting in a "continuous beam". Differently of the case of LASER beam, the excitation by synchrotron radiation could generate not only excitation but also ionization of a polyatomic/poly-molecular systems (indeed considering the whole sample), instead of monoatomic system. Thus, the presence of individual MASER (Molecular Amplification by Stimulated Emission of Radiation) beam generated by SR-TXRF could be considered. A MASER produces coherent electromagnetic waves through amplification by stimulated emission (process based on the that was proposed and argued by Albert Einstein between 1916-1917). In lower ranges of energies than the corresponding to X-rays of electromagnetic spectrum like the Ultraviolet region, the Phosphotungstates molecules ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) exhibit very interesting phenomenon as the photocromism. This phenomenon occurs when the molecules mentioned above are irradiated with ultraviolet light, which brings these molecules to an excited electronic state. The reduced phosphotungstate obtained ($[\text{PW}_{12}\text{O}_{40}]^{4-}$) exhibit a bluish color, being called heteropolyblue. This bluish color disappears in the presence of oxygen, the discoloration time is dependent on the time in which the sample was irradiated, or on the composition/thickness of the film. It is also possible found photoluminescence in the Phosphotungstates, which is due to the multiples multielectronic collisions. For ormosil films were shown the possible pathways of electron transfer of Phosphotungstates (could be internal and external), which are based on the presence of a high number of double chemical bonds between Tungsten and Oxygen atoms. In these mechanisms, the key aspect to consider is that the molecular structure of phosphotungstates remains intact after the preparation of these materials by Sol-Gel process. Taking as base the molecular mechanisms mentioned above, one model for the generation of maser rays has been proposed, considering the phosphotungstate molecule as a Super-atom (structure built of many atoms) due to its stability structural in these films. It would be possible the generation of Multi-Maser beams by SR-TXRF also, if it is taking in consideration the processes of ionization in the whole sample.

Keywords: MASER, Synchrotron Radiation (SR), Total Reflection X-ray Fluorescence (TXRF), Organic Modified Silicates (ORMOSIL), Phosphotungstates (PWA)

1. Introduction

Ormosil (Organic Modified Silicates) are hybrid materials, whose contain as inorganic part a matrix host based on 3D silicates bearing silanols (—Si—OH—) and siloxane bonds (—Si—O—Si—), as well as —Si—C— bonds and organic groups. These hybrid materials usually have unique

properties that traditional composites and conventional materials do not have. They may combine the advantages of the inorganic materials (rigidity, high thermal stability) and the organic polymers (flexibility, dielectric characteristics, ductility and ability to processing). The ormosil that were

studied are composed of Silicates Organically Modified with amino($-\text{NH}_2$), nitrile($-\text{CN}$), diol($\text{HO}-\text{R}-\text{R}'-\text{OH}$) and ether($-\text{R}-\text{O}-\text{R}'-$) groups and doped with Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot \text{XH}_2\text{O}$), Titania (TiO_2), and Zinc cations (Zn^{2+}). These ormosil are prepared by the Sol-Gel process, in which the particles may grow without becoming crystalline, showing disordered regions [1, 2]. Ormosil constitute photoactive materials are presenting enhanced photochromic and photocatalytic behavior. One advantage of the Sol-Gel process is that takes place at very low temperatures, allowing that inorganic or organic materials to be added forming nanocomposites. Furthermore, by this process is possible obtain materials with molecular-level control under different configurations, such as monoliths, films, fibers and particles with low energy consumption [3, 4].

1.1. Total Reflection X-ray Fluorescence (TXRF) Principles

One of the broadest analytical methods that make use of X-rays as a means of excitation and analytical signal is X-ray Fluorescence (XRF). Nonetheless, the bases for the qualitative and quantitative determinations of X-ray Spectrometry were given by Moseley in 1913. From the introduction of the first commercial spectrometer in 1948, XRF began to become a standardized multi-element analytical method in many research laboratories industries (such as the cement industry). The development of X-ray optics in the 1980s and 1990s allow the confinement of the interaction volume of the primary X-ray beam with the analyzed material [5]. Unlike what happens in conventional XRF measurements, where the excitation develops in a uniform electromagnetic field, TXRF excitation occurs in a heterogeneous electromagnetic field of standing waves over an optically flat substrate or in thin layers over several substrates. X-rays, as in the case of other electromagnetic waves, experience full reflection for a particular angle of incidence, when these rays pass from a material with a higher refractive index to a material with a lower refractive index. Among the principles of this method of analysis are considered interference and standing wave phenomena [5].

X-ray Standing Waves (XSW)

The interference mentioned in the previous item referred to the superposition of one or more beams propagating in the same direction, but it is also possible if the propagation takes place in different directions. The pattern of these waves can propagate with a certain speed or be stationary. In this later case, the observed phenomenon is called Standing Wave Field, which is of fundamental importance for TXRF. A way to produce standing waves is the superposition of wide incoming and a wide reflected waves in the following cases: 1) In front of a totally reflecting surface of a thick substrate, 2) Within a thin layer on such a substrate, 3) Within a multilayer system [5]. In TXRF, incident radiation appears as a field of standing waves, with locally dependent oscillations or as a field of evanescent waves.

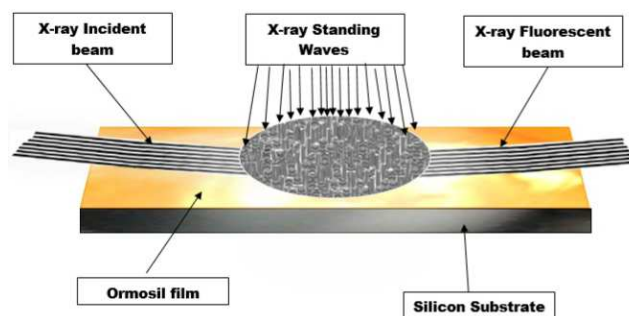


Figure 1. X-ray Standing Waves (XSW) for TXRF condition in Ormosil films [3, 15].

The analytic method of Total Reflection X-ray fluorescence (TXRF) is a variation of Energy-Dispersive XRF, where the primary beam strikes the sample at a glancing angle of less than 0.1° , reaching depth of analysis of nm thickness. TXRF is primarily used for chemical micro- and trace analyses. TXRF has some advantages: 1) Excitation of the sample by photon interference from incident beams and beams Reflected; 2) Reduction of Background; 3) Sample thickness too thin (small sample volume); 4) Short distance between the sample and the detector; 5) The detection limits are at pg (10^{-12} g) levels [5].

1.2. Maser-Rays

A MASER (initially named microwave amplification by stimulated emission of radiation) is a device that produces coherent electromagnetic waves through of the amplification by stimulated emission. The maser is based on the principle of stimulated emission proposed by Albert Einstein in a 1917 [6]. In this year, Albert Einstein published a master-piece of analysis about the stimulated emission, from which the laser physics is based on. This article was entitled in German: "Zur Quantentheorie der Strahlung" (On the Quantum Theory of Radiation), is also notable for first introducing the concept of photon. In this article Einstein argues that in the interaction of matter and radiation there would be a process of stimulated emission, in addition to the processes of absorption and spontaneous emission. Already in 1916, Einstein had deduced theoretically the existence of stimulated emission, process by which electromagnetic waves of the right frequency can "stimulate" an excited atom or molecule in order to emit more waves [7]. First, Einstein proposed that an excited atom in isolation can return to a lower energy state by emitting photons, a process he dubbed spontaneous emission. Second, Einstein's theory predicted that as light passes through a substance, it could stimulate the emission of more light. If one has a large collection of atoms containing a great deal of excess energy, they will be ready to emit a photon randomly. However, if a stray photon of the correct wavelength passes by, its presence will stimulate the atoms to release their photons early. In a maser, a cascading effect ensues: as the crowd of identical photons moves through of the atoms, ever more photons will be emitted from their atoms to join them [8]. When the atoms

have been induced into an excited energy state, they can amplify radiation to the element or molecule used as the masing medium [6]. Experimental results have been obtained with the maser as a spectrometer and as an oscillator. The sensitivity of the maser depends in part on the physical separation of quantum states (by the focuser), and with the dipole moment of the molecule to be studied [8]. Einstein also asserts that the radiation produced in stimulated emission is identical in all relevant aspects to the incident radiation. Einstein postulated that photons prefer to travel together in the same state [8, 9].

Between 1940s and 1950s the physicists found a use for the concept of stimulated emission. Charles Townes—after the end of denominated World War-II—turned his attention to molecular spectroscopy. Nonetheless, this analysis was limited by the wavelength (microwave region) of the light produced (from scattered radiation, result of bombardment with incident light). Townes noticed that as the wavelength mentioned above was shortened, stronger was the interaction of light with the molecules. Thus, Townes together with Arthur Schawlow designed one prototype laser (based on the stimulated emission), which was fitted with a pair of mirrors, one at each end of the lasing cavity, in order to generate the desired frequencies. Photons of specific wavelengths would then reflect off the mirrors and travel back and forth (through the lasing medium), which in turn cause other electrons to relax back into their ground states, emitting even more photons in the same wavelength [8]. In 1955 was presented the device in order to generate Maser-rays, utilizing a molecular beam based on ammonia, in which the molecules in the excited state of a microwave transition were selected. Between the types of masers can be mentioned: Hydrogen maser and Astrophysical maser. The interaction between these excited molecules and a microwave field produced additional radiation and hence amplification by stimulated emission [8]. For their research in the field of stimulated emission, Townes, Basov and Prokhorov were awarded by the Nobel Prize in Physics in 1964 [6]. Charles Townes suggested replacing "microwave" with the word "molecular", for this reason the acronym maser nowadays mean "Molecular amplification by stimulated emission of radiation" [6]. The phenomenon of stimulated emission does not apply only to atoms. Electrons confined by crossed electrical and magnetic fields in wave cavities can under stimulation produce microwave radiation. [10]. Due to the energy produced by spontaneous emission (and their corresponding background) is lower than the corresponding to the stimulated emission, the energy emitted by a maser oscillator is usually a monochromatic wave. The most convenient method for supplying excited atoms is the excitation at frequencies corresponding to infrared and optical bands, which would have a high order of monochromaticity and tunability. In the microwave range frequencies, a maser oscillator is almost inherently a very monochromatic device, which offers the possibility of coherent amplification. The monochromaticity of a maser oscillator is very closely

connected with the noise properties of an amplifier. Photoelectric tubes can use as photon detectors, in order to detect one or few quanta (corresponding to a noise temperature of $h\nu/k$) in the microwave region of the electromagnetic spectrum. The realization of technology of maser has mainly been postergated, due to the inconvenience of the operative necessary conditions: atomic and free-electron masers require vacuum chambers and pumping; and the requirement of cryogenic refrigeration for solid-state masers. Furthermore, masers also require strong magnets and/or magnetic shielding. The active material within a conventional solid-state maser is a dielectric crystal (for example ruby) containing paramagnetic ions, that is maintained to temperatures typically below 10K, and exposed to a strong d.c. magnetic bias field [11]. Javan and Sanders have been successfully applied an optical pumping technique to a fluorescent solid (the active material used was ruby), resulting in the attainment of negative temperatures and stimulated optical emission at a wavelength of 6943 Å [12]. There are a good many crystals, notably rare earth salts, which have spectra with sharp absorption lines, some of them exhibiting lifetimes corresponding to radiative (e.g. fluorescence, phosphorescence), and non-radiative processes. Furthermore, in some cases have been found lifetimes as long as 10^{-3} sec or even more. A solid state maser can also normally be tuned over a rather large fractional variation in frequency (difficult to obtain in the infrared or optical regions). Frequencies of atomic or molecular resonances can in principle be tuned by Stark or Zeeman effects, as they would be in the radio-frequency or microwave ranges. The problem of populating the upper state does not have as obvious a solution in the solid case as in the gas. Lamps did not exist, which could give just the right radiation for pumping. Thus, it may be feasible to pump atoms to a state above one, which is metastable (possibly by nonradiative processes involving the crystal lattice) and accumulate until there are enough for maser action [13]. Some efforts have been taken towards the realization of solid-state masers at room temperature, using optically excited organic molecules (e.g. C_{60} and porphyrins) in strong d.c. magnetic fields [11]. The principle and concept of stimulated emission has since been extended to more devices and frequencies. Modern masers can be designed to generate electromagnetic waves at not only in the corresponding microwave frequencies range, but also extending to the radio, infrared, and optical regions [6]. The extension of maser techniques to the infrared and optical region were considered, but for shorter wavelengths (e.g. ultraviolet region) maser-type amplification appears to be quite impractical. Amplifiers and oscillators using atomic and molecular processes, as do the various varieties of masers, may in principle be extended far beyond the range of frequencies corresponding to infrared, and optical regions. In the infrared region in particular, the generation of reasonably intense and monochromatic radiation would allow the possibility of spectroscopy at very much higher

resolution than is now possible. Maser systems capable of producing coherent amplification at very high frequencies, also they would be able to emit the usual amount of spontaneous emission. This prospect is favorable in applications at the infrared or optical regions [13]. For ultraviolet region and higher frequencies, the implementation of Maser-rays would seem to be impractical. In order to overcome these limitations, for the coherent amplification and generation of very monochromatic radiation, highly reflecting surfaces can be selected. The tunability must be expected to decrease approximately inversely with the increase of frequency [13]. On the other hand, tunability of larger ranges of frequency will require materials with very special properties and/or the use of the Stark or Zeeman effects on the molecular transition frequencies. Masers can serve as high precision frequency references, due to that the amplifiers and oscillators use atomic and molecular processes. Masers are used as narrow-band amplifiers, microwave amplifiers in radio telescopes, spacecraft communication ground stations, and the timekeeping device in atomic clocks.

1.3. Synchrotron Radiation (SR)

The radiation of relativistic electrons in a magnetic field became important in the 1940s. The first synchrotrons were constructed (for uses based on particle physics) by Vladimir Iosifovich in the former Soviet Union and by Edwin Mattison McMillan in the United States in 1945 [5]. In 1947, the light emitted by the Synchrotron was reported for Pollock and colleagues, in an electron accelerator. This phenomenon was consequently called Synchrotron Radiation, which is linked to the emission of electromagnetic waves by a charge that is accelerated or stopped. In this cyclic accelerator, the charged particle experiences a circular motion in a magnetic field, which is uniform in the direction of the particle's trajectory. In 1956, A. A. Sokolov and I. M. Ternov showed that Synchrotron radiation exhibits a pronounced linear polarization, being this complete in the perpendicular plane to the electron radiation orbit [14]. Since the 1970s, the uses of this radiation by scientific community for spectrometry and diffractometry has been increasing. Nowadays, SR is obtained from a storage ring, in which charged particles like electrons (which come from booster, where these are accelerated to almost light-velocity) are stored in several bunches and maintained at high constant velocity or kinetic energy [5]. The properties of this radiation are important, fundamentally because they can be used in experiments. One of the properties of this radiation is the coherence, which exists when the distance between electrons is less than the wavelength of emitted light. Quantum fluctuations, which prevent electrons from getting too close, in Synchrotron radiation are considered in particle motion calculations (very important in the design of electron and positron storage rings). These fluctuations (temporary changes of energy randomly in the space) were based on the Werner Heisenberg's uncertainty principle. Synchrotron radiation (based on theoretical studies) is responsible for the

directional orientation of the electron spin with reference to the applied external magnetic field. This directional orientation leads to self-polarization of the beam, which represents the method of obtaining of spin-oriented relativistic electrons and positrons [14]. The beam from these particles is essential for high-energy physics experiments. Spectroscopy assisted by Synchrotron radiation covers energies ranging from a few eV to tens of KeV, extending from the Infrared region to the X-ray region, respectively. The interaction of Synchrotron radiation with matter is recorded simultaneously with the measured spectrum of this radiation, as in the case of Luminescence (Phosphorescence, Fluorescence and Thermoluminescence) [14]. In addition to the applications of Synchrotron radiation in different fields of science (protein crystallography, surfaces of solids, environmental sciences, materials science, biomicroscopy, catalysis), also has application in the industrial field, for example, in microlithography for the manufacture of microcircuits. X-rays are high-energies (low-wavelengths) electromagnetic waves, which are located in the electromagnetic spectrum between the regions corresponding to the Ultraviolet-rays and the Gamma-rays. Their wavelengths, whose magnitude are tenths of nanometers (nm), makes it possible to analyze atoms and chemical bonds. X-rays are classified, according to their energy, in Hard X-rays, whose energy is in the range of 10-120 keV (0.10-0.01nm respectively); and in Soft X-rays, whose energy is less than 10 keV (>0.10nm). X-rays can be absorbed, scattered and/or diffracted, and emitted (Fluorescence). The interactions between X-rays and matter provide information about the composition of the sample and the position of atoms in it. Synchrotron radiation is a very intense source of X-rays, based on the phenomenon that takes place when electrons in motion change their directions, thereby, they emitting energy. When these electrons are moved fast enough (accelerating to extremely high speeds), they emit X-rays. Synchrotron can emit X-rays as dozens of thin beams, each one of them oriented to a certain line of analysis. The advantages of X-rays produced by Synchrotron are: structure, coherence and polarization. High primary intensity, adjusted excitation energy, and the lowest possible background have resulted in the lowest detection limits achieved by using a Synchrotron beam for excitation. In order to improve the spectral resolution within the low-energy range, can be used the high brilliance of Synchrotron radiation as X-ray source [5]. Three advantages of using Synchrotron radiation as X-ray excitation source compared with conventional source (X-ray tubes) for TXRF analysis that can be mentioned are: 1) The high photon flux and brilliance of a Synchrotron beam result in a drastically increase of the primary X-ray intensity. The gain is 5–15 orders of magnitude in comparison with conventional X-ray tubes. 2) Synchrotron radiation is suitable for energy tuning. 3) The spectral background, already reduced by conventional TXRF, is lowered further because of the polarization of Synchrotron radiation [5, 15].

2. Material and Methods for the Preparation of Ormosil Films

2.1. Materials

Phosphotungstic acid hydrate (HPW), Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnO, tetraethylorthosilicate (TEOS, 98 %), (3-glycidyloxypropyl)trimethoxysilane (Glymo, 98 %) and (4-triethoxysilyl)butyronitrile (BuTs, 98 %) were purchased from Sigma-Aldrich (MA, USA) and used without further purification. Ethanol (99.3 %) was supplied by QHEMIS (SP, Brazil).

2.2. Method of Preparation of Ormosil Films

Ormosil films were obtained according by procedures described in the literature [1, 2].

3. Experimental Section

SR-TXRF measurements were performed at the D09B (15°) bending-magnet XRF beamline of the Brazilian

Synchrotron Light Source (LNLS, Campinas-Brazil) [16]. The experimental setup includes: 1.4 GeV source (storage ring) for Synchrotron radiation (SR); the X-ray beam applied was monochromatic set at 7 keV and 11keV for the determination of Titanium (Ti) and Tungsten (W) respectively; the dimensions of X-ray beam for TXRF were: 5.0 mm (horizontal) x 0.1 mm (vertical); and a HPGe detector (cooled by $\text{N}_2(\text{g})$) operating at energy dispersive mode. For SR-TXRF measurements of the elements Titanium (Ti- $K_\alpha = 4.508$ keV), and Zinc (Zn- $K_\alpha = 8.63$ keV) were not necessary any special filter arrays before of the transmission detector. For SR-TXRF measurements of the Tungsten (W- $L_\alpha = 8.396$ keV) was necessary a special filter array in front of the transmission detector, which consisted in 6 sets of Aluminum foils (total equivalent thickness 120 μm). For the substrates of Monocrystalline Silicon (111), at the energies used, their critical angles were at the range $[0.15^\circ - 0.25^\circ]$ [2, 17]. The time of acquisition of SR-TXRF analysis by sample was 3-5 minutes approximately. The experiments were performed at atmospheric pressure and ambient temperature.

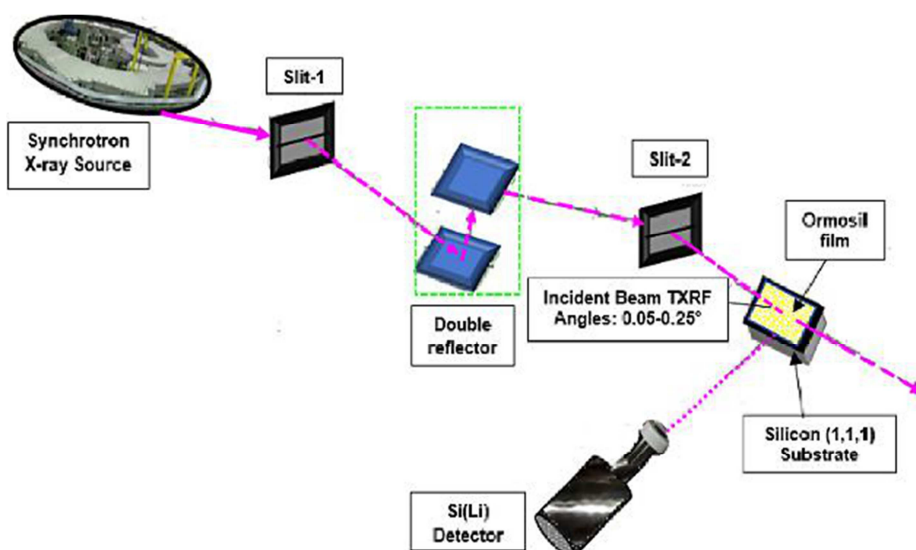


Figure 2. Experimental Setup SR-TXRF [16, 17].

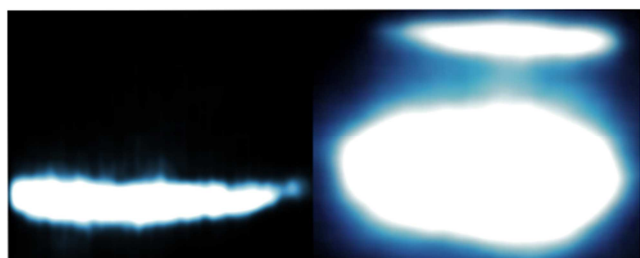


Figure 3. Steps of TXRF condition in ormosil films (LNLS-2012) [18]. At left: the X-ray beam impinges on the Ormosil film producing one brilliant beam. At right: The Total X-ray reflection product of Fluorescence processes.

4. Results and Discussion

In 2012, during the experiments performed at LNLS

(Brazilian Synchrotron Light Laboratory) about Total Reflection X-ray fluorescence assisted by Synchrotron radiation (SR-TXRF) of Ormosil (Organic Modified Silicates) films containing phosphotungstates ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) was observed in Figure 3 the following phenomenon:

From XRF point of view, this image could be interpreted as the result of the transition from the incident Synchrotron radiation X-ray beam (packets of photons explained by modern physics) to a continuous light beam (set of waves explained by classical physics). Considering that the Ormosil films analyzed present thickness of few micrometers ($<3\mu\text{m}$) and exhibit mean roughnesses in the value of 1nm (10 \AA), which is lower than the estimated depths of analyses obtained under Total Reflection X-ray fluorescence (TXRF) condition (40nm approximately), makes that TXRF measurements be viable in Ormosils films ([17], p. 159-162). As was

mentioned above in Section 1.1.1, under TXRF condition the phenomenon called X-ray Standing Waves (XSW) is manifested, which is based on the superposition of one or more X-ray beams propagating in the same direction. These waves exhibit stationary patterns, which depend on the angle of incident X-ray beam, as it is illustrated in Figure 1. Moreover, the brilliant beam observed in Figure 3 could be related to the intensity of Synchrotron radiation applied, which is proportional to the cross-product of the corresponding electric and magnetic field strengths present [5]. Furthermore, from the brilliance of white light beam, it is possible the existence of other phenomena based on luminescence: thermoluminescence, radioluminescence, electroluminescence, photoluminescence, chemiluminescence, atomic fluorescence (e.g. Total Reflection X-ray Fluorescence: TXRF), molecular fluorescence, among others. Another possible phenomenon present also is X-ray scattering [19]. One hypothesis, in order to explain these phenomenon/phenomena is based in the physical and chemical properties of the material analyzed. Being a sample a film (a few micrometers thick) of a hybrid

material, which contains ormosil (organic modified silicates) and phosphotungstates (big molecule), this exhibits some degree of crystallinity at local order, which was measured by XRD [20]. Referent about the physical properties, ormosil films could be the result of a summation of small local crystalline domains (presenting poly-crystalline characteristics), which in individually way respond differently to the X-ray incident beam, but in summatory resulting in a "continuous beam". Referent about the chemical properties, the insertion of molecular clusters as phosphotungstates ($[PW_{12}O_{40}]^{3-}$) changes dramatically the properties and characteristics of these materials. In the case of ormosil films, the phenomena mentioned above can be further amplified, because besides there would have conditions for phosphorescence and refraction phenomena and so on. Furthermore, these films mentioned above constitute a polyatomic system/poly-molecular instead of a monoatomic system. Thus, the presence of an individual Maser beam generated by SR-TXRF can be considered. In the next figure is represented the molecular structure of ormosil films.

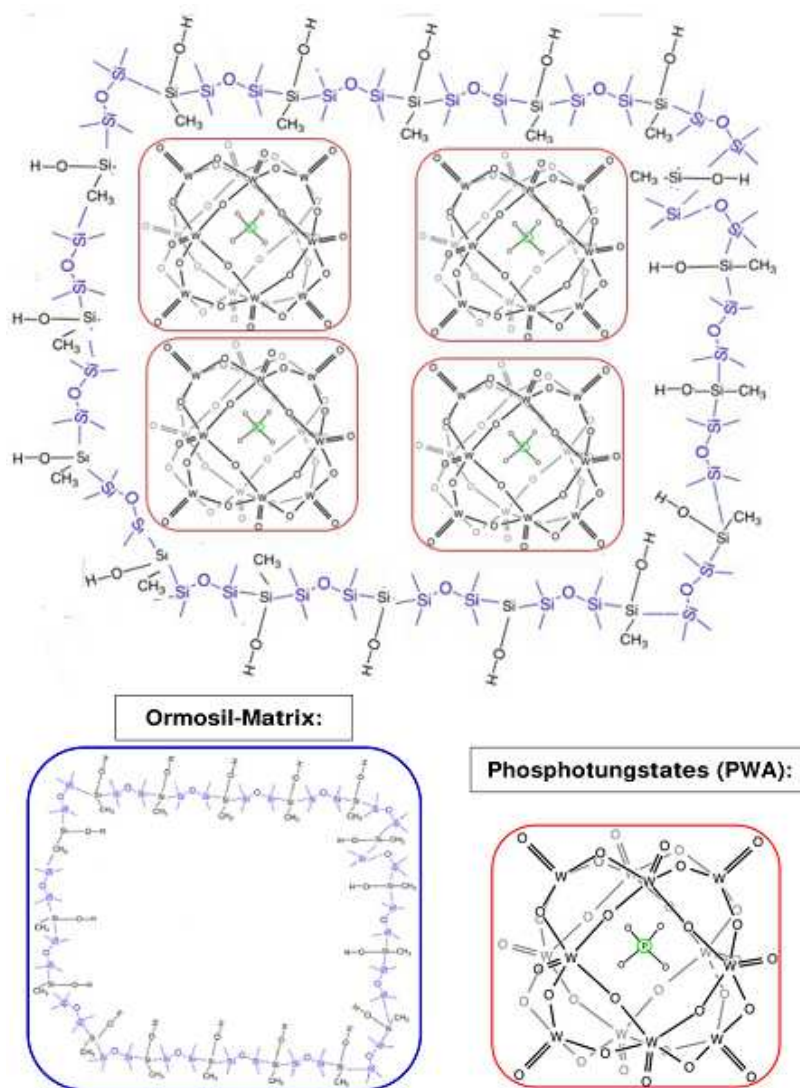


Figure 4. Molecular Structure of Ormosil films [21].

In order to explain the phenomena illustrated at Figure 3, they are presented hypotheses about possible mechanism that occur in the structure of ormosil films, taking in consideration the structure illustrated in Figure 4.

4.1. Molecular Mechanisms

Among the properties of Keggin-type heteropolyacids like phosphotungstates are mentioned: the high polarizability, surface charge distribution, redox potentials for electrons and protons transfer [22]. For ormosil films the pathways of

electron transfer of Phosphotungstates (PWA) could be internal (inside isolated and non-isolated PWA molecules) and external (among PWA molecules and their surroundings). In these mechanisms, the key aspect to consider is that the molecular structure of phosphotungstates remains intact after the preparation of these materials by Sol-Gel process [1, 2].

4.1.1. Internal Molecular Mechanism

Figure 5 illustrates the internal mechanism of movement of electrons inside of the Phosphotungstate (PWA) molecules:

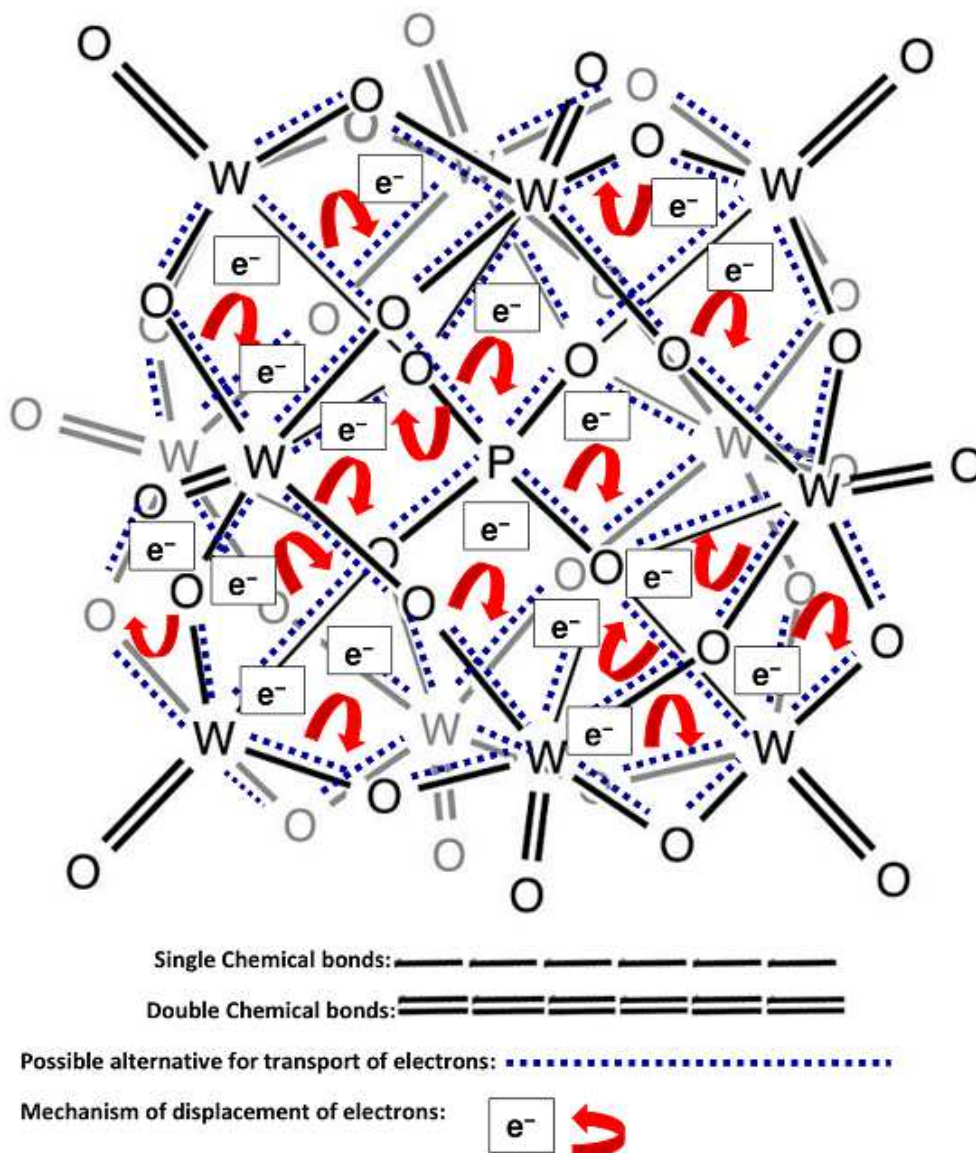


Figure 5. Internal molecular mechanism proposed for the electrons movement in Phosphotungstates (PWA).

From the chemical stability in the structure of the PWA molecules mentioned above, the presence of a number of double chemical bonds between Tungsten and Oxygen atoms (—W=O—), as also between Oxygen atoms (—O=O—) can be deduced. By chemical resonance would establish the presence of electronic movements (displacements) via of these double bonds through of the mentioned structure.

4.1.2. External Molecular Mechanisms

(i). Mechanism Among PWA Molecules and Ormosil Matrix

Figure 6 illustrates the external mechanism of movement of electrons around the Phosphotungstate (PWA) molecules: Considering the existence of resonance among the

chemical bonds —O—O— mentioned above, these could interact with the molecular groups present in ormosil films, as silanol (—Si—OH—) and siloxane (—Si—O—Si—) mainly (mentioned in the Introduction), being able to form temporary bonds as —Si—O—O— , which could conduct electrons outside of the Phosphotungstate structure and surroundings. This mechanism would take advantage of the high electronegativity of Oxygen atoms. The Sol-Gel process leads to the formation of networks of ormosil and particles (like PWA clusters) with an average diameter of around 50\AA , which are interconnected through channels

along the thickness of materials produced [23]. By Laser-Induced Breakdown Spectrometry (LIBS) studies was described the existence of Tungsten gradients in ormosil films ([17], p 177). Take in consideration that the molecular structure of Phosphotungstates (PWA) is keep intact (before the ablation process) in ormosil films, one can deduct also the existence of the gradients of this molecular structure at thickness of these films. Thus, there are indicatives about the presence of channels containing PWA clusters in these materials, which would allow the electronic conduction illustrates in Figure 6.

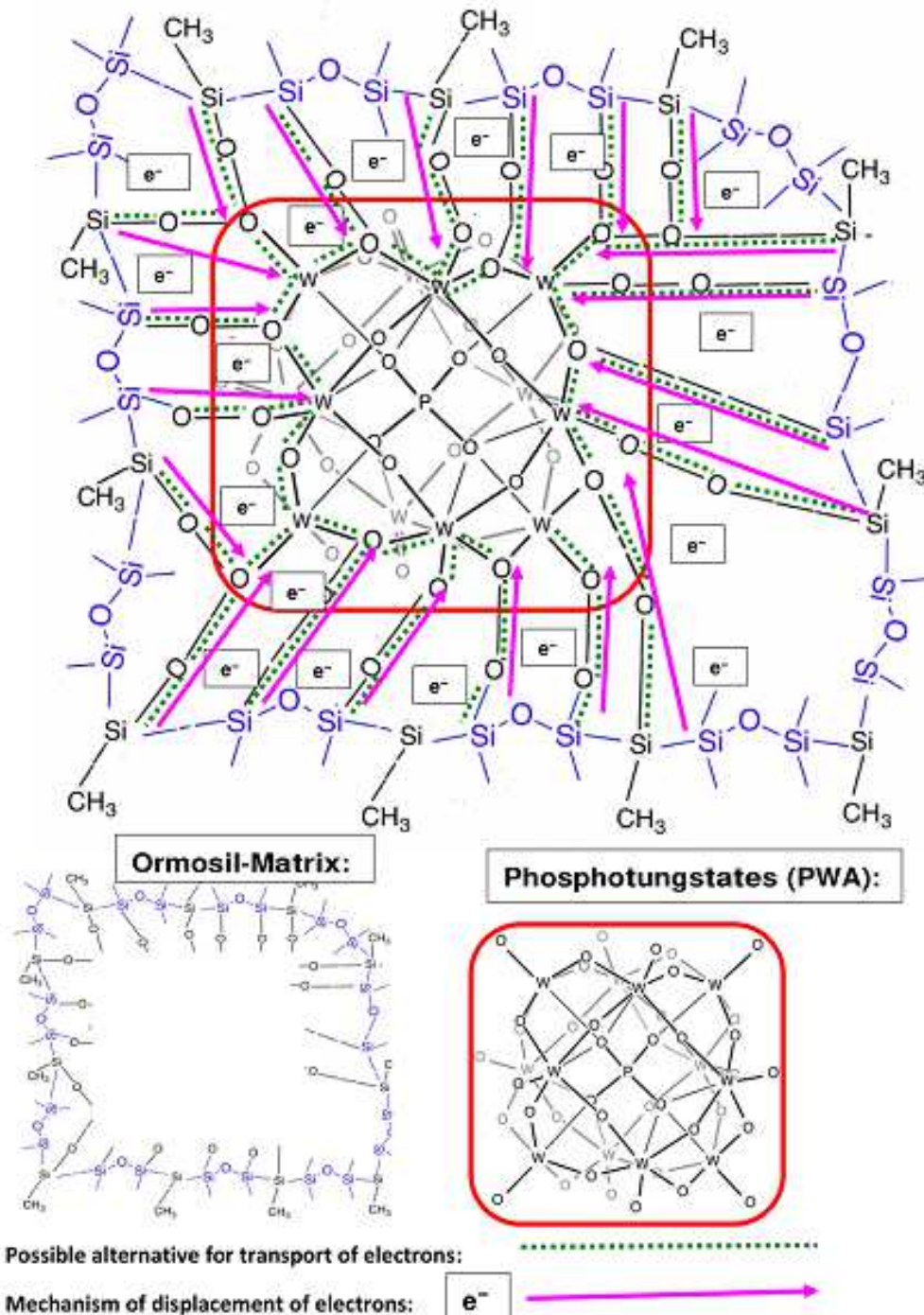


Figure 6. External molecular mechanism proposed for the electrons movement in the surroundings of Phosphotungstates (PWA).

(ii). Mechanism Among PWA Molecules

The intermolecular pathway would be feasible, when the distances between neighbouring PWA molecules are less than

17.0 Å [24]. Figure 7 illustrates the external mechanism of the movements of electrons among the Phosphotungstate (PWA) molecules:

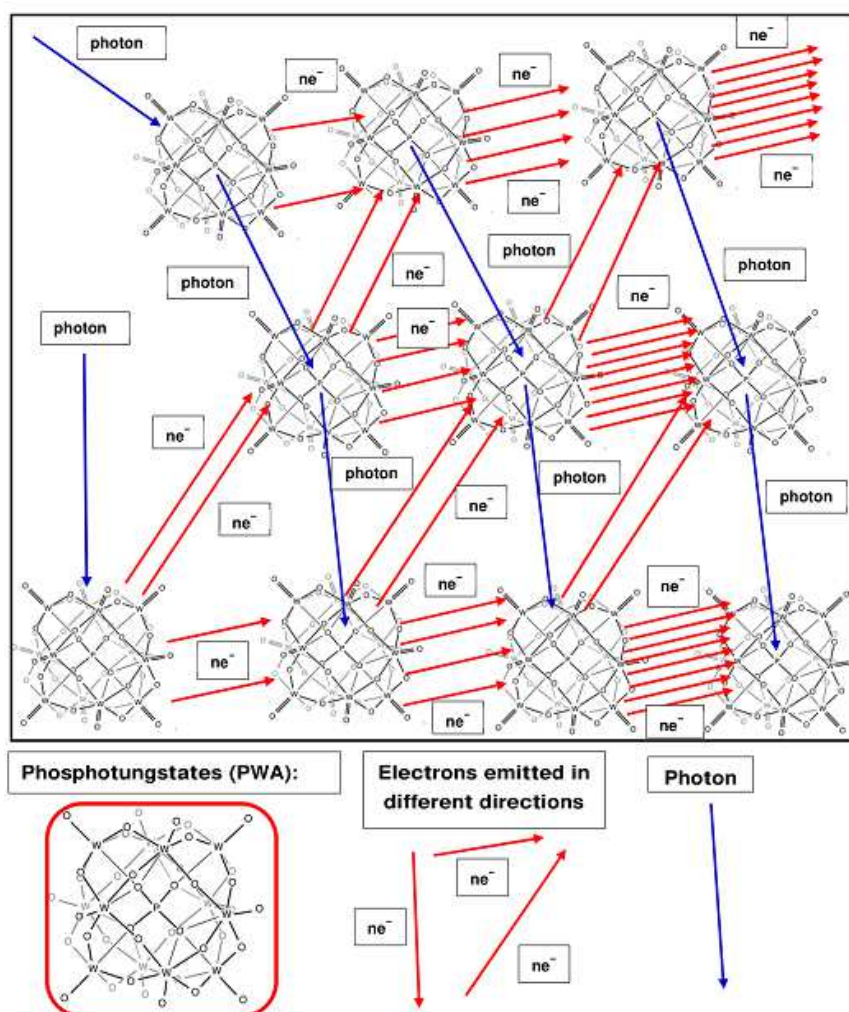
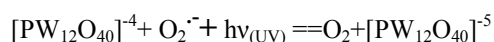
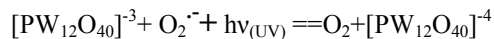


Figure 7. External molecular mechanism proposed for the electrons movement among Phosphotungstates (PWA).

Under the assumption of that PWA molecules are distanced around the value of mentioned above, there are conditions for the presence of intermolecular interactions, based on the incidence of X-ray photons inside of these molecules, taking in consideration the chemical stability of their structure. The hypothesis of this intermolecular mechanism is based on the analogy with the phenomenon that can occur in one photomultiplier tube, which emits electrons when photons of adequate frequency strike it. PWA molecules have the capacity of form clusters, which can exhibit behaving of one crystal (as a collective), being that this structure exhibit high capacity of amplification of generation of electrons. When one photon (coming from Synchrotron X-ray monochromatic beam) impinges on PWA molecules, these can eject electrons from their inner shells of Tungsten atoms being able to generate more photons (secondary emission). Taking in consideration the mechanisms illustrated in Figures 5 and 6, via of double chemical bonds, there are a important number

of electrons that are generated by radiative processes (electroluminescence), as also non-radiative processes (e.g. Auger Effect). In the range of X-ray energies can be manifested also the photoelectric effect produced in the surface of PWA molecules. The presence of PWA (negative charge) significantly increases the positive charge accumulated on Silicon compounds surface and channels (correlated also to the formation of functional groups) in Ormosil films via electrostatic interactions [24-25]. In ranges of energies lower than of the corresponding to X-rays at the electromagnetic spectrum e.g. at the Ultraviolet region, in which the Phosphotungstates exhibit very interesting phenomenona as the photocromism. The phosphotungstate, when irradiated with ultraviolet light around 260nm, is brought to an excited electronic state as a function of an electronic transition of charge transfer from Oxygen to Tungsten ($O(2p) \rightarrow W(5d)$), which involving the heteropolyanion boundary orbitals. The reduced

phosphotungstate exhibit a bluish color, being called heteropolyblue. This bluish color disappears in the presence of molecular oxygen (O_2), the discoloration time is dependent on the time in which the sample was irradiated, or on the composition/thickness of the film, which could take up to 15 hours.



$[PW_{12}O_{40}]^{4-}$ and $[PW_{12}O_{40}]^{5-}$ phosphotungstates species could be assigned to the d-d bands (450-500 nm) and (450-550nm) respectively, and also there is a band corresponding to Inter-valence charge transfer (IVCT:620-750 nm) transition in the corresponding UV-Visible band of spectrum of ormosil films [26-33]. It is possible found some fluorescence effects in the phosphotungstates (e.g. photoluminescence, electroluminescence), which are due to the multiples multielectronic collisions. This aspect can be support on the fluorescence manifested by Tungsten compounds like Tungstates (WO_4^{2-}). In ormosil films the structures of Tungstates is keep partially in the Phosphotungstate ones. Tungstates of Calcium, Strontium, Magnesium and Zinc ($CaWO_4$, $SrWO_4$, $MgWO_4$, $ZnWO_4$ respectively) are known to show luminescence upon excitation by short-wave Ultraviolet radiation (range of temperatures from -100°C to 100°C). This luminescence is even increase more, when this chemical compounds are present as very thin coatings [34-36]. The crystal PWA Keggin structure depends on the amount of water of crystallization contained, result from its molecular composition, besides of their anions (heteropolyanions) and cations (H^+ , H_3O^+ , $H_5O_2^+$, and others that act as counter-cations). The corresponding anions and cations possess high mobilities [22, 37, 38].

These hydrated species located inside, on, and around of the 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) molecules were reported in the study Marcos de Oliveira, Jr. et al, based on analysis by 1H NMR spectroscopy [39].

4.2. Generation of Maser-Rays

The principles of the Maser-rays and the Laser-rays are based on induced emission, spontaneous emission, thermal emission, and fluorescence. In thermal equilibrium, the population of high-energy states in an atomic system is considerably less than the population of lower states. An electron, when excited, will jump to a high-energy level. However, it will not stay in the high-energy level for a long time, and jump back to the lower energy state which is more stable; and, thereby, emit light. The quantum mechanical state of the atom is also affected by external photons which are at a frequency associated with the atomic transition. Some atomic systems may have inverted populations of energy levels with a higher state occupied to a greater degree than the ground state. Depending on the system, a certain proportion of excited atoms will raise their energies during

the collisions [40].

Model for Generation of Maser-Rays

The hypothesis in order to generate Maser-rays is take in consideration one molecule of phosphotungstate ($[PW_{12}O_{40}]^{3-}$) as one Superatom (structure built of many atoms), inasmuch as compound of Tungsten exhibit clustering capacity in solution [41]. Differently of the case of generation of laser beam, the excitation by Synchrotron radiation could generate not only excitation but also ionization (due to its high-intensity) of a polyatomic/poly-molecular systems, as are shown in Figures 5, 6 and 7, instead of monoatomic systems with the corresponding emission of many electrons and photons. We are presenting the steps of model of generation of Maser-rays based on Synchrotron radiation-Total Reflection X-ray Fluorescence (SR-TXRF), which take in consideration the processes of atomic excitation only:

- 1) Phase-I: Excitation of Super-Atoms (Phosphotungstate molecule: $[PW_{12}O_{40}]^{3-}$). Let us consider a three-level atomic system: State-0 (Lower E_0), State-1 (Intermediate E_1), and State-2 (Higher E_2), in which the intermediate State-1 is metastable, which means that the transition from said state to the ground state is prohibited by selection rules. The system can be raised to State-2 by absorption of radiation of frequency $\nu = (E_2 - E_0)/h$.
- 2) Phase-II: Super-Atoms excited (Phosphotungstate molecule: $[PW_{12}O_{40}]^{3-}$). Atoms in State-2 have an existence of approximately 10^{-8} seconds on their way to a permitted transition by spontaneous emission, so that they could fall to metastable State-1 or stable State-0 almost instantaneously. If the higher State-2 is very little occupied, there will be little induced emission and the main consequences that occur are the absorption of incident photons by the atoms in the State-0 (ground state) and the subsequent spontaneous radiation of photons of equal frequency.
- 3) Phase-III: Rapid Transition of some Super-Atoms to the Metastable State (E_1), by mean of Spontaneous Emission of photons: $h\nu = E_2 - E_1$ (black-arrow). In the State-1 (metastable state) could present values of lives superior to even a second on their way to spontaneous emission, and consequently its energy level can continue to be raised until there is a larger population in the State-1 than there would be in the State-0.
- 4) Phase-IV: Induced emission of Maser-rays. With the population partially inverted at the E_1 level, the induced emission of new transitions is produced, when the photons of energy $h\nu = E_1 - E_0$ (blue-arrow) impinge on the photons emitted from the level mentioned above. Induced emission occurs when it is sent direct radiation of frequency $\nu = (E_1 - E_0)/h$ to the atomic system mentioned above, then the induced emission of this frequency will exceed absorption, since that there are more atoms in the State-1 (higher) than in the State-0 (lower), and the net result will be a production of radiation of frequency ν greater than that which arrives. Induced emission and

absorption can be explained directly by considering the interaction between an atom and an electromagnetic wave of frequency ν , but spontaneous emission apparently occurs in the absence of such a wave by a comparable interaction. The spontaneous emissions of photons by atoms in the excited state are induced by Fluctuations, which take place even when electromagnetic waves are absent, and when according to classical principles $E = 0$, $B = 0$. As it was mentioned above in the Section 1.4. in Synchrotron radiation are take in consideration the Quantum fluctuations that prevent electrons from getting too close. However, if these fluctuations are controlled adequately can produce coherent rays, in which condition the distance between electrons is less than the wavelength of emitted radiation [14]. The radiated waves from spontaneous emission are incoherent, as might be expected, with random phase relationships in space and time. However, if the radiated waves from the induced emission are in phase with the induced waves, which makes it possible for a maser or a laser to produce completely coherent rays [40].

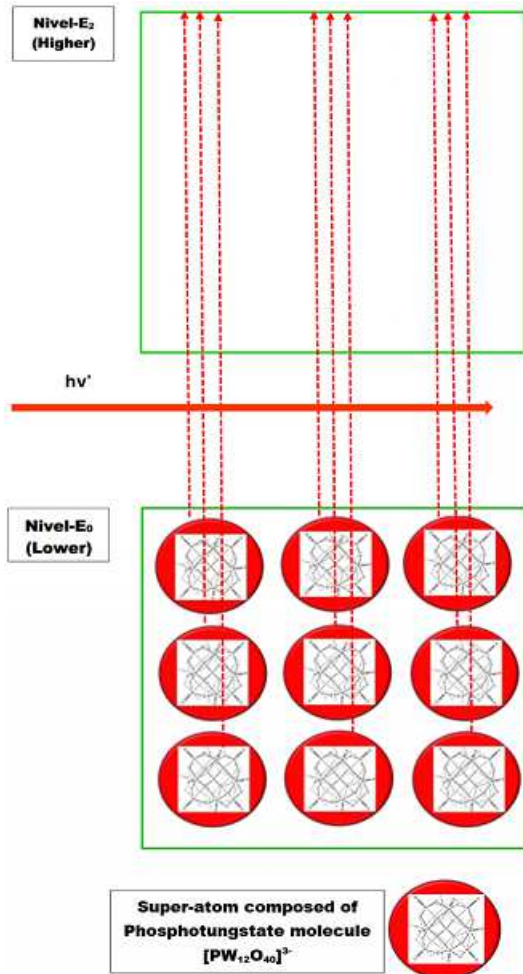


Figure 8. Model for generation of Maser- rays. Phase-I: Excitation of Super-Atoms (Phosphotungstate molecule: $[PW_{12}O_{40}]^{3-}$) from E_0 level to E_2 level: $h\nu' = E_2 - E_0$, (red-arrow).

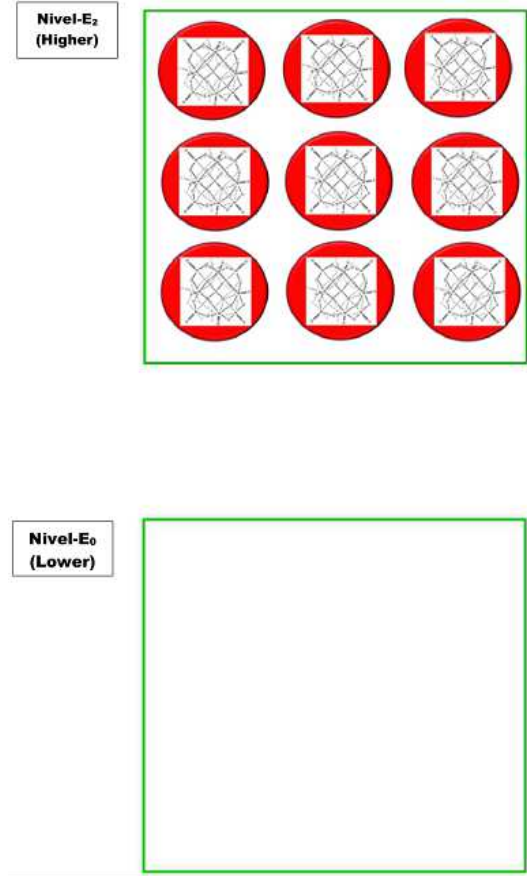


Figure 9. Model for generation of Maser-rays. Phase-II: Super-Atoms excited (Phosphotungstate molecule: $[PW_{12}O_{40}]^{3-}$ at E_2 level).

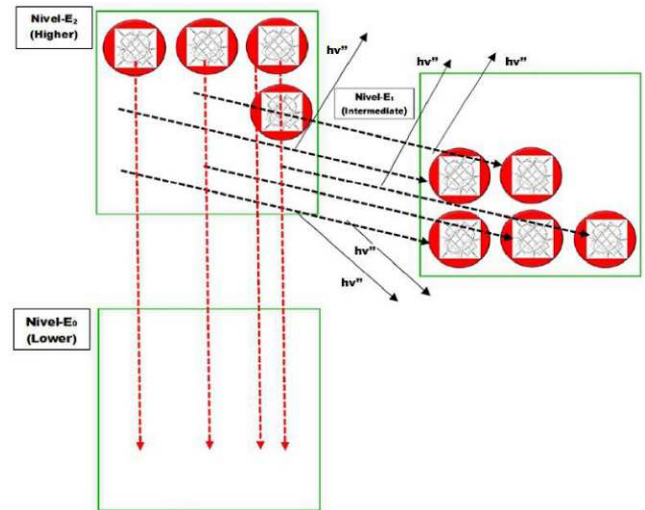


Figure 10. Model for generation of Maser-rays. Phase-III: Rapid Transition of some Super-Atoms to the Metastable State (E_1), by mean of Spontaneous Emission of photons: $h\nu'' = (E_2 - E_1)$ (black-arrow). Furthermore, Spontaneous Emission of photons: $h\nu' = E_2 - E_0$ (red-arrow).

In addition, take in consideration the whole sample this hypothesis of the generation of Maser-rays could be scaled-up up to Multi-Maser beams (based in the effects generated by processes of ionization mainly) produced by Synchrotron Radiation Total Reflection X-ray fluorescence (SR-TXRF). For this case, the electrons could be eject-out from the

structure of Superatom considered, generating diverse radiative and non-radiative new processes. Furthermore, these processes of excitation-ionization in polyatomic system jointed with the polycrystallinity condition mentioned above for ormosil films (Section 4. Results and Discussion, page 5), could constitute a summation of multi-polyatomic/multi-poly-molecular systems, considering the totality of the atoms/molecules constituents of the sample respectively.

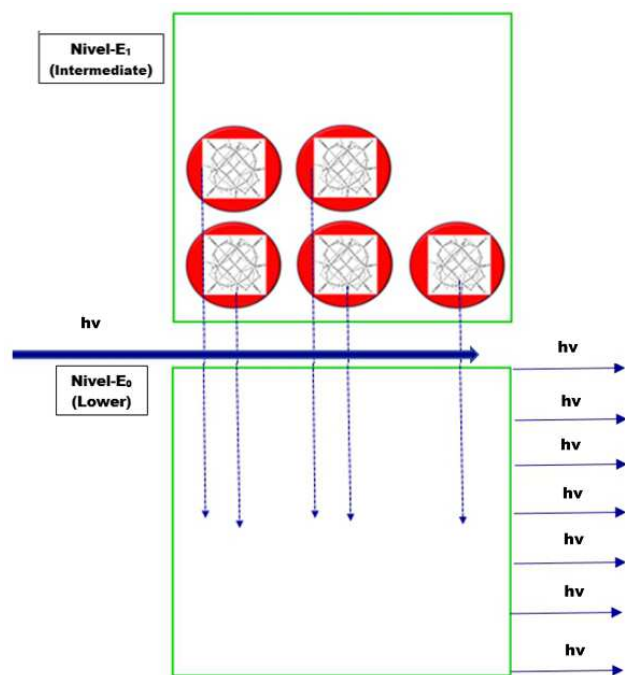


Figure 11. Model for generation of Maser-rays. Phase-IV: With the population partially inverted at the E_1 level, the induced emission of new transitions is produced, when the photons of energy $h\nu = E_1 - E_0$ (blue-arrow) impinge on the photons emitted from the level mentioned above.

5. Conclusions

In 2012, during the experiments performed at LNL (Brazilian Synchrotron Light Laboratory) based on SR-Synchrotron Radiation-Total Reflection X-ray Fluorescence (SR-TXRF) measurements of Ormosil films containing phosphotungstates ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) was observed an image that could be interpreted as the result of the transition from the incident X-ray beam (packets of photons) to a continuous light beam (set of continuous waves). The phenomenon observed, from X-ray point of view, could be supported on the presence of X-ray Standing Waves (XSW), which are based on the superposition of one or more X-ray beams propagating in the same direction or in different directions. One hypothesis in order to explain the image mentioned above could be based on a summation of effects on small local crystalline domains contained in these films, which respond differently to the incident X-ray beam, resulting in a "continuous beam". Another hypothesis, in order to explain the white brilliant beam observed in the Figure mentioned recently is based on Luminescence beams. Differently of the case of laser beam, the excitation by Synchrotron radiation could generate not only

excitation but also ionization (due to their high-intensities) in these materials. Besides of this, the Ormosil films mentioned above constitute a polyatomic system/poly-molecular instead of a monoatomic system. Thus, the presence of an individual maser beam generated by SR-TXRF can be considered. A MASER (initially named Microwave Amplification by Stimulated Emission of Radiation) is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The maser is based on the principle of stimulated emission proposed by Albert Einstein in a 1917, who argued that in the interaction of matter and radiation there would be a process of stimulated emission, in addition to the processes of absorption and spontaneous emission. Already in 1916, Einstein had deduced theoretically the existence of stimulated emission, process by which electromagnetic waves of the right frequency can "stimulate" an excited atom or molecule, in order to emit more waves. In a maser, as the crowd of identical photons moves through of the atoms, ever more photons will be emitted from their atoms to join them, constituting a cascading effect. When the atoms or molecules have been induced into an excited energy state, they can amplify radiation to the element or molecule used as the masing medium. The principle and concept of stimulated emission has since been extended to more frequencies and for the elaboration of devices. In 1950s the physicists found uses for the concept of stimulated emission. Charles Townes and Arthur Schawlow designed one prototype maser at wavelengths corresponding to the microwave region of the light produced. Townes noticed that insofar the wavelength corresponding to the region of the electromagnetic spectrum mentioned above shortened, stronger is the interaction of light with the molecules. In 1955 was presented the device in order to generate Maser-rays utilized a molecular beam based on ammonia, in which molecules in the excited state of a microwave transition are selected. Modern masers can be designed to generate electromagnetic waves at not only in the corresponding microwave frequencies range but also extending to the radio, infrared, and optical regions. In the regions of electromagnetic spectrum mentioned above, Maser systems are capable of producing coherent amplification at very high frequencies, also being able to emit the usual amount of spontaneous emission. On the other hand, in order to overwhelming the limitations for implementation of Maser-rays at ultraviolet region and higher frequencies is necessary a very monochromatic radiation, which can be coherent amplified. Furthermore, highly reflecting surfaces are necessary also. Thus, Synchrotron Radiation-Total Reflection X-ray Fluorescence (SR-TXRF) measurements in ormosil films could generate the conditions for production of maser-rays: 1) Synchrotron radiation generate quantum fluctuations that can produce coherence in X-rays. 2) Synchrotron radiation is suitable for energy tuning. 3) In Total Reflection X-ray Fluorescence (TXRF) assisted by the radiation mentioned above, the X-ray beam applied was monochromatic, polarized and brilliant. In this XRF mode of analysis is necessary that the surfaces used be reflectors. In addition of the possible presence of Maser-rays, from the brilliance of white light beam

observed in the figure mentioned, it is possible to deduce the existence of other potential phenomena based on luminescence (fluorescence and phosphorescence). In lower ranges of energies than the corresponding to X-rays of electromagnetic spectrum like the Ultraviolet region, the Phosphotungstates exhibit very interesting phenomena as the photochromism, which occurs when these molecules are irradiated with ultraviolet light around 260nm. This irradiation brings these molecules to an excited electronic state, which is a function of an electronic transition of charge transfer $O(2p) \rightarrow W(5d)$, involving the heteropolyanion boundary orbitals. The reduced phosphotungstate ($[PW_{12}O_{40}]^{-4}$) exhibit a bluish color, being called heteropolyblue. This bluish color disappears in the presence of oxygen, the discoloration time is dependent on the time in which the sample was irradiated, or on the composition/thickness of the film. It is also possible to find photoluminescence in the phosphotungstates, which is due to the multiples multielectronic collisions. This aspect can be supported on the fluorescence manifested by Tungsten compounds like Tungstates (WO_4^{2-}) and that the luminescence manifested is increased more, when these chemical compounds are present as thin coatings. For Ormosil films were shown the possible pathways of electron transfer of Phosphotungstates (PWA) that could be internal (inside isolated and non-isolated PWA molecules) and external (among PWA molecules and their surroundings), which are based on the presence of a high number of double chemical bonds between Tungsten and Oxygen atoms. In these mechanisms, the key aspect to consider is that the molecular structure of phosphotungstates remains intact after the preparation of these materials by Sol-Gel process. Taking as base the molecular mechanisms mentioned above, which could occur in the structure of ormosil films, one model for the generation of Maser-rays has been proposed, considering the phosphotungstate molecule as a Super-atom (structure built of many atoms), which is due to its stability structural in these films. It would be possible the generation of Multi-Maser beams by SR-TXRF also, if it is taken into consideration the processes of ionization in the whole sample.

Acknowledgements

The author thanks to the São Paulo Research Foundation (FAPESP) by the research grants (2011/08120-0, 2011/06019-0, 2013/05279-3) and to the CNPq Brazilian agency by the financial support (research grants 141880/2011-2 and 160515/2011-4). We also extend our gratitude to the Dr. Carlos Perez for his help at the SR-TXRF/SR-GRXRF measurements done at Brazilian Synchrotron Light Source (LNLS), to the CNPEM-LNLS facilities for SR-TXRF/SR-GRXRF measurements (proposal numbers: XRF-14217, XAFS1-14254 respectively), and to the Inorganic Hybrid Materials Chemistry Group (IQSC-USP). Finally the author wishes to express his gratitude and acknowledgement to Prof. Dr. Luis Cisneros V. by his help and advices during my studies of Physical Sciences at the Universidad Nacional de Ingeniería, Lima-Perú.

References

- [1] E. Ferreira-Neto, S. Ullah, O. Elguera Ysnaga, et al. "Zn²⁺ doped Ormosil-Phosphotungstate Hybrid Films with Enhanced Photochromic Response". *J. Sol-Gel Sci. Technol.* 2014. 72 (2): 290–300. <https://doi.org/10.1007/s10971-014-3404-7>.
- [2] L. Gonçalves, E. Ferreira-Neto, S. Ullah, et al. "Enhanced Photochromic Response of Ormosil-Phosphotungstate Nanocomposite Coatings Doped with TiO₂ Nanoparticles". *J. Sol-Gel Sci. Technol.* 2015. 76 (2): 386–394. <https://doi.org/10.1007/s10971-015-3787-0>.
- [3] D. Bradley. "Metal alkoxides as precursors for electronic and ceramic materials". *Chem. Rev.* 1989. 89 (6): 1317–1322. <https://doi.org/10.1021/cr00096a004>.
- [4] G. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin. "Chemical Strategies To Design Textured Materials: from Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures". *Chem. Rev.* 2002. 102 (11): 4093–4138. <https://doi.org/10.1021/cr0200062>.
- [5] R. Klockenkämper, A. Von Bohlen. "Total Reflection X-ray Fluorescence Analysis and Related Methods. In: Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications". Mark F. Vitha, Series Editor. 2015. New York: John Wiley, 2nd Edición, Vol. 181, Chap. 4. Pp. 141–143.
- [6] <https://www.nobelprize.org/prizes/physics/1964-townes/facts/> (accessed 17-Jun-2020).
- [7] Invention of the Maser and Laser. 2005. *Phys. Rev. Focus* 15, 4. <https://physics.aps.org/story/v15/st4> (accessed 17-Jun-2020).
- [8] Einstein Predicts Stimulated Emission. *APS News*. 2005 14 (8). <https://www.aps.org/publications/apsnews/200508/history.cfm> (accessed 17-Jun-2020).
- [9] Coherence in Stimulated Emission. <http://www.applet-magic.com/stimem.htm>. (accessed 17-Jun-2020).
- [10] J. Gordon, H. Zeiger, and C. Townes. "The Maser—New Type of Microwave Amplifier, Frequency Standard, and Spectrometer". *Physical Review*. 1955. 99 (4), 1264–1274. <https://doi.org/10.1103/PhysRev.99.1264>.
- [11] M. Oxborrow, J. Breeze, & N. Alford. "Room-temperature solid-state maser". *Nature*. 2012. 488, 353–356. <https://doi.org/10.1038/nature11339>.
- [12] T. Maiman. "Stimulated Optical Radiation in Ruby". *Nature*. 1960. 187: 493–494. <https://doi.org/10.1038/187493a0>.
- [13] L. Schawlow and C. Townes. "Infrared and Optical Masers". *Physical Review*. 1958. 112 (6): 1940–1949. <https://doi.org/10.1103/PhysRev.112.1940>.
- [14] I. Ternov, V. Mikhailin and V. Khalilov. *Synchrotron Radiation and Its Applications-Department of Physics. Moscow State University. Moscow, USSR., 1980. Translated from Russian by S. J. Amoretti. New York: Harwood Academic Publishers, 1985.*
- [15] A. Balerna, S. Mobilio. "Introduction to Synchrotron Radiation". In: S. Mobilio, F. Boscherini, C. Meneghini. editors. *Synchrotron Radiation Basics, Methods and Applications*. 2015. Springer-Verlag Berlin Heidelberg 2015. Springer, Berlin, Heidelberg, 2015. DOI <https://doi.org/10.1007/978-3-642-55315-8>. eBook ISBN: 978-3-642-55315-8. Chap. 1, Pp.3–28.

- [16] C. Pérez, M. Radtke, H. Sánchez, H. Tolentino, et al. "Synchrotron Radiation X-ray Fluorescence at the LNLS: Beamline Instrumentation and Experiments". *X-ray Spectrom.* 1999. 28 (5): 320–326. [https://doi.org/10.1002/\(SICI\)1097-4539\(199909/10\)28:5<320::AID-XRS359>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1097-4539(199909/10)28:5<320::AID-XRS359>3.0.CO;2-1).
- [17] O. A. Elguera Ysnaga. Métodos de Análise de Materiais Híbridos: Um Estudo Comparativo Entre Fluorescência de Raios-X Com Detecção Dispersiva em Energia Usando Fonte Tradicional e Luz Síncrotron. [Doctor of Science in Analytical and Inorganic Chemistry, Thesis]. Instituto de Química de São Carlos. São Carlos, São Paulo-Brasil: Universidade de São Paulo (IQSC-USP), 2015. Pp. 249–301. Unpublished.
- [18] TXRF/GIXRF Measurements in Ormosil Thin Films contained Zn. LNLS 2012 Activity Report. Brazilian Synchrotron Light Laboratory.
- [19] D-M. Smilgies. "Grazing-Incidence Small-Angle Scattering (GISAXS)". Cornell High Energy Synchrotron Source (CHESS). In: The SAXS Guide, 4th edition. Anton Paar Company, 2017. <https://smilgies.github.io/dms79/gisaxs/SAXS-Guide-Smilgies.pdf>
- [20] L. Gonçalves. Nanopartículas de Titânio como aditivos em materiais híbridos inorgânicos fotocromicos baseados em fosfotungstos. [Master in Materials Engineering, Dissertation]- Instituto de Química de São Carlos. São Carlos, São Paulo-Brasil: Universidade de São Paulo (IQSC-USP), 2011. Pp. 89–92. Unpublished.
- [21] R. Pardo, M. Zayat, D. Levy. "Thin film photochromic materials: Effect of the sol-gel ormosil matrix on the photochromic properties of naphthopyrans". *Comptes Rendus Chimie*, 2010. 13 (1–2): 212–226. <https://doi.org/10.1016/j.crci.2009.05.006>.
- [22] I. Kozhevnikov. "Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions". *Chemical Reviews*. 1998. 98 (1): 171–198. <https://doi.org/10.1021/cr960400y>.
- [23] C. Brinker, B. Bunker, D. Tallant, K. Ward, and R. Kirkpatrick. "Structure of Sol–Gel-Derived Inorganic Polymers: Silicates and Borates". In: M. Zeldin, K. Wyne, Alcock, H. Allcock editors. *Inorganic and Organometallic Polymers*. ACS Symposium Series, 1988. Albuquerque: American Chemical Society. Vol. 360, Chapter 26, Pp. 314–332. DOI: 10.1021/bk-1988-0360.ch026.
- [24] Y. Zhou, J. Yang, H. Su, J. Zeng, S. Ping-Jiang, W. Goddard. "Insight into Proton Transfer in Phosphotungstic Acid Functionalized Mesoporous Silica-Based Proton Exchange Membrane Fuel Cells". *Journal of the American Chemical Society*. 2014. 136 (13): 4954–4964. <https://doi.org/10.1021/ja411268q>.
- [25] Y. Liu, Y. Lu, A. Haragirimana, I. Buregeya, N. Li, Z. Hu, S. Chen. "Immobilized phosphotungstic acid for the construction of proton exchange nanocomposite membranes with excellent stability and fuel cell performance". *International Journal of Hydrogen Energy*. 2020. 45 (35): 17782–17794. <https://doi.org/10.1016/j.ijhydene.2020.04.159>.
- [26] G. Brown, M. Noe-Spirlet, W. Busing, H. Levy. "Dodecatungstophosphoric acid hexahydrate, (H₅O₂⁺)₃(PW₁₂O₄₀³⁻). The true structure of Keggin's 'pentahydrate' from single-crystal X-ray and Neutron-Diffraction Data". *Acta Crystallographica Section B-Structural Science*. 1977. 33 (1): 1038–1046. <https://doi.org/10.1107/S0567740877005330>
- [27] X. López, et al. "Electronic properties of polyoxometalates: a DFT study of α/β - [XM₁₂O₄₀]ⁿ⁻ relative stability (M) W, Mo and X a main group element)". *Journal of the American Chemical Society*. 2001. 123 (39): 9571–9576. <https://doi.org/10.1021/ja010768z>
- [28] A. Ioannidis, E. Papaconstantinou. "Photocatalytic generation of hydrogen by 1:12 heteropolytungstates with concomitant oxidation of organic compounds". *Inorganic Chemistry*. 1985. 24 (3): 441–443. <https://doi.org/10.1021/ic00197a037>.
- [29] Y. Guo, C. Hu. "Heterogeneous photocatalysis by solid polyoxometalates". *Journal of Molecular Catalysis A: Chemical*. 2007. 262 (1): 136–148. <https://doi.org/10.1016/j.molcata.2006.08.039>.
- [30] M. Varga Junior, E. Papaconstantinou, T. Pope. "Heteropolyblues. IV. Spectroscopic and Magnetic Properties of Some Reduced Polytungstates". *Inorganic Chemistry*. 1970. 9 (3): 662–667. <https://doi.org/10.1021/ic50085a045>.
- [31] R. Zhang, et al. "Preparation of photochromic sol-gel composites films containing dodecaphosphotungstic acid". *Materials Chemistry and Physics*. 2003. 78 (2): 380–384. DOI: 10.1016/s0254-0584(02)00160-8..
- [32] T. Yamase. "Photo and electrochromism of polyoxometalates and related materials". *Chemical Reviews*. 1998. 98 (1): 307–326. <https://doi.org/10.1021/cr9604043>.
- [33] E. Ferreira-Neto, M. Simões, J. Noveletto, J. Yabarrena, S. Ullah and U. Rodrigues-Filho. "The Effect of Ormosil Matrix Composition and Alkaline Earth Metal Doping on the Photochromic Response of Ormosil-Phosphotungstate Films". *J. Braz. Chem. Soc*. 2015. 26 (12): 2598–2606. <http://dx.doi.org/10.5935/0103-5053.20150282>.
- [34] Scheelite (accessed 05-Nov-2021) <https://www.fluomin.org/uk/fiche.php?id=202>. (accessed 05-Nov-2021).
- [35] <https://www.naturesrainbows.com/> (accessed 05- Nov-2021).
- [36] F. Kröger. "Fluorescence of Tungstates and Molybdates". *Nature*. 1947. 159: 674–675. <https://doi.org/10.1038/159674b0>.
- [37] A. Yaroslavtsev, D. Gorbachev. "Proton mobility in the solid inorganic hydrates of acids and acid salts". *Journal of Molecular Structure*. 1997. 416 (1–3): 63–67. [https://doi.org/10.1016/S0022-2860\(97\)00035-5](https://doi.org/10.1016/S0022-2860(97)00035-5).
- [38] J. Keggin. "The structure and formula of 12-phosphotungstic acid". *Proceedings of the Royal Society of London. Series A*. 1934. 144 (851): 75–100. <https://doi.org/10.1098/rspa.1934.0035>.
- [39] M. de Oliveira, U. P. Rodrigues-Filho, J. Schneider. "Thermal Transformations and Proton Species in 12-Phosphotungstic Acid Hexahydrate Studied by ¹H and ³¹P Solid-State Nuclear Magnetic Resonance". *The Journal of Physical Chemistry C*. 2014. 118 (22): 11573–11583. <https://doi.org/10.1021/jp501887x>.
- [40] A. Beiser. *Conceptos de Física Moderna*. Primera Edición, Revisada. McGraw-Hill Book Company Inc. (in spanish), 1965. Pp. 270–274.
- [41] V. Alexéiev. "Semi-microanálisis Químico Cualitativo". Editorial Mir-Moscú-URSS, 1963, Pp. 518.