

# From the Mining to the Obtaining of Ferroelectric Ceramics

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## Abstract

Enjoy and learn by looking for the ancient techniques of working the pottery from the clay, led to the obtaining of more convenient materials and better mineral extractive processes. This is what has allowed the development of the great variety of domestic ceramic materials and the emergence of electro technical ceramic. The piezoelectric and ferroelectric ceramics depend on the origin of their raw materials, what has been the process of obtaining them? As well as on the variations of the ceramic process used. Five examples are presented of how the reagents, their purity, granulometry and present phases can modify the properties and characteristics of ferroelectric ceramics.

The work will make a panoramic visualization of the materials and their origins, arriving at the obtaining of ferroelectric ceramics and the influence of the raw material (obtaining process) and the properties of the desired product.

**Keywords:** Ceramic materials; Ferroelectric phases; Piezoelectricity

## Introduction

The first question we would ask for the development of this work would be what is a ferroelectric?

A ferroelectric is a dielectric material that has the characteristic of being piezoelectricity, which is also pyro electric and which is characterized by a hysteresis loop (Figure 1).

These characteristics do not appear in any material, they are manifested only in materials that physically possess one or more *ferroelectric phases* [1], this being a property that has a select group. Of the 32 point groups of symmetry in which all the crystalline materials can be classified, only 10 of them fulfill the following characteristics [2]:

- Do not have center of symmetry (necessary condition for piezoelectricity)
- Present spontaneous polarization (necessary condition for the piroelectricity)
- Reverse its polarization to an external electric field.

At present many types of ferroelectrics have been studied, in particular we will focus on those with perovskite structure  $ABO_3$ . The second question that we would ask ourselves would be what is its importance?

These materials are widely used for the manufacture of ultrasonic equipment, for their properties as resonators and filters (clocks, tuning forks, filters for radio and television, telecommunications), delay lines (color television sets), pushbuttons and keyboards (telephones, printers, game machines, calculators, computers) among others and because the ceramic process used is relatively cheap.

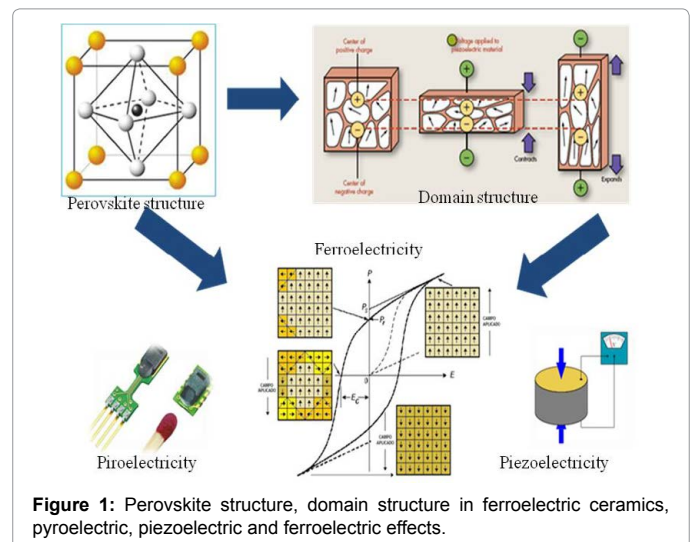
The applications of these ceramics range from physicians in diagnosis and physiotherapies to industrial. Modifications are now being made to the obtaining procedures, which allow for cheaper ceramics yet with higher performance. The piezoelectricity is the most interesting characteristic of these materials; however, with the miniaturization of the devices, the Ferro electricity has received a substantial increase for the development of the same in applications as storage of information.

The third question to be asked is: What role does mining and extractive processes play in the properties of ferroelectric ceramics?

This will be answered in the development of the work being the main objective of the same.

## Development

Under the general name of ceramics, objects are grouped that differ substantially from one to another in their bases composition, terracotta, stoneware, porcelain, on the exterior in which their shape can be covered by glaze or enamel, and in the how the cooking: temperature, oxidation atmosphere or reduction was carried out. It is a very fine type of earth that is composed of hydrated aluminum silicates that are produced by the decomposition of minerals.



**Figure 1:** Perovskite structure, domain structure in ferroelectric ceramics, pyroelectric, piezoelectric and ferroelectric effects.

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Received February 07, 2017 Accepted February 23, 2017; Published March 06, 2017

Copyright: Rodríguez MDD (2017) From the Mining to the Obtaining of Ferroelectric Ceramics. J Powder Metall Min 6: 160. doi:10.4172/2168-9806.1000160

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Ceramic is the oldest industry of humankind [3], is a genius idea of man and fruitful since it has developed extensively throughout history not only in quantity but also in the variety of products, some of them, of transcendental importance for Technologies [4].

The manufacture of bricks appears in areas where the stone is scarce and the clay abounds. Ceramic material is the product of various raw materials (mainly clays) made in a powdery or pasty state (to easily communicate the form) and acquiring the stone consistency by physicochemical processes when cooking these clay.

### Mining and extractive techniques

Mining is the selective extraction of minerals and other materials from the earth's crust, from which an economic benefit can be obtained, as well as the primary economic activity related to it.

Depending on the type of material to be extracted, the mining is divided into metallic, non-metallic, ornamental stones and construction.

The mining process involves different stages, which are carried out to develop a mining project:

- The search and estimation of resources
- Extraction of ore
- Pre-treatment of ore
- Reduction to free metals
- Purification

Mining extractive can be classified in opencast mining or subterranean mining:

#### Opencast mining

Also denominated of surface is realized by the elimination of the vegetation and of the superior layers of rock, to be able to arrive at the buried deposits. It can be divided into:

- *Open pit mining*
- *Quarries*
- *Strip mining*
- *Mountaintop removal mining or mountaintop mining*

#### Subterranean mining

Sometimes called underground mining is done by building tunnels or galleries, with the goal of penetrating the rock to reach the sites. It is classified according to the access form:

- *drift mining*
- *slope mining*
- *shaft mining*

Or according to the extraction technique: [5,6]

- sinking, within these are found: block caving, sublevel caving y panel caving,
- for "caserones", within these are found: sublevel stoping, vertical crater retreat (VCR), cut & fill and shrinkage, open stopes and room & pillar.

In order to analyze the extractive techniques used, we must know or present the materials that are developed ferroelectric ceramics. Historically, materials of the lead titanate-zirconate system (PZT) have been developed with different dopant, and more recently lead-free materials due to environmental campaigns to avoid contamination with lead, in particular sodium-potassium niobium, also with different dopant elements. Therefore, we will analyze the extractive processes of the majority elements: Na, K, Ti, Zr, Nb, Pb and of the minority ones: Li, Nb, La, Ta.

### Extractive mining of the interest elements

**Lead (Pb):** is widely distributed throughout the planet in the form of galena, cerusite and anglesite, which is lead sulfide. It occupies the 36th place in abundance among the elements of the earth's crust.

The extraction of lead from the galena [7,8] is carried out by calcination the ore, converting it into oxide and reducing the oxide with coke in high furnaces. The process of obtaining the metallic lead is summarized in Figure 2, however to obtain the ferroelectric ceramics the lead is in the form of oxide (PbO) or carbonate (PbCO<sub>3</sub>), which would be what is obtained from the second and third steps of the process.

The structural forms in which lead minerals can be found are four: galena, cerusite, anglesite and litharge, distributed geographically throughout most of the planet but with greater abundance in America, Europe and Africa and Australia (Table 1).

**Zirconium (Zr):** Zirconium [9] is a hard metal with characteristics similar to steel. It is one of the elements of the periodic table with more presence and greater distribution in the terrestrial crust. In nature, it is only found combined with other elements giving rise to minerals such as zircon, whose chemical formula is ZrSiO<sub>4</sub> or as a zircon oxide (ZrO<sub>2</sub>). It is a transition metal, shiny, greyish white, hard, corrosion resistant and steel-like appearance. The main commercial source of zirconium is zirconium (zirconium silicate, ZrSiO<sub>4</sub>), which is found mainly in deposits in Australia, Brazil, India, Russia and the United States, as well as in smaller deposits around the world. 80% of zircon mining is produced in Australia and South Africa. As a curious fact, the first practical application of zirconium was using it as a flash in photography (Figures 3-6).

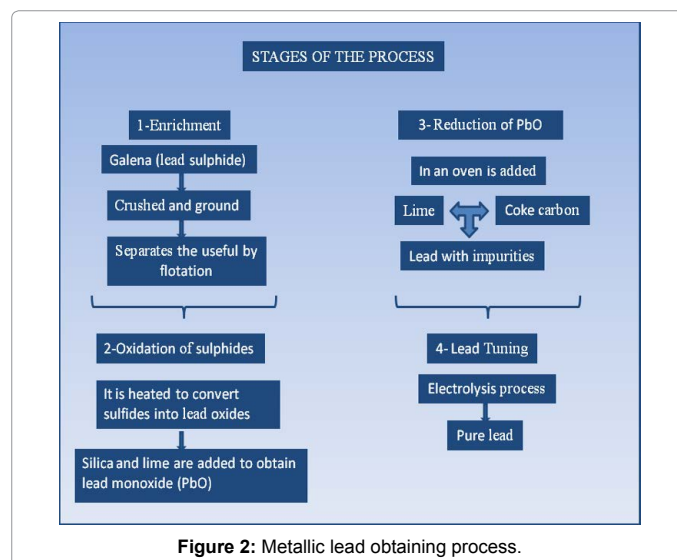
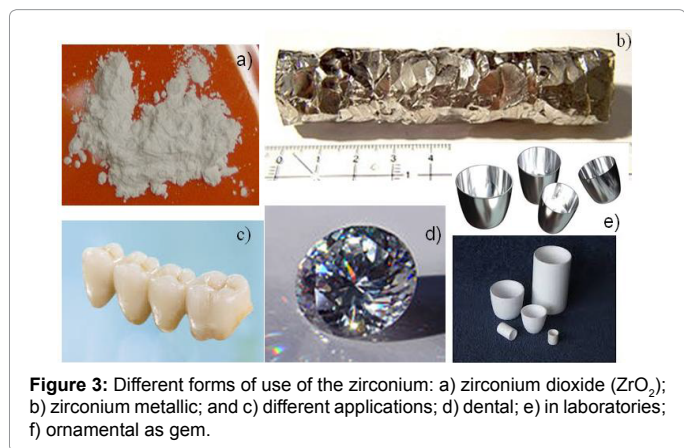


Figure 2: Metallic lead obtaining process.

Pb Mineral	Chemical formula	Crystal system	Density (g/cm <sup>3</sup> )	Location
Galena	PbS	cúbico	7.6	Chile, Bolivia, Peru, Mexico, USA and Spain
Cerusita	PbCO <sub>3</sub>	Ortorrómbico	6.58	Nassau, Saxony, England, USA and Spain
Anglesita	PbSO <sub>4</sub>	Ortorrómbico	6.3	Namibia, Germany, USA, Spain, Australia and Mexico
Litargirio	PbO	Tetragonal	9.35	Appears in conjunction with Galena or Hydro-Cerucite

**Table 1:** Crystallographic forms in which the lead mineral appears in the earth, also density and global location.



**Figure 3:** Different forms of use of the zirconium: a) zirconium dioxide (ZrO<sub>2</sub>); b) zirconium metallic; and c) different applications; d) dental; e) in laboratories; f) ornamental as gem.

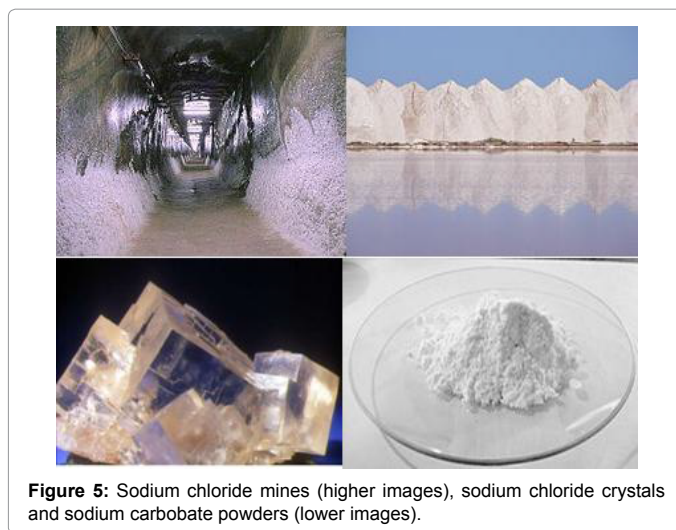


**Figure 4:** Forms in which the titanium is presented: Rutile and Anatasa and its multiple current applications.

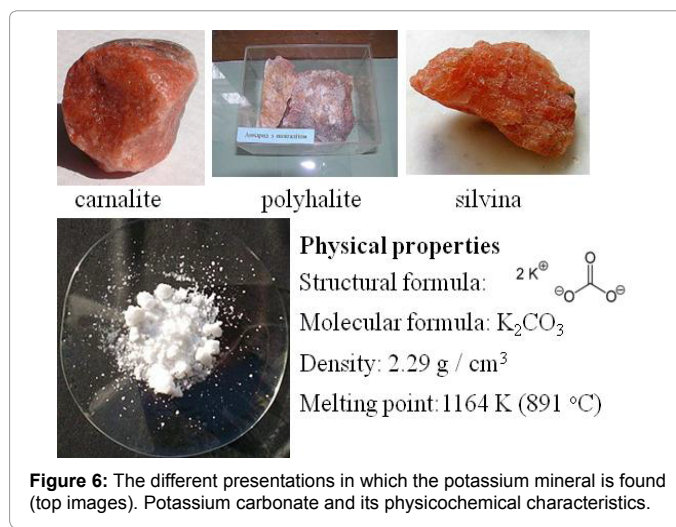
There are two main methods for obtaining the zirconium: the Kroll and the Van Arhel process.

The so-called Kroll process is the most commonly used for obtaining zirconium. It is a process of reductive chlorination in which the preparation of the chloride is made to go to a second phase of reduction using magnesium.

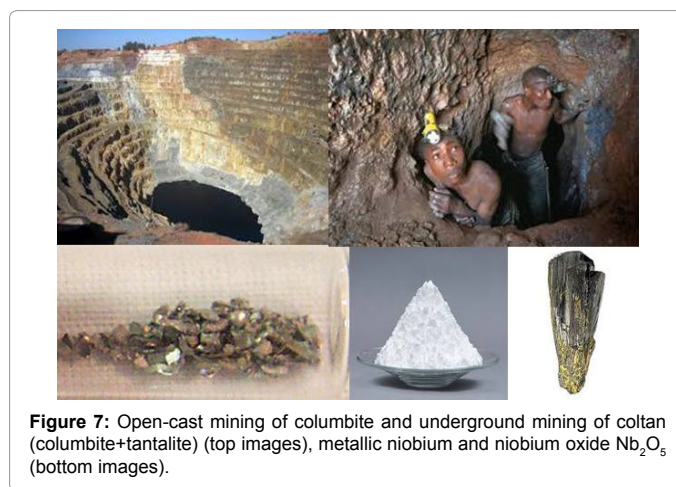
The Van Arhel process is based on the dissociation of zirconium iodide. Through this process is obtained zirconium of greater purity than with the Kroll process. When dissociating the zirconium iodide a metallic zirconium sponge is obtained, Which is melted to obtain the zirconium ingot (Figures 7-9).



**Figure 5:** Sodium chloride mines (higher images), sodium chloride crystals and sodium carbobate powders (lower images).



**Figure 6:** The different presentations in which the potassium mineral is found (top images). Potassium carbonate and its physicochemical characteristics.



**Figure 7:** Open-cast mining of columbite and underground mining of coltan (columbite+tantalite) (top images), metallic niobium and niobium oxide Nb<sub>2</sub>O<sub>5</sub> (bottom images).

### Applications

• 90% of the consumption is used, in the form of alloy (zircaloy) in nuclear reactors, due to its resistance to corrosion and to have very low neutron capture section.



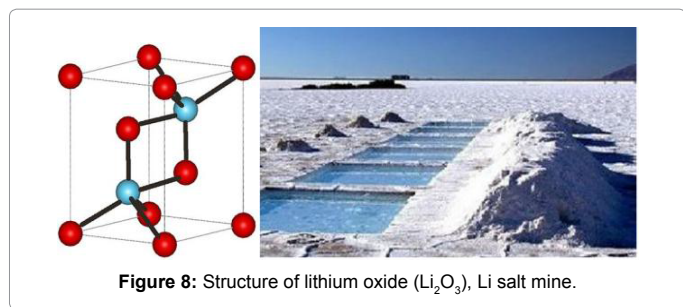


Figure 8: Structure of lithium oxide (Li<sub>2</sub>O<sub>3</sub>), Li salt mine.

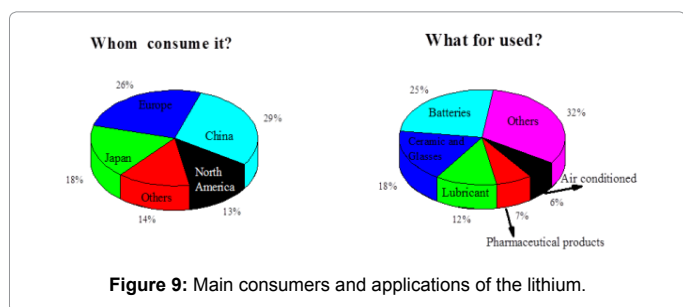


Figure 9: Main consumers and applications of the lithium.

- As an additive in steels obtaining very resistant materials. Also in alloys with nickel for the chemical industry for its resistance against corrosive substances, especially for valves, pumps, pipes and heat exchangers.

- Manufacture laboratory crucibles, furnace lining and refractory material in ceramic and glass industries.

- Yttrium stabilized zirconium oxide is widely used in dentistry for the manufacture of fixed prostheses, removable prostheses and implant abutments. In addition, it is used for the replacement of joints since it is a more biocompatible material like the titanium.

- Heat exchanger, vacuum tubes and light bulb filaments.

- For military purposes it is used as an incendiary agent, such as the Dragon Breath Cartridge.

- In alloys to obtain materials with superconductivity and magnetism at low temperatures.

- In jewelry; Is an artificial gem called zirconite that imitates the diamond.

- In an industry in its infancy: the manufacture of cutting blades, are extremely durable and resistant to steel.

- Used as an additive to make synthetic sand.

**Titanium (Ti):** Titanium [10,11] receives its name from the ancient Greek, white earth (its rust is of the purest whites). It was discovered in 1790 by the English chemist William Gregor and in 1795 the German chemist Martin Klaproth gave it the name titanium.

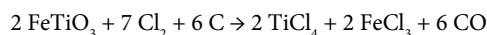
It is the fourth most common metal in nature, is present in igneous rocks, materials formed by decomposition of igneous rocks, many minerals, especially those with iron and all plant and animal organisms.

Titanium is extracted first from rutile (titanium oxide), abundant in coastal sands. For this, the titanium must undergo a refining process before, to prevent its reaction with substances such as nitrogen, oxygen and hydrogen.

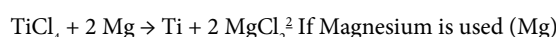
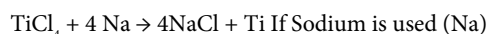
To obtain pure titanium, from the minerals that contain it, is mostly

used the so-called Kroll Method, which consists of the reduction of titanium tetrachloride with magnesium, in an atmosphere of argon or helium that prevents its oxidation. The process is the following:

- Obtaining of titanium tetrachloride by chlorination at 800° C, in the presence of carbon, according to the reaction:



- The TiCl<sub>4</sub> is reduced with magnesium or ground sodium in an inert atmosphere according to:



The Kroll method, traditionally used since 1937, has been tried to modify to obtain titanium powder used in the coating of reinforcements and aerospace components, transport and chemistry to increase the strength of surfaces.

Titanium dioxide is a compound whose formula is (TiO<sub>2</sub>). It is in a black or brownish form known as rutile. The natural forms found less in nature are the anatase and brookite. Both the pure rutile and the anatase are white. The basic black oxide, (FeTiO<sub>3</sub>), is in natural form as the mineral called ilmenite. Titanium dioxide is the main commercial source of titanium. Approximately 95% of the titanium consumed is in form of titanium dioxide, due has many industrial applications.

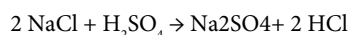
**Sodium (Na):** Sodium is a chemical element of symbol Na (from the Latin, natrium) with atomic number 11, was isolated by Sir Humphry Davy in 1807. It is a soft alkaline metal, silverish, very abundant in nature, being in the sea salt and halite ore. It is very reactive, burns with yellow flame, oxidizes in the presence of oxygen and reacts violently with water. Sodium is present in large quantities in the ocean in ionic form. It is also a component of many minerals and an essential element for life [12].

Halites are the ores associated with the production of sodium chloride, although it is usually associated with magnesium chloride, calcium and potassium. A mining activity is carried out in two possible ways:

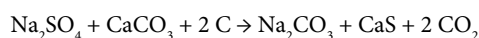
- Ore is extracted and pulverized until the desired appearance
- Water is pumped and dissolved with the minerals extracting a kind of mud-brine that is then dried by evaporation.

The methods used depend largely on the geological characteristics of the salt deposits. However the way it is used in ceramics is in Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>), is a white and translucent salt, used among other things in the manufacture of soap, glass and dyes. It can be found in nature or obtained artificially, thanks to a process devised and patented in 1791 by French Nicolas Leblanc, which consists of:

1ero- Common salt with sulfuric acid



2do- Na<sub>2</sub>SO<sub>4</sub> with limestone and coal:

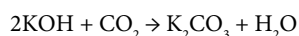
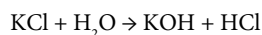


Later this method was replaced by the one devised by the Belgian chemist Ernest Solvay, his method was able to lower the process and eliminate some of the problems presented by the Leblanc method. This method uses as raw materials sodium chloride (common salt), ammonia and calcium carbonate [13,14].

**Potassium (K):** constitutes about 2.4% by weight of the earth's crust being the seventh most abundant. Due to its solubility, it is very difficult to obtain the pure metal from its minerals. However, in ancient seabed and lakes there are large deposits of potassium minerals (carnallite, polyhalite and sylvite) in which the extraction of the metal and its salts is economically viable [15].

Potassium carbonate is a white water-soluble (alcohol-insoluble) salt of the chemical formula  $K_2CO_3$ . Form strong alkaline solutions. It is usually formed as a product of the chemical reaction between potassium hydroxide or caustic potassium (KOH) and carbon dioxide ( $CO_2$ ). Is a hygroscopic substance, which often appears as a water-based solid. It is commonly used for the manufacture of soap and glass and is the main component of caustic potash as found in nature.

Potassium carbonate was obtained from the leaching of ash from wood or other burned vegetables. The first industrial method to obtain it is the Leblanc process already in disuse. Nowadays, potassium carbonate is commercially produced from the reaction between carbon dioxide and potassium hydroxide obtained by electrolysis of the potassium chloride according to:



**Niobium (Nb):** is a chemical element of 41 atomic number, located in 5 group of the elements periodic table. It is a transition metal, ductile, gray, soft and little abundant [16]. It is found in the mineral niobita or columbita. It is mainly used alloy in steels, conferring them a high resistance by adding only 0.1% of Nb. It is also used in welding, industries: nuclear, aerospace, electronics, optics, medical, numismatics and jewelry. In the last three applications, its low level of toxicity makes it highly quoted and with advantages over other materials.

It is estimated that niobium is the 33 most common elements on the Earth's surface, but is not found free in nature. It is found in combination with other mineral elements, such as tantalum, both of great importance in today's microelectronics industry. Australia is the world's largest producer, so are Brazil, Nigeria, China, Thailand and the Scandinavian countries. Recent research estimates that most of the potential global reserves of tantalite are located in Africa, 80% of which are in the territory of the Democratic Republic of Congo.

The metal is obtained in two stages:

1- Separation of tantalum by solvents and transformation into  $Nb_2O_5$  [17].

2-  $Nb_2O_5$  is reduced in two stages with carbon

- First one at 800° C, NbC is formed,
- In the second stage the NbC at 2000° C, acts as a reducer of the oxide and the metal is produced.

In addition, the extracted ore is finely milled and separated by flotation and magnetic separation of high intensity.

**Lithium (Li):** is a chemical element of atomic number 3. In the periodic table, it is in-group 1, between the alkaline elements. In its pure form, a soft, silver-white metal rust quickly in air or water. It is the lighter solid element and is used especially in heat conducting alloys, in electric batteries and their salts in the treatment of bipolar disorder [18].

It is the lightest metal, like the other alkaline metals, it is univalent and highly reactive, although less than sodium, so it is not found free in nature.

It was discovered by Johann Arfvedson in 1817 in the spodumena and lepidolite of a petalite mine ( $LiAl(Si_2O_5)_2$ ) on Utö Island (Sweden) that he was analyzing. In 1818 C.G. Gmelin was the first to note that lithium salts make the flame a bright red color. Both attempted, unsuccessfully, to isolate the element from their salts, which eventually got William Thomas Brande and Sir Humphrey Davy by electrolysis of lithium oxide.

In 1923 the German company Metallgesellschaft AG started producing lithium by electrolysis of molten lithium chloride and fused potassium chloride.

Since 2010, lithium batteries have become the primary method of replacing pollutants with fossil fuels. The "triangle of lithium" composed of the salar Uyuni in Bolivia, salar Atacama in Chile and salar Hombre Muerto in Argentina account for between 50 and 85% of the world's reserves of that mineral [19]. There are other smaller salar such as Puna in Argentina and Manaure in Colombia, as well as in Afghanistan, recently discovered, whose magnitude is yet to be precisely determined. The accelerated growth in the use of lithium-ion has caused the accelerated increase of its price in 7 times its value in six years.

#### Applications

- Heat transfer applications due to their specific high heat.
- Anode for electric batteries, due to their high electrochemical potential.
- As a drying agent, due to its high hygroscopicity in form of chloride and bromide of lithium.
- In medical treatments of psychopathologies such as manias and bipolar depression, lithium salts ( $Li_2CO_3$ ) are used.
- Stearate is a general purpose lubricant in high temperature applications.
- In the synthesis of organic compounds, for the coordination of ligands through the lithiated intermediate.
- As an air purifier extracting carbon dioxide, used in spacecraft and submarines.
- In alloys used in aeronautical construction as well as in the manufacture of ceramics and lenses.
- In nuclear applications.

Lithium is industrially obtained from the electrolysis of molten lithium chloride (LiCl). The main minerals from which it is extracted are lepidolite, petalite, espodumena and amblygonite (Figure 10).

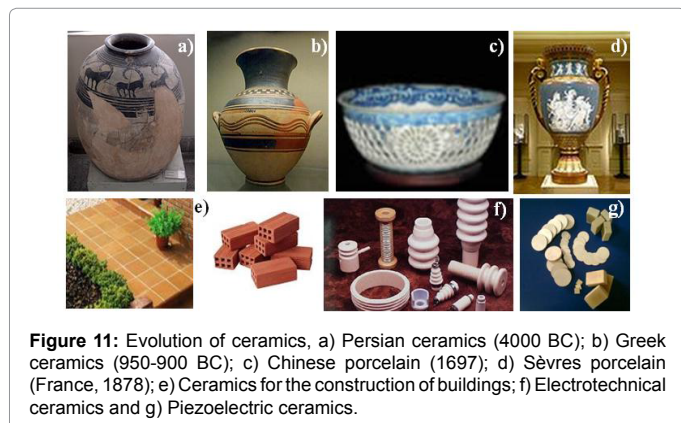
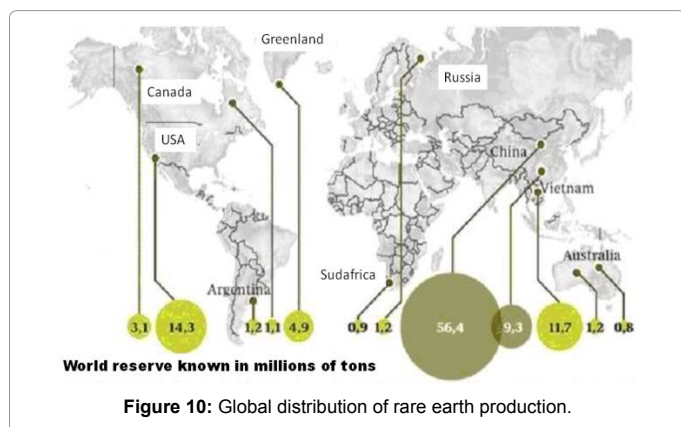
**Lanthanides or "rare earths":** The series of lanthanides is the group of chemical elements that follow the lanthanum in-group IIIB of the periodic table. Their atomic distinction is that they occupy in electronic sublevel 4f. At first, they were only the elements with atomic numbers from 57 to 71, because the minerals in which they were accumulated were unknown and were isolated as oxides (or "lands") hence their name [20]. Compared with many other elements, rare earths are not "rare", their absolute abundance in the lithosphere is relatively high, but the study of these elements has been hazardous because of the similarity of their chemical characteristics. At this moment, this group is composed of: Lanthanum (La 57), Cerium (Ce 58), Praseodymium (Pr 59), Neodymium (Nd 60), Prometio (Pm 61), Samario (Sm 62), Europio (I 63), Gadolinium (Gd 64), Terbio (Tb 65), Dysprosium

(Dy 66), Holmium (Ho 67), Erbium (Er 68), Tulio (Tm 69), Ytterbium (Yb 70), Lutetium (Lu 71), Yttrium (Y 39) and Scandium (Sc 21), for having similar characteristics [21-23].

Lanthanides are found in many minerals, mainly in the monazite (which is essentially a lanthanide orthophosphate); their distribution in minerals is La, Ce, Pr and Nd constitute approximately 90%, with Cerium being the most abundant element and Tulio the scarce. Pure lanthanides are silver metals with high boiling points. They react slowly with air, except Samarium, Europium, and Ytterbium, which are much more reactive with oxygen. Metals are preparations of fluorides or oxides by treatment with a strong metal reducer, such as calcium, or salts of chlorides and flowers by electrolysis at high temperatures. Lanthanides are typically insolubilized in a group by precipitating their insoluble hydroxides, oxalates or phosphates. Then they are separated by an ion exchange.

Until recently the only commercial use of rare earths was as a mixture of metal, mainly cerium, lanthanum, and neodymium, for lighter stones. However commercial production of these rare earths today is growing because of its multiple applications in metallurgy (to remove sulfur and oxygen), obtaining permanent magnets with a demand growth of 15% per year in the last 10 years. In production of television screens and energy efficient lamps; such as catalysts, ultraviolet light filters in glass, batteries for hybrid vehicles, dissimilar electronic components of mobile telephony and laptops (Figure 11).

In particular, the lanthanum is used in the production of piezoelectric ceramics increasing the dielectric permittivity and the gadolinium can decrease the temperature of the phase transitions of the PZT.



### Ceramic Method for Piezoelectric Ceramics

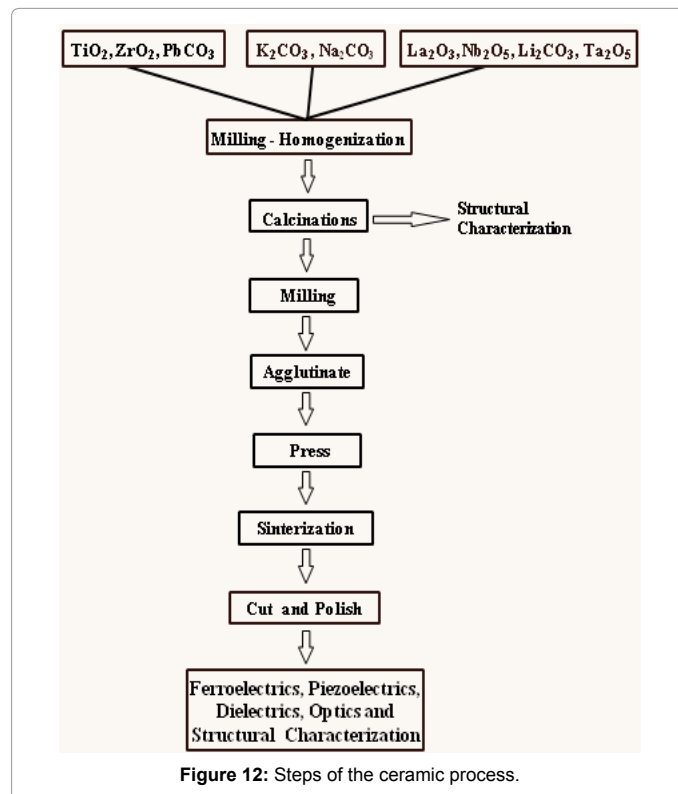
Under the name of the general term of pottery, objects are grouped that differ substantially from one another in the composition of their base, terracotta, stoneware, porcelain, on the exterior in which their shape can be covered by glaze or enamel, and in the How the cooking, temperature, oxidation atmosphere or reduction was carried out.

Pottery is the oldest industry of humankind, is a genius idea of man and fruitful since it has developed extensively throughout history not only in quantity but also in the variety of products, some of them, of transcendental importance for Technologies.

The manufacture of bricks arises in areas where the stone is scarce and the clay abounds. Ceramic material is the product of various raw materials (mainly clays) made in a powdery or pasty state (to easily communicate the form) and acquiring the stone consistency by physicochemical processes when cooking these clay soil.

Ceramics are the synthesis of one or more chemical compounds, which for the traditional ceramic process are usually oxides and/or carbonates. There is a strong influence on the desired final characteristics of the starting materials used. For the ceramist, it is important to consider the process (Figure 12) as a whole in formulating the powder composition [24] (Figure 12).

The interaction of the materials during the ceramic process is so complex that the total quantitative description of all the events and their interactions is not possible. To understand the role of powders it is necessary to join a significant number of factors, such as the characteristic of the powders and agglomerates of the starting materials. If they are large or if the tendency is to form dense agglomerates, intimate and homogeneous mixing will be difficult or impossible. Also if the particles are hard (abrasive) can mean a source of contamination during the grinding process. These interacting factors may have a



dominant effect on the formation kinetics of the compound during subsequent heat treatments [25].

### Grinding and Calcination

The operation with mills is used to homogenize powders, reduce particle sizes and break agglomerates. It is of special attention in the process of technical ceramics the type of mill to be used and the time of grinding. It has been observed that the particle size decreases and the amount of contaminant increases with the grinding time.

Calcinations is one of the most studied parts of the ceramic process [26,27], since it has a strong influence on the characteristic of the powders. Four stages [28,29] have been found for the case of ceramics type PZT.

Stage 1: Begins the decomposition of the starting materials (carbonates, oxalates, nitrates).

Stage 2: Lead oxide reacts with titanium dioxide.

Stage 3: The composition of the desired compound is initiated; the zirconium dioxide is reacted with the mixture obtained in the previous step.

Stage 4: Homogenization of the reaction.

The selection of the reactants, grinding time and calcinations regimes is sustained on the experience obtained by previous studies [30,31]. To confirm that occurred the formation reaction of the PZT system completely without the presence of other phases, is carried out X-ray diffraction on the calcined material.

### Sintering

This stage of the ceramic process has as its object the union between particles, reducing the porosity and obtaining the ceramic body. During the same, the porosity of the samples decreases from 35-50% at the initial time to 5-10% at the end of the process.

The force that governs sintering is the reduction of the surface energy of the particle. This reduction is achieved by the transport of matter from the center of the particles to the "neck" or contact between particles, these causes a reduction of the surface area that leads to a reduction of the free energy in the system, thus ruling the sintering [32]. In the process, the following steps are well defined:

- Removing the binder.
- Reaction of components
- Densification.
- Grain growth.

The sintering process is divided into two regions. The first region (and the most critical during heating) is between 60° C and 350° C [33]. In this region, the moisture and the binder are volatilized and extracted. Before starting densification, it is necessary to remove the binder, which has fulfilled its function in the compaction process, as well as the residual moisture contained in the compacted ceramics; this operation must be carried out very slowly, to avoid cracks and pores that decrease the density of the ceramic body. For simple shapes of shaped parts a heating of approximately 10° C/min can be performed, being tolerated without structural difficulties.

In the second region from 350° C to the sintering temperature, the reaction of the raw material residues that have not yet done so in the calcination step occurs, and then the densification process begins.

It must be taken into account if the material is volatile or not, in the PZT the lead is a highly volatile element as in the KNN the sodium and the potassium are it, reason why the process must be realized in closed crucible and with atmosphere control. After sintering, chemical analyzes are performed to confirm the desired stoichiometric or to determine the obtained [34,35].

The percentage of binder used to facilitate the molding of the ceramic by dry pressing is about 5% by weight, depending on the binder used; the most common are starch and polyvinyl alcohol.

## Results and Discussion

In this section, we will present examples of how they influence the origin of the reagents, their purity, granulometry, crystalline phase and the process of obtaining in the characteristics and properties of the piezoelectric and ferroelectric ceramics. There is an extensive literature that generalizes these aspects [36], but here we will present specific examples of each behavior (Tables 2-4).

### Reagents of equal purity and different granulometry

The formation reaction (calcination) of PZT ceramics is analyzed to obtain the composition  $Pb(Zr_{0.52}Ti_{0.48})O_3$ . Combinations of raw materials that react completely in the shortest possible time are analyzed, were used the reagents show in Table 4.

The starting reagents are analyzed to corroborate the purity and crystallographic structure provided by the manufacturers. Differential thermal analysis (ATD) was performed according to reference 27. In this example, the granulometry of lead carbonate was a determining factor in the PZT formation reaction process. For  $PbCO_3$  Merck the particle size was <1 μm and for  $PbCO_3$  Reachin (blue band) it was 0.01-5mm. The reagents for the  $TiO_2$  and the  $ZrO_2$  presented similar granulometry (Tables 2-4).

This implies that in the process of obtaining the PZT, a longer grinding time is required for the Reachin  $PbCO_3$  than for the Merck. If identical processes are carried out, what occurs in Figure 13, for the mixture a) the peaks present between 200 and 460°C correspond to the

Country	Thousands of tons	% of total
Australia	1291	30,6
South Africa	850	20,1
Canada	767	18,2
Norway	382	9,1
Ukraine	357	8,5
Total of 5 countries	3647	86,4
Total world	4221	100

Table 2: Main titanium oxide producers and production in 2003.

Potassium mineral	Chemical formula	Crystal system	Density (g/cm <sup>3</sup> )
Carnallite,	KMgCl <sub>3</sub> ·6H <sub>2</sub> O	Orthorhombic	1,60
Polyhalite	K <sub>2</sub> Ca <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>4</sub> ·2H <sub>2</sub> O	Triclinic, pinacoidal	2,77
Sylvite	KCl	Cubic	2,00

Table 3: Forms in which the potassium mineral is presented, chemical formula of the same, crystalline system and density.

Sample	Reagent		
	PbCO <sub>3</sub> (%)	ZrO <sub>2</sub> (%)	TiO <sub>2</sub> (%)
a)	Merck (99)	BDH (99)	Sigma (99.5)
b)	Reachim (99.5)	Riedel (99)	Riedel (99)

Table 4: Reagents used.



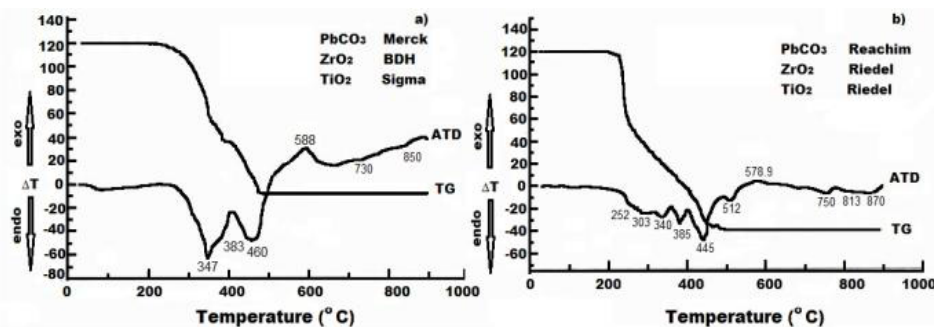


Figure 13: Thermal analysis of the mixtures of powders used.

stages of dissociation of the carbonate and formation of lead oxide in its structural modifications tetragonal (litargiro) and Rhombic (massicot) [37], these transformations produce weight loss, as evidenced in the TG curve (Figure 13). The formation of lead titanate (PT) is considered to occur between 450-650°C [38,39], in this mixture appears an exothermic peak at 588°C associated with this process, as observed this process does not imply either gain or loss weight. In the range of 700-900°C appears lead zirconate (PZ) and lead titanate-zirconate (PZT) formation.

For the mixture b), the peaks present between 200 and 512°C correspond, in addition to the dissociation of the lead carbonate, already explained above, to structural water and hydroxides present in the composition. Although the peak associated to the PT appears 10°C lower than case a), the rest of the processes between 700-900°C appear shift at higher temperatures. This ratifies the importance of granulometry in the reaction process and formation of the desired product.

### Mixing of phases in raw materials

The unknown mixtures of phases in the row materials provoke properties not wanted. It is for that, very important analyze the reagents used to confirm the information of the suppliers [40]. Structural characterizations of all ceramics process are very important for the results, in this case the zirconium powders there were different activity, and were necessary study what happened. Was made the XRD and DSC (Figure 14), both show the difference between the zirconium powders.

The solution was calcinated, made against XRD, and observed what happened. Ceramics obtained with the zirconium powders calcinated have a good structural resolution. The XRD show the patter of perovskita with tetragonal and rhombohedra phase (Figure 15). The properties for sensor construction are the best.

### Different phases of one reagents and similar results

In this example were used different lead oxide  $PbO$ ,  $PbO_2$  and  $Pb_3O_4$  as Pb sources, were mixed with  $TiO_2$  and  $ZrO_2$  following stoichiometric ratios to obtain PZT samples with a composition of  $Zr/Ti=53/47$ , near to the morphotropic phase boundary (MPB) [41]. In this case was studied the milling time and calcinations temperature to obtain perovskite structure. The previous study of row materials contributes that: in  $PbO$  were identified orthorhombic and tetragonal phases, whereas in  $PbO_2$  and  $Pb_3O_4$  platnerite and minium were identified, (both having tetragonal phase), the samples were identified as A( $PbO$ ), B( $PbO_2$ ) and C( $Pb_3O_4$ ).

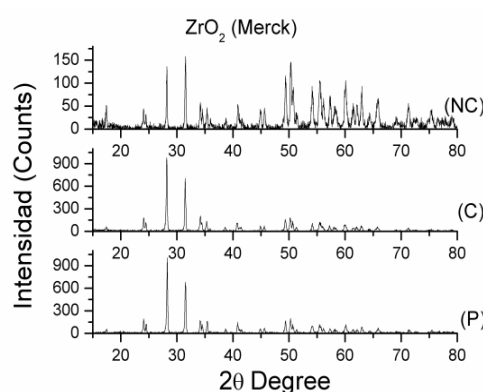


Figure 14: XRD patters of  $ZrO_2$  problem not calcinated (NC),  $ZrO_2$  problem clacinated (C) and  $ZrO_2$  patter not calcinated (P).

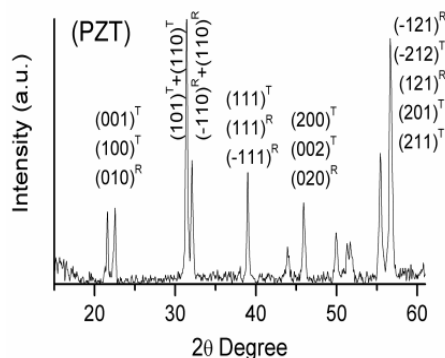
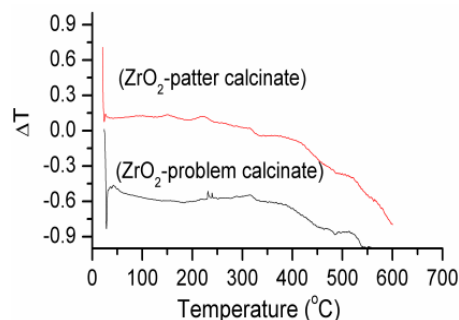


Figure 15: DSC of  $ZrO_2$  problem calcinated and  $ZrO_2$  patter calcinated, also DRX patter of PZT obtaining of  $ZrO_2$  problem calcinated, appear a classic perovskite structure with mixing of tetragonal and rhombohedral phases.



The results of milling and thermal process shows that A samples need more temperature for obtain the wanted result, only obtained at 900°C but too appear pyrochlore phase undesirable, for B and C samples this result was obtained at 700°C with pyrochlore phase, that disappear completely at 900°C (Figure 16). The most important result is present in Table 5.

In this example the author obtain by mechanical activation process reduce the particle size, accelerating the process of obtaining of the PZT (350°C), compared to the synthesis of traditional methods, the ceramics powders are homogeneous and with sub-micrometric size. Although for the PbO and the Pb<sub>3</sub>O<sub>4</sub> similar results are obtained, they are better those obtained for the Pb<sub>3</sub>O<sub>4</sub>, because it has smaller coercive fields (Ec) and bigger remaining polarization (Pr) (Table 5).

### Differences caused by variations in the ceramic process

Milling process produce different influence as grain size of powder and specific initial surface that causes difference in final density of material. BaTiO<sub>3</sub> ceramics obtained from powders of BaCO<sub>3</sub> and TiO<sub>2</sub> stoichiometric, exhibit properties that reveal the presence of a memory effect related to the value of specific surface of the starting powders. This magnitude change alternatively with maxima and minima depending on the milling time, a lattice distortions of BaCO<sub>3</sub> takes place, no similar effects were detected for TiO<sub>2</sub> (Figure 17).

In the second examples in this topic, we present the influence of conformation pressure and sintering temperature in ceramics of niobate of sodium-potassium (KNN) [42,43]. The increase of the conformation pressure from 10 MPa to 80 MPa causes a great effect in the transition temperature (Figure 18a), decreasing it near room temperature; additionally there is an increase of the grain size (Figure 18c) and smaller polarization state (Figure 18b). The information

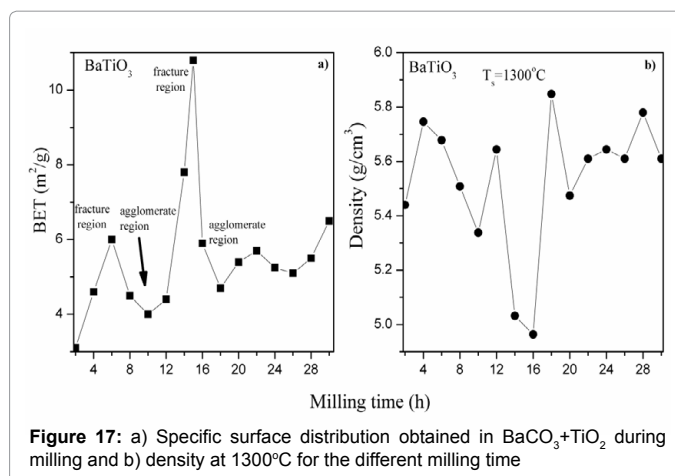


Figure 17: a) Specific surface distribution obtained in BaCO<sub>3</sub>+TiO<sub>2</sub> during milling and b) density at 1300°C for the different milling time

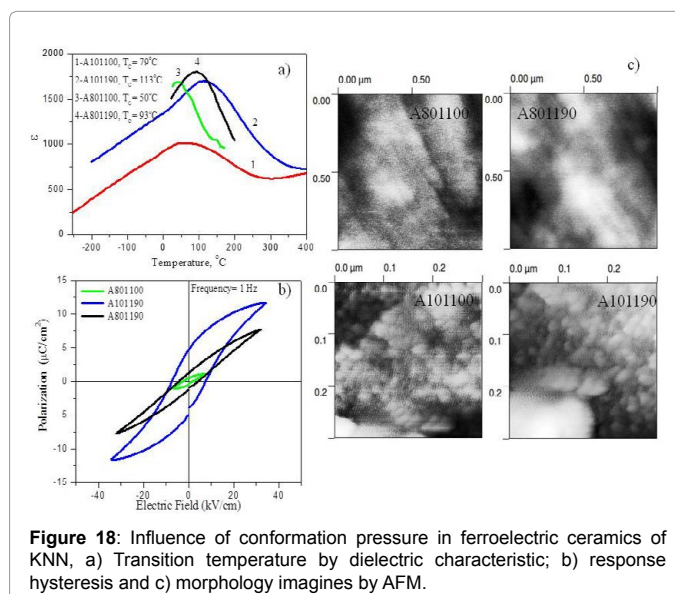


Figure 18: Influence of conformation pressure in ferroelectric ceramics of KNN, a) Transition temperature by dielectric characteristic; b) response hysteresis and c) morphology images by AFM.

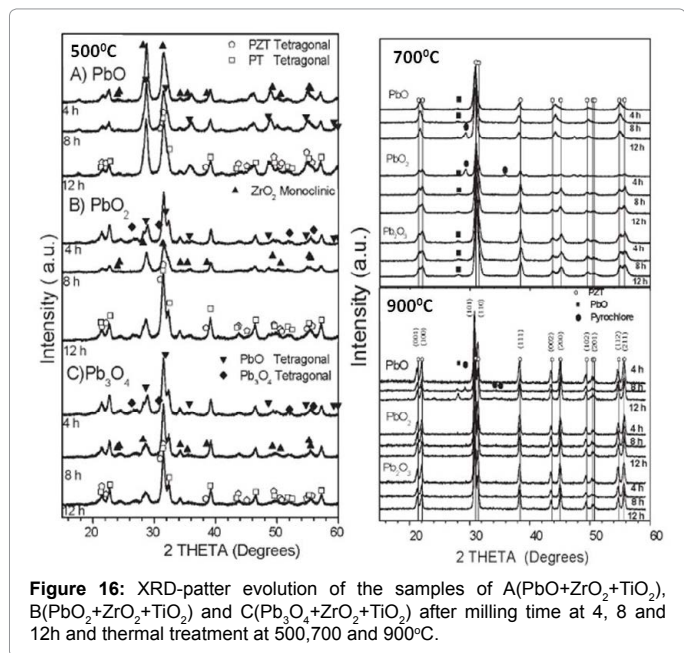


Figure 16: XRD-pattern evolution of the samples of A(PbO+ZrO<sub>2</sub>+TiO<sub>2</sub>), B(PbO<sub>2</sub>+ZrO<sub>2</sub>+TiO<sub>2</sub>) and C(Pb<sub>3</sub>O<sub>4</sub>+ZrO<sub>2</sub>+TiO<sub>2</sub>) after milling time at 4, 8 and 12h and thermal treatment at 500,700 and 900°C.

Sources of Pb	T <sub>sint.</sub>	E <sub>max</sub>	P <sub>r</sub>	E <sub>c</sub>	P <sub>r</sub> /P <sub>max</sub>	ρ (g/cm <sup>3</sup> )	T <sub>c</sub> (°C)
Pb <sub>3</sub> O <sub>4</sub>	1250	53.62	34.02	11.3	0.99	7.47	396
PbO	1250	55.34	31.35	18.1	0.94	7.54	394

Table 5: Some results of ferroelectrics ceramic obtained of different lead sources.

obtained from the distribution of ferroelectric domains indicates that a greater extension of the domain size and the presence of greater area fraction of out-of-plane domains appear to be associated with good ferroelectric behavior, as in the case of samples A101190 and A801190. The microstructure was studied with atomic force microscopy, AFM. The grain size for samples obtained at bigger pressure (A801100 and A801190) was 1.0 μm, while for samples at smaller pressure (A101100 and A101190) was 28 ± 8 nm.

Other examples in KNN ceramics was obtained by López-Matus [44], modifying the process presented previously had milled with mechanic-synthesis. This allowed diminishing the time of having milled from 12 h to 1.5 h. The results are comparable to those of a PZT.

### Introduction of dopants to modify properties

We will present three examples that show how small concentrations of an element can change significantly the properties of the material. Both examples are in PZT ferroelectric ceramics. In this example, the visible photoluminescence effect is analyzed at room temperature in a sintered Pb<sub>0.95</sub>Sr<sub>0.05</sub>(Zr<sub>1-x</sub>Ti<sub>x</sub>)<sub>1-y</sub>Cr<sub>y</sub>O<sub>3</sub> perovskite-type structure system, doped with Sr and Cr. The excitation bands used were 267, 325, 373, 457, 635 and 680 nm, but the best result was obtained at 373 nm [45].

The intensity and energy of such emission in this system have been studied by changing the molar Cr concentration ( $0 < y < 0.005$ ) and the Ti content ( $x$ ), with  $x=0.20, 0.40, 0.53, 0.60$  and  $0.80$ , on both sides of the morphotropic phase boundary (MPB) zone (Figure 19 and Table 6). The principal emission bands are at the energies 1.73, 1.87 and 3.03 eV. The changes that were caused by Zr or Ti ions in the symmetry presented in the rhombohedral or tetragonal side of the MPB are more important.

The second example is gadolinium (Gd) doped PZT [46], this causes a decrease in the ferroelectric temperature transition (from rhombohedral ferroelectric phase to tetragonal ferroelectric phase). Determinants by different techniques that said transition was ferroelastic transition (Figure 20).

The third examples are La, Nb and La + Nb doped PZT ceramics obtained by traditional ceramic method. In the case it is analyzed how these dopants modify the conduction band (CB), the valence band (VB) and the band forbidden ( $E_g$ ) of the materials, as well as its dielectric characteristics. From this, it is proposed a model of the possible recombination process of the electrons ejected by photons (Figure 21), measured through the photoluminescence and absorption spectrum of each material [47].

### Conclusions

The ceramic process has evolved with man's development, as well as

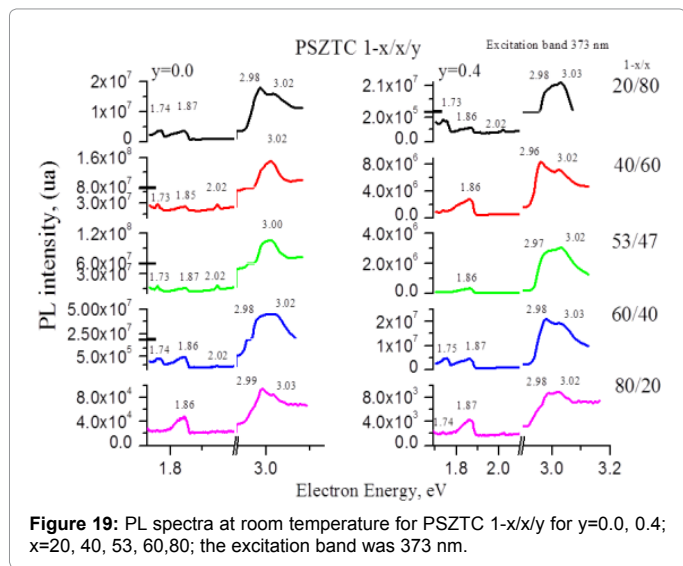


Figure 19: PL spectra at room temperature for PSZTC 1-x/x/y for y=0.0, 0.4; x=20, 40, 53, 60, 80; the excitation band was 373 nm.

Samples	Emission energy (eV) for different λ excitation (nm)					
	267 nm	325 nm	373 nm	457 nm	635 nm	680 nm
PSZTC 80/20/0.0	3.99	3.36	1.87	2.84	1.79	1.74
	4.09	3.46	3	2.52	1.85	1.77
			3.04	2.57		
PSZTC 80/20/0.4			2.61			
	3.98	2.19	1.87	2.47	1.79	1.71
	4.24	2.65	2.03	2.49	1.84	1.73
		3.36	2.66	2.56	1.86	1.75
		3.49	2.99		1.89	
			3.04			
		3.08				

Table 6: Room temperature PL spectra fixing the excitation band at 267, 325, 373, 457, 635 and 680 nm for PSZTC 80/20/0 and PSZTC 80/20/0.4. Similar results were obtained for the rest of the samples in study.

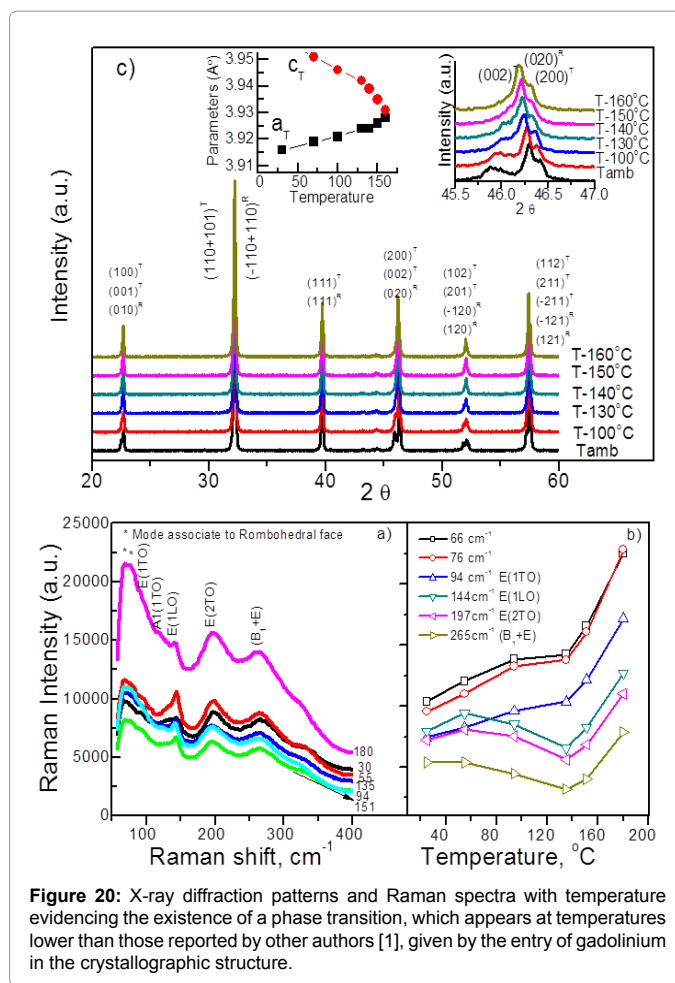


Figure 20: X-ray diffraction patterns and Raman spectra with temperature evidencing the existence of a phase transition, which appears at temperatures lower than those reported by other authors [1], given by the entry of gadolinium in the crystallographic structure.

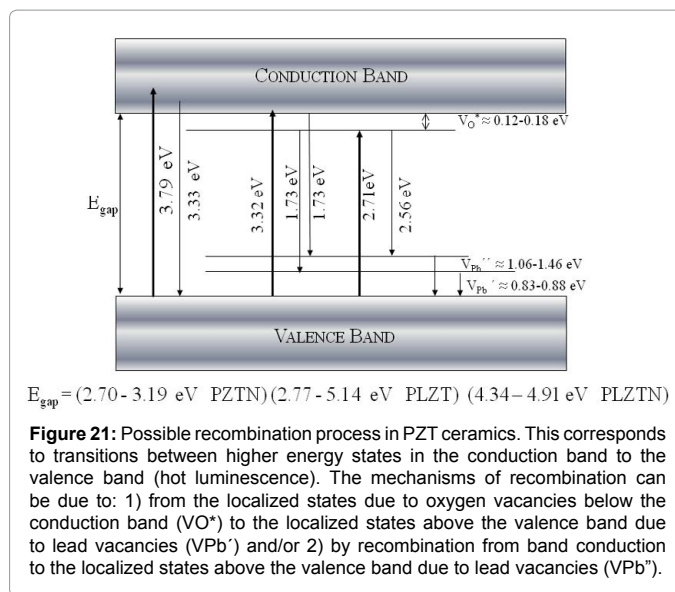


Figure 21: Possible recombination process in PZT ceramics. This corresponds to transitions between higher energy states in the conduction band to the valence band (hot luminescence). The mechanisms of recombination can be due to: 1) from the localized states due to oxygen vacancies below the conduction band ( $VO^*$ ) to the localized states above the valence band due to lead vacancies ( $VPb^*$ ) and/or 2) by recombination from band conduction to the localized states above the valence band due to lead vacancies ( $VPb^*$ ).

with his needs. As seen in the examples, the influence of each step in the desired product is important. The ceramic process has been used and will continue to be used for its simplicity and versatility, in dissimilar objects from the great industry to the delicacy of an ornamental object.

In the particular case of ferroelectric ceramics with perovskite structure, in order to achieve the desired results, it is very important to pay the highest attention to the purity, crystalline structure and granulometry of the raw materials used. Each of these aspects can cause changes in the process, since the raw materials obtained cannot always be discarded, especially at the laboratory level.

The introduction of dopants and changes to the obtaining process can enrich the material or deteriorate the properties required.

#### Acknowledgments

The author would like to thank the national programs of CITMA-Cuba and the Sabbatical Programs of CONACYT-Mexico for their financing support of research, as well as Dr. Fathi Habashi of Laval University of Quebec, Canada for suggest me to write this work.

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**Citation:** Rodríguez MDD (2017) From the Mining to the Obtaining of Ferroelectric Ceramics. J Powder Metall Min 6: 160. doi:[10.4172/2168-9806.1000160](https://doi.org/10.4172/2168-9806.1000160)

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