

# Theoretical approach, elaboration and physical characterization of ceramic materials. Modelisation of the electrostatic potential considering multipolar moments.

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In this review paper, a summary of works developed by our research group is presented. First, we describe a theoretical model for calculating the physical parameters and some experimental results of the type  $ABO_3$  ferroelectric ceramic materials with perovskite structure, and then we present a new sol-gel process for the elaboration of silicates which permits an improvement of the synthesis temperature and the control of grains size. Finally, we describe a theoretical model of the electronic density and electrostatic potential involving multipolar moments.

## I. INTRODUCTION

Many solid materials have been elaborated which are widely utilized for consuming goods fabrication and consequently influence the human mode life. Traditionally, and according to their properties and characteristics, their methods of elaboration and their uses, these materials have been classified as metals, ceramics, glasses, textiles, polymers and composites materials. Each of these categories has its own nomenclature, methodology and norms so that a comparison between these materials is too difficult. But, since many years, a unified theory has been developed for all these materials. This theory is based on the molecular structure, their mechanical (ductility, fragility, plasticity) or physical (electrical conductivity, magnetism, ferroelectricity, supraconductivity, etc.....) properties are interpreted by the different binding types between the elementary constituents; metallic, ionic, covalent, hydrogen, etc., or by their crystalline structure and defects (dislocations, distortions, lacunas,...). Structurally speaking, material science has been developed after the discovering of the X rays diffraction in 1911 by W. H. Bragg which reveals the atomic architecture of the crystalline materials.

The transmission electronic spectroscopy developed in the thirties of the twentieth century, and the scanning electronic spectroscopy developed in the sixties have permitted the micro-structural characterization of different materials giving useful information about their morphology, composition crystallography as well as the repartition of their constituents. Presently, it's known that the mechanical as well as physico-chemical properties of the solid materials are due to the arrangement of their atoms, defects and interatomic forces. All the macroscopic properties of the solid materials may be interpreted from their atomic arrangement and their molecular structures which are characterized by their binding type.

## II. CERAMIC MATERIALS

Ceramic materials are known and utilized many years ago, but due to the technological progresses a great interest has been made again in these materials. Indeed, new techniques, elaboration and growing procedures have been

developed allowing a best knowledge of the physical properties of these materials.

### A. Ferroelectric ceramic materials

The study of the ferroelectric ceramic materials developed in the forties has given important information in the dielectric constant, piezoelectric module and pyroelectric properties. A fundamental study of the physical and physico-chemical mechanisms which are responsible of the physical properties observed in some of the ceramic materials used in microelectronic industry is necessary for the comprehension of these properties as well as their variation as a function of external constraints like temperature, electrical field, etc. Many theoretical as well experimental works have been already made for studying the ferroelectrical properties of the  $ABO_3$  perovskite structure type.<sup>1-6</sup>

In 1949, Roberts<sup>1</sup> evaluated the electronic polarizability of different ions exploiting the Clausius-Mossotti relationship as well as experimental data of the dielectric constant. Slater<sup>2</sup> has improved the calculation of these electronic polarizabilities using a model assuming that all ions possess a dipole moment and only the titanium ion has a non zero spontaneous displacement. The refractive indexes have been calculated from Kinase<sup>3</sup> works and Lawless<sup>4, 5</sup> has introduced the oxygen electronic polarizability anisotropy to get agreement between the calculated and measured birefringency.

According to Bilz and Migoni<sup>6</sup>, the oxygen electronic polarizability should play an important role in the appearing of the ferroelectric state for the  $ABO_3$  perovskites type compounds. Indeed, we can firstly notice that 90 % of the ferroelectric compounds contain oxygen. In the opposite all of the fluorid perovskites present antidistorsive transition.<sup>7</sup> Indeed, in the  $ABO_3$  structure, the oxygen electronic polarizability increases by hybridization of the  $O^{2-}$  p orbitals by the B metal d orbitals; this property is verified in the  $KNbO_3$  case when calculating the electronic band structure.<sup>8</sup> This effect occurs particularly because of the anisotropic environment of the  $O^{2-}$  oxygen, which favored a large polarizability along the binding with the B ion than along the plane



normal to these bindings. The specific role of the oxygen electronic polarizability has been proposed to explain the intensive second order Raman spectrum in the cubic phase of all oxygenated perovskites.<sup>6</sup>

Among the most studied materials, we can cite the pure barium titanate ( $\text{BaTiO}_3$ ), barium titanate doped with iron ( $\text{BaTiO}_3\text{:Fe}$ ), potassium niobate ( $\text{KNbO}_3$ ) and lead titanate ( $\text{PbTiO}_3$ ). These materials present a double interest:

- technologically because of their dielectrical, pyroelectrical, piezoelectrical, optical, electrooptical and ferroelectrical properties. These materials are consequently presented as potential materials for making large capacitance condensers, optical memories and other electronic and optoelectronic devices.

- theoretically because of some of their complex fundamental properties such as the nature of observed phase transitions and optical anisotropy.

According to the "point dipole" microscopic model<sup>9, 10</sup>, the crystalline lattice is constituted by the superposition of five cubic simple sub-lattices, each one corresponds to one type of atoms. In each sub-lattice, each atom is associated to a p electrical dipole moment orientated along the c-axis, considered in the tetragonal phase as the spontaneous polarization direction. We can notice that the fundamental physical parameters of the model are: lattice deformation, shearing and effective charges of different ions in the unit-cell.

This microscopic model permits to first studying the oxygen electronic polarizability of the  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$  and  $\text{PbTiO}_3$  materials in ferroelectrical phases and second to study its dependence on the temperature and wavelength and also the spontaneous polarization.

The results obtained<sup>11-14</sup> show the existence of anisotropy of the oxygen electronic polarizability, particularly these of the  $\text{O}_3$  oxygen (situated along the titanium ion direction) in the tetragonal phase and the  $\text{O}_1$  and  $\text{O}_2$  (situated in the normal plane to the titanium ion direction) in the orthorhombic phase. This confirms clearly the correlation between the optical indexes (macroscopic properties) and oxygen electronic polarizabilities (microscopic properties).

This model may be applied to other  $\text{ABO}_3$  type compounds pure or doped or in solid solution such as  $\text{LiNbO}_3$ ,  $\text{PbZrO}_3$ , PZT ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ),  $\text{KNbO}_3\text{:Fe}$ , KTN ( $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ ).

Experimentally, copper, nickel and antimony  $\text{BaTiO}_3$  and  $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$  doped fine powders have been prepared using the hydrothermal method and analyzed by EPR spectroscopy. Study of the doping rate have been systematically conducted on these materials. A comparative analysis of the ions doping behavior in each of these compounds shows<sup>15</sup>:

- that a hyperfine structure attributed to the  $^{47}\text{Ti}^{3+}$  appears in the antimony doped  $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$  and pure  $\text{BaTiO}_3$ .

- the spectra of the nickel and copper doped samples present signals attributed to the corresponding ions. Oxygen lacunas ( $\text{Vo}$ ) appear by introducing these ions in the perovskite matrix to compensate charges excess which implies the Ni-Ti-Vo and Cu-Ti-Vo dipoles formation.

## B. Elaboration of ceramics by the sol-gel technique

The sol-gel process is widely used for elaborating materials utilized in high technology fields. This elaboration technique permits a precise control of the synthesis parameters and then the final material characteristics. Among the advantages of this elaboration process, one can cite: purity, homogeneity and shaping diversity.<sup>16, 17</sup>

From the chemical point of view, the sol-gel process consists on starting from a precursing solution to form an in situ oxide lattice by inorganic polymerizing reaction. According to the nature of the precursor, one can distinguish two ways:

- the organo-metallic way in which the precursor is an alcoxide dissolved in an organic solvent.

- the inorganic way in which the precursor is simply a metallic salt in water solution.<sup>18</sup>

The classical sol-gel process based on using metallic alcoholates present more advantages: abundance of this chemistry, synthesis of bimetallic alcoholates, possibility to obtain purified reactives,...<sup>19</sup> But the use of these products present some disadvantages: products too expensive and difficult to manipulate, large reactivity gap between the different alcoholates, etc. For this, it is necessary to search new sol-gel ways permitting to benefit from the advantages of this method by eliminating its disadvantages in order to elaborate good ceramic materials.

We have developed a new technique (in collaboration with the CM2 - CEMES at the CNRS in Toulouse, France) to prepare silicates via the aqueous way.<sup>20</sup> The use of alkaline silicates which are soluble in water, specifically  $\text{KHSi}_2\text{O}_5$ , permits to obtain easily silicic acid solutions, by ionic exchange of the alkaline, as a precursor. This method permitted us to obtain variable silicon concentration solutions which are relatively stable. This permits a control of the gelification time. The major advantage of this method is that the mixture of the silicic acid solution with the metallic salt solutions (acid pH) take place without heterogeneous gelification.

The evaporation of such a solution leads to the formation of a more stable transparency gel. The entity containing silicon which initiates the gelefication presents a less cumbersome coordination sphere (hydroxides) and then susceptible of making bridges with other metallic entities which are present in the solution. Whereas the silicon ethanolate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) which the ethanolate groups induced a constrained effect, presents a worse reactivity towards metallic salts.<sup>21</sup>



Zircon or zirconium silicate ( $\text{ZrSiO}_4$ ) is industrially important due to its refractive properties and hardness. It is also utilized as a colored pigment in ceramics after doping by d or f transition metals. To extend its application as a pigment for plastic materials, the mean crystallites dimensions must be so smaller than one micron. Zircon at low temperature,  $100^\circ\text{C}$  instead of  $900^\circ\text{C}$  given in the literature, with controlled grains size ( $< 0.5 \mu\text{m}$ ) has been elaborated by using this new method.<sup>20</sup>

Other silicates, such as  $\text{CaSnOSiO}_4$ ,  $\text{KSbOSiO}_4$  and  $\beta\text{-LiAlSi}_2\text{O}_6$ , have been synthesized using this new sol-gel way. In all cases, the appearing temperature is so smaller than obtained using other traditional methods (solid chemistry for instance), and the grains size control is generally so easy.<sup>22, 23</sup>

The present conducted research works concern the coloring of two silicate matrixes:  $\text{ZrSiO}_4$  and  $\text{CaSnOSiO}_4$  to obtain pigments for plastics industry capable to replace the conventional ones. In fact, the lathers contain heavy metals such as Cd, Pb, Hg,... which may cause environmental pollution. The two other silicates may be used to make ionic conductors.

### III. MODELISATION OF THE ELECTROSTATIC POTENTIAL

The atomic moments are very useful for calculating the intermolecular interaction energies, more precisely for proteins and enzymes containing a large number of atoms. The atomic multipolar moments  $Q_{lmi}$  are determined using the Buckingham model:

$$V(\mathbf{r}) = \sum_i \sum_{lm} \frac{Q_{lmi}}{|\mathbf{r} - \mathbf{R}_i|^{l+1}} Y_{lm}(\theta, \varphi) \quad (1)$$

where  $V(\mathbf{r})$  represent the electrostatic potential at a point  $\mathbf{r}$  obtained from high resolution X rays diffraction

measurements,  $R_i$  characterizes the position of an atom  $i$  of the molecule,  $Y_{lm}$  are the spherical harmonics.

Due to the reliability of the dipolar moments obtained by the adjusting method which consists of an adequate choice of the points  $\mathbf{r}$ , we have calculated the molecular moments. The obtained results<sup>24</sup> permit to get precise information on the global electronic distribution. In other respects, the molecular moments are directly linked to the macroscopic physical properties such as the permittivity, polarizability and birefringency. The molecular moments are also useful in interaction energy calculations because they permit to reduce the calculation sites. Indeed, we can reproduce exactly the electrostatic potential beyond the Van der Waals sphere of a molecule of 30 atoms and only 6 sites, one site is an atom fragment. The mathematical development consists of a movement of translation of  $Q_{lmi}$  atomic moments towards the mass center chosen and sum between them the concerned fragment moments. It is to be noticed that there is a difficulty due to the fact that the atomic moments calculations are expressed in a local framework. They must be then transformed via a number of relations in the same framework and perform a movement of translation on the real harmonic functions  $Y_{lm}$ . This calculation has been applied to determine the molecular dipolar moment of crystallized water in other compounds which the electronic densities and electrostatic potential have been obtained by high resolution X rays diffraction.

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