

ELABORATION AND STRUCTURAL CHARACTERIZATION OF A COMPOSITE MATERIAL BASED ON CERAMIC / POLYMER

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ABSTRACT

The polycrystalline samples of « Ba (Zr_xTi_{1-x})O₃ », x = 0.50, were prepared by high temperature solid state reaction technique. The formations of the compounds were confirmed by X-Ray diffraction (XRD) analysis. Fourier transform infrared spectroscopy (FTIR) analysis confirms the formation of perovskite structure. The polymer/ceramic composites were prepared using polyvinyl chloride (PVC) as polymer matrix and Ba (Zr_xTi_{1-x})O₃ noted (BZT) as ceramics powder In a weight percentage 50/50 . We present the various preparation steps of the synthesis reaction, then we will detail the different analysis techniques applied to this material, we start first by the x-ray diffraction, thermal analysis, following FTIR spectroscopy. These studies are carried out under air atmospheric conditions help us to accumulate as much information on these materials.

KEYWORDS: BZT / polymer / composite / diffraction of x / IRTF rays.

1 INTRODUCTION

In recent years material scientists around the globe are involved in research and development of new multifunctional ceramic materials for many device applications such as multilayer capacitors, optical shutters and modulators, computer memory and display, microwave communication devices, piezoelectric detectors, ferroelectric random access memory (FRAM) etc [1-2].

Ferroelectric materials can be studied in the form of single crystal or in the form of polycrystalline ceramic oxides. For the study of ferroelectric properties, homogeneous single crystal is usually preferred due to minimum effect of surfaces and imperfections. But single crystals require particular care in their preparation, cutting and polishing to make them suitable for device applications. The presence of grain boundaries gives rise to additional effect and play an important role for various physical properties, which is not present in single crystals. Ceramics oxides also possess good thermal, chemical and mechanical stability [1, 2].

Barium titanate (BaTiO₃) is the first ferroelectric ceramic belongs to perovskite structure discovered in 1945 and is used in capacitor application and piezoelectric transducer devices applications [1].

The most important group of ferroelectric ceramic is the family of oxygen octahedral which can be further classified into four types. They are (1) Perovskite type, (2) Tungsten-Bronze type (3) Spinel structure (Layered structure) , (4) Pyrochloro type .Among them perovskite ferroelectric ceramics oxides is the most studied one because of their

wide variety of technological applications. The perovskite structure needs some explanation as the material under investigation belongs to this group. The simple perovskite structure has a general formula ABO₃, where A is a large mono or divalent cation, B is a small tetra to pentavalent cation. It is cubic with A atoms at the cubic corner, B atoms at the body center and oxygen atoms at the face center. Most studied ferroelectric ceramics oxides with the perovskite structure due to their excellent physical properties (i.e., high dielectric constant, piezoelectric properties, ferroelectric properties) include lead titanate (PbTiO₃), lead zirconate titanate (Pb(Zr_xTi_{1-x})O₃ or PZT), [3]. Despite their excellent ferroelectric & piezoelectric properties these materials contain a large amount of lead (> 60 wt. %) which is toxic. Therefore there is growing interest in developing lead free ferroelectric ceramics to replace lead based ferroelectric due to toxicity and concern for environmental protection [4]. Among various lead free perovskite systems, (Ba(Zr_xTi_{1-x}) O₃) (BZT) is expected to be the candidate for lead free piezoelectric materials. [5]. the tetragonal–rhombohedral transition corresponds to a transformation from an antiferroelectric to a ferroelectric (FE) state [6]. However, this ceramic has drawbacks such as high conductivity and large coercive field , which cause problems during poling. This compound also possesses low piezoelectric and electromechanical properties and K_p coupling coefficients [6, 7].

2 POLYMER COMPOSITE

Now a days ferroelectric polymer composite also received

considerable attention as compared to ferroelectric ceramics in view of their technological importance in devices such as sensors, actuators, transducers etc [8,9]. Fabrication of composite materials means to combine two or more different materials having different properties to obtain the desirable material properties that often cannot be obtained in single-phase materials. Ceramics are less expensive and easier to synthesize than polymers or single crystals. Ceramics also have relatively high dielectric constants as compared to polymers and good electromechanical coupling coefficients. Ferroelectric polymer such as PVDF exhibits piezoelectric and pyroelectric response, low acoustic impedance which matches water and human skin and more over their properties can be tailored as per the requirement of the device. The best compromise in properties can be obtained by the judicious combination of piezoelectric ceramics and polymers. Piezoelectric ceramic/polymer composites possess high electromechanical coupling, low acoustic impedance, and an intermediate dielectric constant. Moreover, composites are flexible, and are moderately priced. In view of the above importance of the ferroelectric polymer composites, our objectives are as follows:

1. Synthesis of (BZT) doped ceramics using solid state reaction techniques.
2. Structural characterization of powders by X-ray diffraction technique.
3. Vibrational characterization using FTIR techniques.
4. Synthesis of PVC-BZT composite.
5. Characterization of the prepared composite by XRD and FTIR techniques.

3 SAMPLE SYNTHESIS

3.1 General Methods for Preparing Ceramic powders

There are several techniques available in the literature for the synthesis of ceramic samples used chemical methods are (a) Sol-gel methods, (b) Co-precipitation method, (c) Hydrothermal Method (d) Combustion Method etc. Both the chemical and mechanical methods have their own advantages and disadvantages. [10]. In the present study, The polycrystalline samples of ceramic were prepared from the following carbonates and oxides: Barium carbonates (BaCO_3), Plomb Oxides (PbO), Titanium Oxide (TiO_2), and Zirconium Oxide (ZrO_2). Their characteristics are summarized in Table 01.

Table 01: Features of the starting materials

Commodities	molar mass (g / mol)	Chemical purity(%)	Supplier
BaCO_3	197.34	99%	Biochem

ZrO_2	123.22	99%	Biochem
TiO_2	79.87	99%	Biochem
PbO	223.20	99%	Biochem

A conventional solid state reaction technique has been adopted to prepare the materials. The ingredients were thoroughly mixed and ground in acetone for 2h in an agate mortar to get homogenous mixture of the materials. Then the mixed powders of the compounds were calcined at 900°C in an alumina crucible for 2 h in an air atmosphere. The quality and formation of the compounds were checked by an X-ray diffraction (XRD) technique. The fine and homogeneous powder of the above compounds were pressed into cylindrical pellets of 10 mm diameter and 1-2 mm thickness under a uniaxial pressure of $6 \times 10^5 \text{ N/m}^2$ using a hydraulic press. The pellets were then sintered for 2 h at 1100°C in air atmosphere. The binder was burnt out during the high temperature sintering. The formations of the prepared compounds were studied by an X-ray diffraction technique (XRD).

3.2 Preparation of Composites

This stage involves the production of a mixture: polymer (polyvinyl chloride) with the ceramic (BZT) which was previously prepared; these mixtures in different percentages in the presence of THF (tetra hydro furan) as a solvent, because it does not react with the compounds and in addition it has a low boiling temperature. After mixing for a few hours (or minutes, depending on the composite formulation produced), the next step is the evaporation of the solvent to obtain Films.

4 TECHNICAL ANALYSIS

4.1 X-Ray Diffraction Technique on powders "XRD"

As part of this work, we used a type of diffractometer D8 Advance Bruker AXS using $\text{K}\alpha_1$ cancellation of a copper anticathode ($\lambda = 1.54056\text{\AA}$). This analysis provides a number of information about the structural characteristics such that the phases present, their amount and their crystal structure.

4.2 Fourier Transform Infrared Spectroscopy "FTIR"

The infrared absorption (IR) resulting from the change of the vibrational and rotational states of a molecular bond. It allows to show the presence of specific atomic groups in a given phase. We used the infrared spectral analysis technique by Fourier transform, measures FTIR spectra were carried out with IR apparatus (Shimadzu IR-84) operating in the range of $400\text{-}4000 \text{ cm}^{-1}$, with a spectral resolution of 4 cm^{-1} . However, each sample was pelletized

into Bromide Potassium "KBr" through a hydraulic press with a proportion of (product 0.02g and 0.2g of KBr), the spectra obtained in the range 4000 to 500 cm^{-1} .

4.3 Differential thermal analyse (DTA) and thermogravimetric (TG)

The differential thermal analysis and thermogravimetric under ambient atmosphere were performed to study the thermal behavior changes that accompany the changes induced in the picture materials degraded compared to virgin material. The experimental design used is of type Linseis 2400, operating in the temperature range 25 - $1200\text{ }^{\circ}\text{C}$ with different heating program. The used heating rate is $5\text{ }^{\circ}\text{C}$ per minute.

5 RESULTS AND DISCUSSION

5.1 Sample characterization by XRD

In order to verify the incorporation of the reinforcement ($\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$) and has a structure in the matrix of polyvinyl chloride (PVC), we carried out the characterization of the samples by X-ray diffraction Figures 1, 2 and 3 show, respectively, the XRD patterns of the PVC polymer, and BZT ceramic and the 50/50 in mass blend of the two materials: PVC / BZT. The diffractogram of PVC is characteristic of amorphous body and has a broad line and diffuses to $2\theta = 24\text{ }^{\circ}$ to 25 ° . XRD spectra of the composite charge 50% BZT (Fig. 3), show more diffraction peaks of other purposes PVC peaks characteristic of the perovskite structure in its crystalline form in the tetragonal system. Vicinity of $2\theta = 30\text{ }^{\circ}$, it is found two peaks this implies the existence of two phases. The results obtained by X-ray diffraction allow to see that the organic and inorganic phases are present, the first amorphous, the second well crystallized in the composite BZT / PVC obtained. The crystallites in the amorphous matrix explain the modification as well, the thermal stability of resistance to photodegradation. Indeed, the crystallites prevent chains relax in the nanocomposites and limit mobility which delays a little the decomposition phenomenon of the loaded products. [11]

The spectra also show a bigger mess in the polymer matrix, the diffraction line profile is larger in the diffraction patterns of nano composites. The splitting of the DRX peaks in the case of the composite relative to that of the pure BZT ceramic, means the existence of interactions between the PVC matrix and the ceramic inclusions (They may be due to the affinity of LC for BZT) resulting in deformation of the tetragonal structure of the BZT symmetry .figure 4.

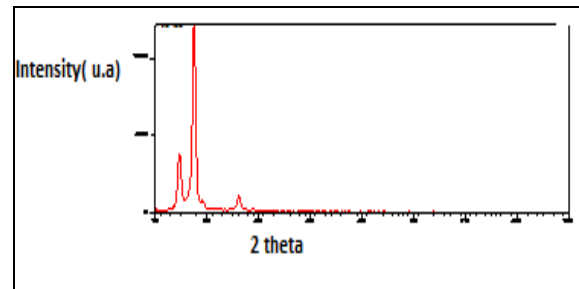


Figure 01: Diffractogram of PVC

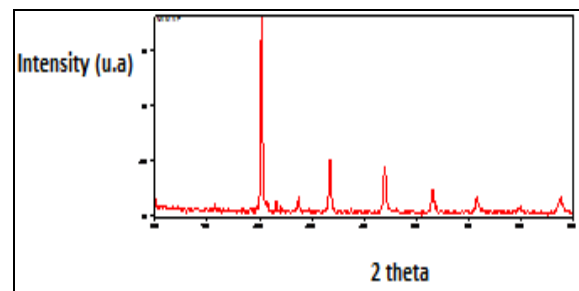


Figure 2. Diffractogram of BZT

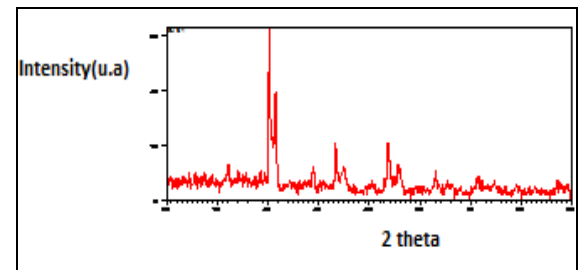


Figure 03: Composite diffraction for PVC / BZT = 50/50 by mass

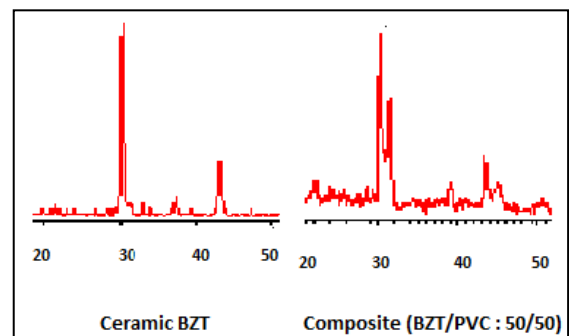


Figure 04: A DRX spectrum zoom ($20 < 2\theta < 50$)

5.2 The thermal stability of the synthesized material is followed by ATD ATG

The DTA thermogram of the composite material PVC / BZT: 50/50 by mass, shown in (Figure 5) makes it possible to locate the thermal accidents during heating .The curve has two peaks endothermic material, a first endothermic peak at 80 - $90\text{ }^{\circ}\text{C}$ combined from water followed by another peak around 280 - $290\text{ }^{\circ}\text{C}$ attributed to the decomposition of PVC. The width of this peak indicates that the polymer chains do not decompose directly, the start of the peak corresponding to the cuts of the ends of the channels, the end is cut followed by decomposition of the

macromolecules. Under the action of heat, the PVC degrades ie there is formation of a hydrogen chloride (HCl) and appearance of a double bond.

The Cl atom immediately following the one that was lost in HCl form occupies said position. Compared to the double bond formed this structure, called allyl structure, is well known for its high sensitivity to heat: thus form a set of double bonds in this subsection "the tail" [4-5]. ... $\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{CH} = \text{CH} \dots$ So we can assign the exothermic peak at around 450°C to training polyenes from the dehydrochlorination of PVC. And the second exothermic peak at around 700°C to the total degradation of polymer (PVC), giving monomers. Finally the last two endothermic peak attributed to the inactive forms; Since a certain amount of stabilizers (resulting from the decomposition of carbonates and oxide-based ceramics) has been consumed as a result of chemical reactions with hydrochloric released by the PVC and finds converted to an inactive form acid (ZnCl_2 , BaCl_2 CHOH and $\text{CHCl} \sim \sim$) [5]

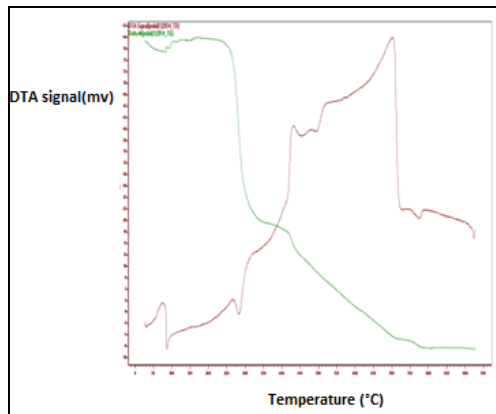


Figure 05: Thermogram of composite material (PZT/ BZT :50/50)

5.3 Fourier transform infrared spectroscopy (FTIR)

IR spectroscopy is routinely used for identifications (polymers, ceramic, ..) and for quantitative analysis of additives or structural irregularities determined well in relatively homogeneous family of materials (control production) [6]. When we compared the two spectra of pure BZT compounds before and after the calcination (figure 6-7), the disappearance is noted of the peak which is between 1400 and 1500cm^{-1} in the first spectrum (BZT before calcination) and increase the peak which is between 500 - 600cm^{-1} , mean that the formation of the perovskite structure. from figure 9, it is noted in this spectrum the presence of the perovskite phase between 550 - 700 and the presence of weak peaks of C-Cl, and it explains the mixture of the two phases. Note the strong presence of the perovskite phase and oxides and it returned to the majority in the percentage of ceramics and dispersion of bands C-Cl.

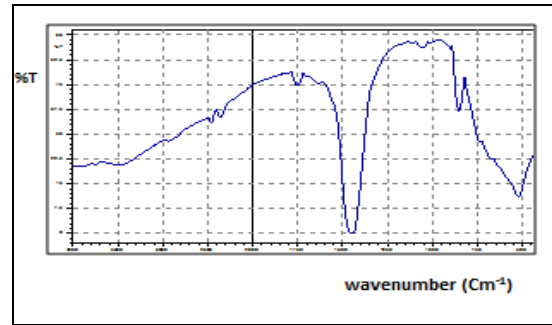


Figure 06: Infrared spectrum of pure BZT before calcination

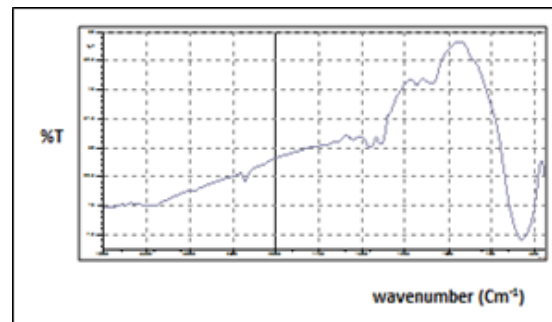


Figure 07: Infrared spectrum of pure BZT after calcination

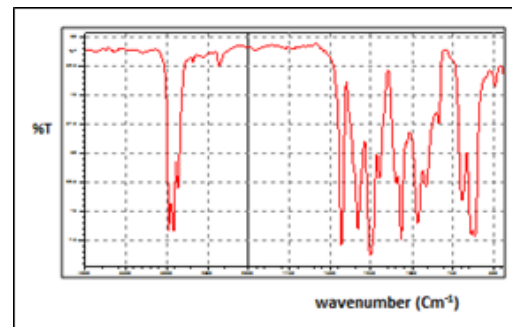


Figure 08: Infrared spectrum of pur PVC

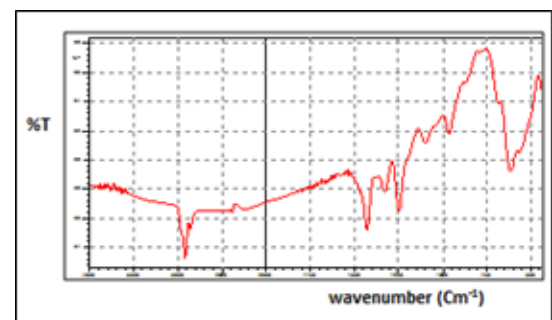


Figure 09: Infrared spectrum of PVC + BZT (50/50 by mass)

6 CONCLUSION

We studied the ceramic BZT: Ba (Zr_{1-x}, Ti_x) O₃ with x =0.50, mixed with polymer PVC (Poly Vinyl Chloride) In a weight percentage 50/50. This study is carried out by making mixtures between the BZT with PVC. So our goal is to synthesize new materials with interesting properties, our ceramic was developed by solid method or dry and following mixing between (the polymer and the prepared ceramic) was carried out with the solvent THF (Tetra Hydro furan) for obtaining a composite material in the form of a film.

The results obtained by X-ray diffraction allow to see that the organic and inorganic phases are present, the first amorphous, the second well crystallized (perovskite phase) in PVC / BZT composites obtained. The splitting of the DRX peaks in the case of the composite relative to that of the pure BZT ceramic, means the existence of interactions between the PVC matrix and the ceramic inclusions (They may be due to the affinity of Cl for BZT) resulting in deformation of the tetragonal structure of the BZT symmetry. The crystallites in the amorphous matrix explain the modification as well, the thermal stability and the resistance to degradation. Indeed, the crystallites prevent chains to relax in composite and limit mobility which delays a bit the phenomenon of decomposition of the loaded products. And that we found by differential thermal analysis (DTA / TG), and as confirmed by FTIR spectroscopic study.

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