International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 06, June-2020

Research on Building Process Technology of Synthetic Piezoelectric Materials System PZT - SZN Doped Mn and Application

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***Abstract*—Materials science is the field of synthesizing, analyzing and applying new materials. Piezoelectric materials on the doped PZT base materials are used to manufacture ultrasonic transmitters and receivers. Regarding technology monopoly, commercial piezoelectric ceramic companies only publish the parameters and applications while the material formulas and technological processes are always kept secret. In this paper, we present the results of research on building technological process of synthesizing hard-doped PZT material system. To evaluate the technological process, a composite of PZT - SZN doped Mn^{4+} was conducted. As a result, we have successfully fabricated ceramic system $(Pb_{0.95}Sr_{0.05})((Zn_{1/3}Nb_{2/3})_{0.2}(Zr_{0.53}Ti_{0.47})_{0.8})O_3$ + 0,5% Wt MnO_2. In particular, this technological process has lowered the material heating temperature, the 1st burning temperature at 700^0C, sintering temperature at 1000^0C. Dielectric, electric iron and piezoelectric parameters: ρ= 7,8 (g/cm^3), k_p = 0,58, d_{33} = 330 (pC/N), $T_c = 342^0$C, Q_m = 1000. Results of the study shows that the characteristic parameters clearly show the properties of hard piezoelectric materials, suitable for manufacturing power ultrasound transducer.**

Keywords - Piezoelectric ceramic; PZT doped Mn^{2+}; hard piezoelectric ceramic; piezoelectric coefficient d_{33}; Curie temperature T_C.

I. INTRODUCTION

From the properties of the forward and backward piezoelectric effect, piezoelectric ceramic is the basis for the manufacture of electrical - mechanical, mechanical - electrical energy conversion elements, in which the typical ultrasound transmitters and transceivers is made from piezoelectric ceramic based on doped PZT, also from here to develop the field of ultrasound, hydrography and applications. Currently, ultrasound technology is rapidly developing and widely used in many fields: science and technology, industry, agriculture, environment, medicine ... In military, underwater ultrasound technology is called hydrodynamic, which is applied in Sonar passive and active equipment to actively equip for system of underground hunting of the Navy[1, 2].

Overview of the research and application of piezoelectric materials, in the world there is Morgan - USA producing commercial piezoelectric ceramic and there are many scientific works that have announced different types of piezoelectric ceramics depending on application purpose [1, 2]. However, it exists a situation of monopoly of technology; commercial piezoelectric ceramic manufacturers and scientific works only announce trade names, typical parameters and application while material formulas, technological processes are always kept secret. Thus, with the goal of proactively manufacturing doped PZT ceramic systems suitable for application requirements, the issues that need to be posed and must be solved are:

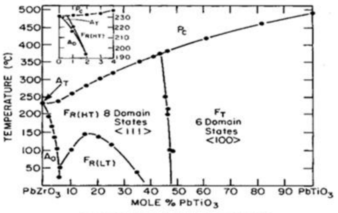
Firstly, it is necessary to study and determine the PZT base materials formula, composition and doped concentration in order to create a hard and soft doped PZT ceramic system with high characteristic parameters, especially stable under conditions of high stimulus for a long time. Hard piezoelectric materials are used to make ultrasonic transmitters, soft piezoelectric materials are used to manufacture ultrasonic transducers and ultrasonic sensors [1].

Secondly, it is necessary to study and develop a process of synthesizing piezoelectric materials based on doped PZT.

Thirdly, it is necessary to identify the characteristic parameters according to international standards IRE - 61 and IRE - 87 on piezoelectric materials.

II. THEORETICAL BACKGROUND OF PIEZOELECTRIC MATERIAL

Piezoelectric ceramic is a material of polycrystalline structure, exists many domains in the microcrystalline in different directions, when it is not polarized by electric fields, the total electric dipole moment of the crystal is zero. After polarization by the electric field, the domain structure is rearranged in a fixed direction, the electric dipole moment is non-zero and the material exists piezoelectric nature. When the domain structure is rearranged, the direction of the external electric field is applied to the piezoelectric ceramic plate and the mechanical oscillation direction, whereas the direction of the mechanical stress on the ceramic plate and the generated electric field is determined. This is a decisive factor for the properties of forward,backward piezoelectric effect [4].



Lead zirconate titanate phase diagram.

Fig. 1. Morphotropic Phase Boundary – MPB according to the temperature of the PZT piezoelectric ceramic

Figure 1 is a Morphotropic Phase Boundary – MPB according to the temperature of the PZT piezoelectric ceramic based on two components having the Perovskite ABO_3 structure, $PbTiO_3$ and $PbZrO_3$. This is the basis for selecting the PZT component and determining the Curie temperature Tc of the material [4].

From the diagram, the horizontal axis represents the Zr / Ti component ratio, the right side is rich with Ti, the left side is rich in Zr, the vertical axis represents the temperature dependence according to the Zr/Ti component ratio. The temperature transition diagram is divided into three main areas: P_C is the cubic crystal phase region, F_T is the quadrilateral crystal phase region and F_R is the rhomboidal crystal phase. The dividing line between the cubic and quadrilateral phases, the rhombic surface represents the variation of temperature, the dividing line between the quadrilateral phase and the rhombic phase is called the Morphotropic Phase Boundary (MPB). At room temperature, MPB lies adjacent to the Zr/Ti component ratio: 51/49, 52/48, 53/47. It is worth noting that the MPB has a stable and quite high temperature of 360^0C. On the other hand, the adjacent MPB always exists two quadrilateral and rhombus surface so the material has very good piezoelectric properties. When the temperature is higher than the Curie temperature, the material changes to the cube phase so the material loses its piezoelectric properties. Thus, the selection of material system with the proportion Thus, the selection of the material system has the proportion of components adjacent to the morphological phase margin with high piezoelectric and Curie temperature is one of the important issues of piezoelectric ceramic manufacturing technology process [5] .

The morphological phase diagram is the basis for selecting PZT base materials according to Zr / Ti component ratio adjacent to MPB from two solid materials $PbTiO_3$ and $PbZrO_3$. A more important issue of the synthesis of piezoelectric materials based on PZT is that it is doped to have basic parameters suitable for the purpose of application. With piezoelectric materials on the basis of perovskit ABO_3 structure, hard and soft doping method is oftend used. The softening effect of soft impurities is the creation of Pb defects (Vacancy Pb) in the network. The result when doping hard or soft into PZT-based piezoelectric material will produce the defect effect of Pb, O atoms in perovskit ABO_3 structure network, leading to easier movement of atoms, from which Domain walls will also be easier to deform even under the influence of electric fields or small stresses [6, 8].

III. TECHNOLOGY PROCESS - THEORETICAL BACKGROUND OF PIEZOELECTRIC MATERIAL

Stage 1: Prepare the materials

The material is prepared on the basis of the formula of the selected ceramic system, the initial compositing components are oxides, PZT base materials including PbO, ZrO_2, TiO_2, $SrCO_3$, ZnO, Nb_2O_5 and the doped component are MnO_2. All ingredients must be above 99% purity, electronically balanced to an accuracy of 10^{-4} grams.

Stage 2: Grinding, mixing for 1st time

This stage is very important to create the homogeneity of the ceramic, it is necessary to make the particles reach fineness and mix evenly, easily creating solid phase reactions according to the principle of atomic diffusion in the stage of heating, it requires a diameter of particles less than 2μm. Attention should be paid to impurities mixed in the grinding and mixing process. To minimize this effect, the grinding and mixing process was carried out by PM400/2 –MA-Type planetary crusher using zirconia balls for 20 hours [7].

After grinding and mixing for the first time, the material needs to analyze DTA-TG differential temperature to determine the material transition temperature. The results of DTA-TG will determine the 1st burning temperature and sintering temperature. According to the DTA-TG diagram, there are 2 peaks absorbing heat and the weight loss at 370^0C and 900^0C with analytical sample volume is only 50.63 mg. Experiments show that the fabricated samples with large volume need to investigate higher burning temperature. In this technological process, the first burning temperature was selected at 650^0C, 700^0C and 750^0C, selecting sintering temperature at 950^0C, 10000C and 1050^0C. The result chosing the first calcination temperature at 7000C and the sintering temperature at 1000^0C is the best. This is the basis for selecting the burning temperature for 2nd times in the process of synthesizing hard piezoelectric materials system PZT - SZN doped $Mn^{4+.}$

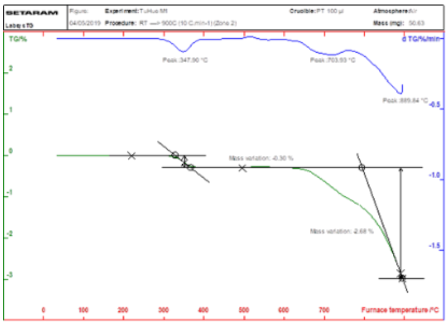


Fig. 2. Differential thermal analysis scheme DTA-TG

Stage 3: Press, preheat

The solid material mixture after the first grinding is pressed into a 30 mm diameter disc tablet, 1500 kg/1cm^2 compression force. With doped PZT material, the temperature of 700^0C is selected, the heating speed is 5^0C/min, keeping the temperature at 700^0C for 2 hours. This stage is the synthesis of compounds by solid phase reaction that occurs when there is the diffusion of atoms between adjacent particles, at a temperature lower than the melting point of each participating material. The mechanism consists of four physical processes that occur during the preheating stage, which are: Linear expansion of particles in the room temperature range to 400^0C; solid phase reactions in the range of 400^0C - 600^0C; shrinkage of material in the range of 600^0C - 750^0C and finally the development of particle size at temperatures above 800^0C [6]

Stage 4: 2nd crushing

After preheating, we conduct a second crushing with a planetary crusher in a period of 15 hours. The purpose of grinding this time is to create a homogeneous compound and reduce particle size, helping substances participating in solid phase reactions occur completely at the sintering stage. The fineness and uniformity of the particles greatly affect the quality of the ceramic after sintering [7].

Stage 5: Pressing, sintering

The mixture of solid materials after the 2nd grinding is pressed into many pellets of 1.2mm diameter, 1.4mm thickness, 150kg/1cm2 compression force. With doped PZT material, sintering temperature of 1000^0C is chosen, heating speed of 5^0C/min and keeping the temperature at 1000^0C for 2 hours.

Stage 6: Sample treating

Create a sample size according to the international standard IRE - 61 on piezoelectric materials, in order to prepare for the measurement and survey of subsequent piezoelectric parameters. The surface of the sample is grinded by a sandpaper with increasing fineness of the Labpol Duo8 machine until it reaches the desired thickness, then rinse the sample with ultrasound before creating the electrode. Pay special attention to the surface flatness and the duplex plane between two sample surfaces.

Stage 7: Creating silver electrodes

Requirements of piezoelectric ceramic electrode: good conductivity, high adhesion and not destroyed when polarizing at high temperatures and electric fields. Electrode coating process is carried out as following: The sample is heated to a temperature of 400^0C and a silver-oxide emulsion layer is applied to the two surfaces in turn for 20 minutes. At a temperature of 400^0C silver oxide in the emulsion layer will be decomposed into Ag metal adhering to the sample.

Stage 8: Polarizing in an electric field

Before polarization, electric iron ceramics do not have piezoelectricity due to the chaotic distribution of electric iron domains. Polarization is the process of orienting and fixing domains in the direction of the electric field. After being processed, the sample has a thickness of 1mm, polarized at 30kV/cm electric field in silicon oil at 120^0C, time is 30 minutes.

IV. GENERAL RESULTS OF VOLTAGE MATERIALS PZT- SZN + 0,5% 5%w_t Mn^{2+}

From the theoretical basis of choosing material formulas, in this study, we choose the system of materials with the formula $(Pb_{0.95}Sr_{0.05})$ $((Zn_{1/3}Nb_{2/3})_{0.2}$ $(Zr_{0.53}Ti_{0.47})_{0.8})O_3$ + 5%Wt MnO_2 (PSZ – SZN + Mn^{2+}). In particular, the PZT basis materials are selected according to the component mass ratio of Zr/Ti = 53/47 adjacent to the morphological phase boundary.

The parameters and properties of the material are surveyed according to international standards IRE-61 and IRE-87. The experiment was conducted according to the established technology process, at the Material Science Laboratory, the Department of Physics - Hue College of Sciences. Dielectric, electric iron and piezoelectric parameters are measured on Hioki 3532 LCR measuring system and automation Impedance HP 4193A equipment, ceramic polarization with adjustable high voltage DC source of 0 - 40 kV. The structure was measured by X-ray diffraction method on D8 ADVANCE - Bruker device, the microstructure was photographed SEM by S4800 – NIHE device. The results of parameters and properties are:

1. *Piezoelectric properties.*

In order to study the piezoelectric properties, we created the sample with shape and size in accordance with the international standard IRE - 61, the samples were made Ag electrode and polarized in appropriate ways in order to obtain the oscillation modes respectively. The selected polarization temperature is 120^0C, polarized electric field of 30 kV/cm, 30 minutes. Resonance vibration spectrum measured on the Hioki 3532 LCR measuring system and automation Impedance HP 4193A equipment.

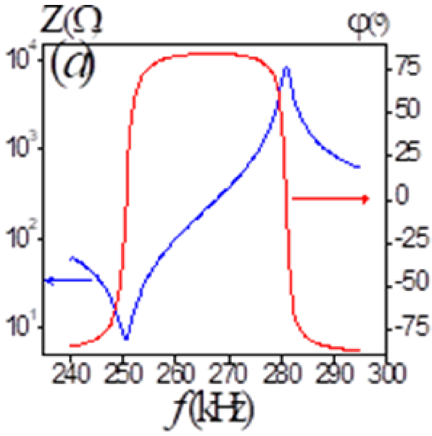


Fig. 3. Resonance spectrum of piezoelectric material PZT- SZN + 5%Wt Mn^{2+}

Figure 3 shows the result of resonant spectroscopy measurements of ceramic samples in radial direction. The characteristic lines represent the phase dependence of the resonant oscillation spectrum, the impedance of the piezoelectric ceramic plate according to the frequency of the excitation signal. From the characteristic lines shows that when the impedance with the smallest value Z_{min}, resonant oscillation starts to occur, the frequency corresponding to Z_{min} is called the resonance frequency. When the impedance with the maximum value Z_{max}, it no longer exists resonant oscillation, the frequency corresponding to Z_{max} is called the anti-resonant frequency. The characteristics of the resonant oscillation spectrum in the resonant and anti-resonance frequency bands have the type of clear square, showing the piezoelectric properties of the material under the effect of the excitation signal source [4].

2. *Structure.*

The structure of the material was measured by X-ray diffraction method on D8 - ADVANCE –Bruker device.

Figure 4 is the diffraction spectrum of the PZT-SZN sample material without doping, Figure 5 is the diffraction spectrum of the sample material with Mn^{2+} phase, the diffraction spectra of the two samples show the structure of the material with a single phase characteristic, no strange phase appears. Diffraction lines of PZT - SZN materials coincide with typical diffraction lines of material $Pb(Zr_{0.53}Ti_{0.47})O_3$ with network parameters a = b = 4.0550 A^0, c = 4.1100A^0, $\alpha = \beta = \gamma = 90^0$. That shows the material with a typical quadrilateral structure, with double lines appearing at positions corresponding to angles 2θ equal to 32^0, $44.5^0 – 50^0$, and single lines at 38.2^0. With such crystal structure, it is concluded that the synthesized material sample has the main component located adjacent to the morphological phase edge completely in accordance with the selected material formula.

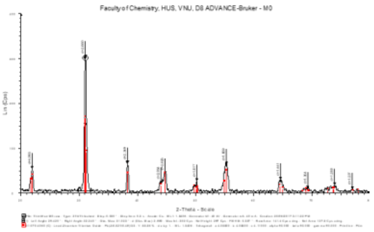


Fig. 4. X-ray diffraction spectra of unadulterated sample PZT- SZN

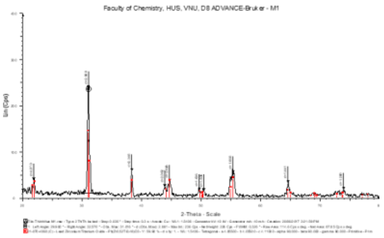


Fig. 5. X-ray diffraction spectra of sample PZT- SZN + 5%Wt Mn^{2+}

3. *Structure.*

Microstructures were surveyed by SEM imaging method on S4800 - NIHE device.

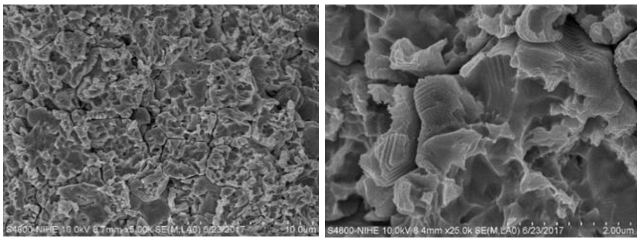


Fig. 6. SEM photos taken in different magnification modes

Figure 7 shows a SEM image of a material sample taken at high magnifications. Samples of material without any chemical treatment, just randomly broken and washed with ultrasound before taking pictures. Noticeability from the microstructure shows that on each particle, there has been the formation of a stacked domain wall structure, the domain wall width is about 150nm, with a plate-type domain wall structure completely suitable for the doped PZT piezoelectric material. This is also the expected result because the material has piezoelectric properties when the material exists the domain wall structure because the domain wall will deform easily under the action of electric fields or generate charges when there is mechanical stress. [6]

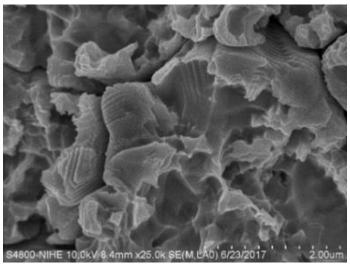


Fig 7. SEM photos taken in high magnification modes

4. *Typical parameters of a piezoelectric material system PZT-SZN + Mn^{2+}.*

Electro-mechanical linking coefficient: $k_P = 0{,}58$
Piezoelectric coefficient: $d_{33} = 330$ (pC/N)
Quality coefficient: $Q_m = 1000$
Curie temperature: $T_C = 342^0$ C
Density: $\rho = 7{,}8$ (g/cm^3)

From the typical parameters, it shows that the PZT- SZN + Mn^{2+} piezoelectric system has the properties of hard piezoelectric materials. Theory and experiment show that, four parameters k_P, d_{33} and Q_m, T_C never increase or decrease at the same time. Depending on the application purpose, hard or soft doping is selected to have the appropriate parameters. With this material, it is possible to fabricate high power ultrasound and application. [4].

V. CONCLUSIONS

A technological process for synthesizing piezoelectric materials has been developed with each stage explaining the mechanism clearly.

From the technological process, we successfully synthesized piezoelectric ceramic material system $Pb_{0.95}Sr_{0.05})((Zn_{1/3}Nb_{2/3})_{0.2} (Zr_{0.53}Ti_{0.47})_{0.8}) O_3 + 5\%Wt\ MnO_2$ (PSZ – SZN + Mn^{2+}). The characteristics of the material are investigated on modern solid analyzers such as Hioki 3532 piezoelectric measuring system and Impedance HP 4193A, XRD, SEM. The results showed that they are consistent with the theory, the typical parameters of the material system (PSZ - SZN + Mn^{2+}) clearly show the properties of hard piezoelectric materials. Accordingly, it is confirmed that the material formula of the chosen hard piezoelectric ceramic system and the established technology process are perfect.

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