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INFLUENCE OF SYNTHESIS ROUTE ON MORPHOLOGY AND DIELECTRIC PROPERTIES OF PZT NANOSTRUCTURES BY SOL-GEL PROCESS

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Abstract- In the present work, we report the synthesis of ($PbZr_{0.52}Ti_{0.48}O_3$)PZT in tubes-like nanostructure by microwave-assisted sol-gel route. According to our knowledge, this is the first report on tubes-like PZT, were obtained by microwave-assisted sol-gel route. To understand the effect of microwave heating on the synthesis, the same experiment was repeated by using conventional way of heating. Round shape nanoparticles of PZT were obtained by the conventional sol-gel route. The crystallization behaviors of the tubes and sol-gel route of PZT are confirmed by XRD. The structural morphologies of the PZT sample are observed by SEM and TEM. The thermal decomposition characteristics of the gel are identified by DTA and TGA. The molecular structures are investigated by FTIR. A pure pervoskite PZT powders were obtained after having been annealed tubes-like structure at 650^{0}C and NPs at 750^{0}C for 3 hr.
Keywords- microwave-assisted sol-gel route, sol-gel route, PZT.

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Introduction

PZT ($PbZr_{1-x}Ti_xO_3$) is an important dielectric and a piezoelectric material [1]. Compositions close to the morphotropic phase boundary (x = 0.52-0.55) exhibit high dielectric constants and electromechanical coupling coefficients [2]. It is widely accepted that the performance of PZT ceramics strongly depends on chemical homogeneity, particle size and morphology of the PZT powders. One dimensional morphology of PZT such as fibers or tubes, rods etc have recently been paid more attention by researchers owing to increased anisotropy, excellent flexibility and improved strength over monolithic PZT.

In recent years, many scientists have focused on the investigation of microwaves as a heating source for synthesizing and processing of materials. The growing interest in microwave heating over conventional is due to the fact that electromagnetic wave interacts with materials at molecular level, which gives rise volumetric heating with more rapid heating rate and helps materials to grow it in different microstructure. In this study, microwave-assisted sol-gel route is used to synthesize PZT. Same experiment was repeated by using conventional way of heating in place of microwave. The crystallization behavior and the microstructure of PZT synthesized by using different way of heating are compared by XRD and SEM. Thermal decomposition characteristics and transition of molecular structure of gel and solid phase are studied by TGA/DTA and FTIR techniques respectively.

Experimental Procedure

Lead acetic acid trihydrate ($Pb(COO)_2.3H_2O$), titanium isopropoxide ($Ti(O\text{-}C_3H_7)_7$), Zirconium propoxide ($Zr(O\text{-}C_3H_7)_4$, procured from Sigma-Aldrich, were used as starting materials, and isopropanol was used as solvent. The atomic ratio of the Pb:Zr:Ti of solution was 1:0.53:0.47 and no excess lead was introduced. After PZT precursor sol was obtained, the mixture of acetic acid and pure distilled water was added into the precursor. The sol was proceed in microwave oven at optimize irradiation conditions that is 600 power level for 30 min. The gel was aged at room temperature for 3 days and dried at 50 - 100^{0}C. The dried powder (PZT-A) was used for further characterization. Same experiment

was repeated using conventional source of heating in place of microwave (The powders is designated as PZT-B).
according to the areas to be discussed. This should be followed by the Acknowledgement (if any) and Reference sections. The first page should contain the title, the authors names (initials and surname only), with an asterisk in front of the name of the principal author.

Results and Discussion

XRD patterns of PZT- powders annealed for 3 h at different temperatures (450^{0}C, 550^{0}C and 650^{0}C) are shown in Figures 2a and b. At an annealing temperature of 450^{0}C, the **PZT-A** are predominantly in the rhombohedral phase, and there is also some pyrochlore phase, but for **PZT-B** an amorphous phase was observed up to 450^{0}C. The rhombohedral phases are enhanced by increasing the annealing temperature up to 550^{0}C, but at this stage a small amount of pyrochlore phase appears.

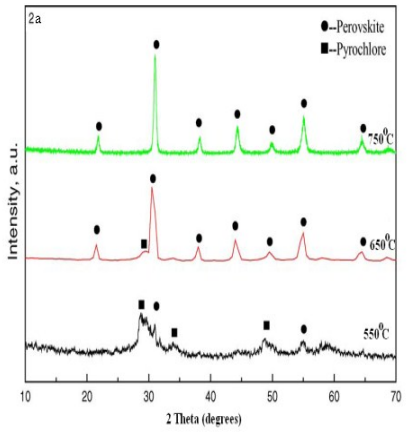


Fig. 1-

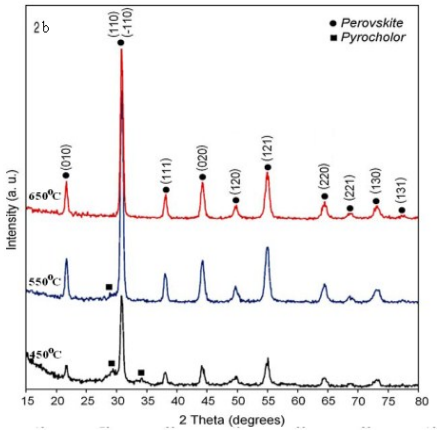
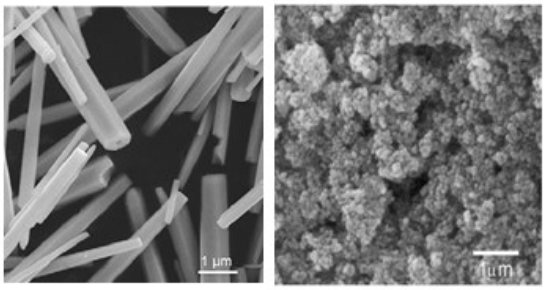


Fig. 2- XRD of PZT (a) PZT-A and (b) PZT-B

At the annealing temperature of 650^{0}C, the pyrochlore phase disappears, while the pure rhombohedral phase is observed. The same trends were observed for **PZT-B** sample at 550^{0}C onwards. The XRD results reveal the existence of a perovskite type phase for the **PZT-B** at 750^{0}C.

The surface morphology of the PZT powders annealed 550^{0}C for 3 h are depicted in Figures 3a and b. The images show the tubes-like structure of **PZT -A** sample and round-shape particles for **PZT -B** sample. Average diameter of tubes is found to be 40 nm and length in several µm. The SEM image of tube clearly indicates that tubes are hollow internally. The particles are observed to be highly agglomerated with average size is measured to be 20 nm.



FIGURES 3: SEM images of PZT (a) Tubes and (b) Particles

Figure 4 shows the results of thermogravimetric analysis, TGA, and differential thermal analysis, DTA of PZT-tubes. The TG curve descends until a horizontal is obtained around 620^{0}C. The horizontal curve obviously corresponds to the existence of PZT. The TG and DTA traces show three main regions. The first is an initial loss of water at around 60^{0}C. It is shown by bend at ***A*** endothermic reaction, and corresponding 4.7% weight loss. Then the decomposition of organic material occurs between 100 and 350^{0}C which corresponds to bend ***B***, accompanied by a 17.439% weight loss. Also, this important deflection at ***B***, whose maximum is around 260^{0}C, is attributed to the formation of the pyrochlore phase and the initiation of crystallization of materials. Finally, the third deflection at ***C*** that occurs around 450 ^{0}C is related to the formation of the perovskite structure of PZT nanostructures accompanied by 4.172% weight loss. The horizontal curves of TG\DTA are achieved around 550 ^{0}C, which indicates that the complete formation of the perovskite PZT- nanostructures is achieved at a furnace temperature of greater than 550^{0}C. The X-ray diffraction indicates that the perovskite structures are formed at around 600^{0}C, which agrees well with the TG\DTA results.

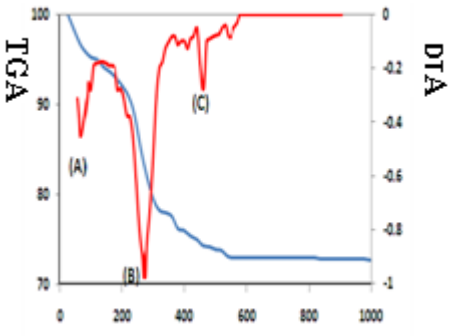


Fig. 4- TGA and DTA of PZT-B

The evolution of the molecular structure of PZT tubes was investigated by FTIR as shown in Figure 5. The absorption at about 3600 - 3000 cm^{-1} was associated to O-H vibration. The 1550 cm^{-1} and 1400 cm^{-1} bands, were ascribed to the symmetric and asymmetric

C-O vibration -COO groups [25, 26]. The 1322 cm^{-1} band, was attributed to the deformation vibration of CH_3 groups. The peak at 932 cm^{-1}, was attributed to the vibration C-C bonds [27]. The peak at about 1020 cm^{-1} was ascribed to vibration of CH_3 groups. All these absorption bands, which were related to the acetic acid, isopropanol and propoxide group, greatly decreased in intensity as the heat treatment temperature increased up to 350^{0}C, which confirmed that the organic was decomposed before 350^{0}C. Along with the increasing heat treatment temperature up to 550^{0}C, the peak at 790 cm^{-1} and 580 cm^{-1}, which were attributed to Ti-O bond and pervoskite phase [25], emerged and become stronger. This result indicated that the perovskite phase was formed at 550^{0}C and increased for higher heat treatment temperature. These results are in agreement with DTA results.

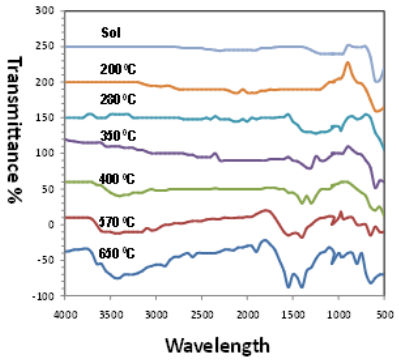


Fig. 5- FTIR spectra of the PZT sol and tubes heat treated at different temperature

Conclusion

Pure PZT in tube-like structure on nanoscale were synthesized by microwave-assisted sol-gel route and results were compared with PZT synthesized by conventional sol-gel route, which prepared nano-size round-shape particles. Both samples were characterized by XRD, SEM, DTA-TGA and FTIR. The XRD diffraction patters showed that the synthesized product were fully crystalline orthorhombic phase at annealing temperature 450^{0}C for tubes and 550^{0}C for nanoparticles. SEM images confirmed the surface morphology of tubes and particles of PZT. The SEM images of PZT calcined at 550^{0}C reveals the average particles size of 40 nm for nanotubes and 20 nm for round-shape particles. The XRD and FTIR patterns indicated that pervoskite PZT were free by pyrochlore phase at 650^{0}C for the tubes, while at 750^{0}C for the nanoparticles. Microwave-assisted heating route may prove to be a potential tool for growing of one dimensional nanostructure of same of pervoskite oxide.

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