The effect of sintering time on grain size of PZT ceramics on ultrasonic transducer

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Lead zirconate titanate (PZT) ceramics were fabricated by powder mixing method. The resultant samples were sintered at a different time and subsequently characterized in terms of both microstructure and dielectric function to study effects of sintering behavior. Microstructure and dielectric function exhibited obvious dependence on sintering time. The grain size of PZT ceramics plays critical roles in determining the magnitudes of dielectric function. With the increase of sintering time, the grain size increased which exerted direct influences on dielectric function.

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1. Introduction

Piezoelectricity is a property possessed by a group of materials, discovered in 1880 by Pierre and Jacques Curie during their study of the effects of pressure on the generation of electrical charge by crystals such as Quartz, converse effect was deduced by Lipmann from thermodynamics principles. In the next three decades, collaborations within the European scientific community established the field of piezoelectricity; and by 1910, Voigt's "Lerbuchder Kristallphysic" was published and became a standard reference work detailing the complex electromechanical relationships in piezoelectric crystals [1]. However, the complexity of the science of piezoelectricity made it difficult for it to mature to an application until a few years later. Langevin et al. [2] developed a piezoelectric ultrasonic transducer during World War I. Their success opened up opportunities for piezoelectric materials in underwater applications as well as a host of other applications such as ultrasonic transducers, microphones, accelerometers, etc…In 1935, Busch and Scherrer discovered piezoelectricity in potassium dihydrogen phosphate (KDP). The KDP family was the first major family of piezoelectrics and ferroelectrics to be discovered. During World War II, research in piezoelectric materials expanded to the U.S., the Soviet Union and Japan. Up until then, limited performance by these materials inhibited commercialization but that changed when a major breakthrough came with the discovery of barium titanate and lead zirconate titanate (PZT) in the 1940s and 1950s respectively. These families of materials exhibited very high dielectric and piezoelectric properties. Furthermore, they offered the possibility of tailoring their behavior to specific responses and applications by the use of dopants. To date, PZT is one of the most widely used piezoelectric materials. It is noted that most commercially available ceramics (such as barium titanate and PZT) are based on the perovskite structure (Fig. 1). The perovskite structure (ABO3) is the simplest arrangement where the corner-sharing oxygen octahedra are linked together in a regular cubic array with smaller cations (Ti, Zr, Sn, Nb etc.) occupying the central octahedral B-site, and larger cations (Pb, Ba, Sr, Ca, Na etc.) filling the interstices between octahedra in the larger A-site. Compounds such as $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $NaNbO_3$ and $KNbO_3$ have been studied at length and their high temperature ferroelectric and antiferroelectric phases have been extensively exploited. This structure also allows for multiple substitutions on the A-site and B-site resulting in a number of useful though more complex compounds such as $(Ba,Sr)TiO_3$, $(Pb,Sr)(Zr,Ti)O_3$, $Pb(Fe,Ta)O_3$, $(KBi)_{TiO3}$ etc.

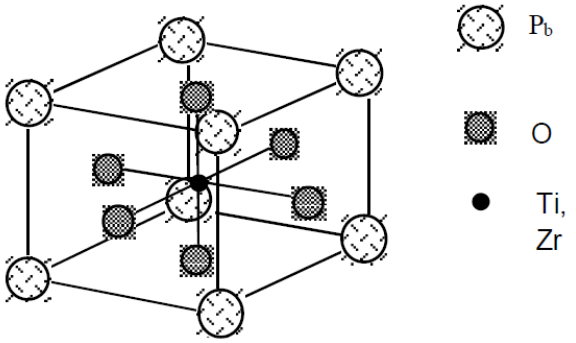

Fig. 1.Perovskite structure.

$Pb(ZrTi)O_3$Or PZT has superior ferroelectric, pyroelectric and piezoelectric characteristics and is widely used in various functional device applications. PZT ceramics show their maximum dielectric and piezoelectric properties, especially in the composition region around the morphotropicphase boundary (MPB).

In the past decade, PZT thin films have been recognized as the most promising capacitor materials nonvolatile and dynamic random access memories, electro-optic modulators, infrared detectors and micro-electromechanical system [3-5]. Dielectric, piezoelectric and pyroelectric materials used in manufacturing electronic, acoustic and thermal devices must have three main properties, (i) having wide band gap, (ii) very high dielectric constant and (iii) high Curie temperature. The solid solution PZT has a wide range of ferroelectric phase transitions and two different ferroelectric phase transitions and two different ferroelectric structures, depending on the Ti/Zr ratio. Fig. 1 shows the well-known phase diagram of bulk PZT materials, which has been referred by many investigators [6,7].

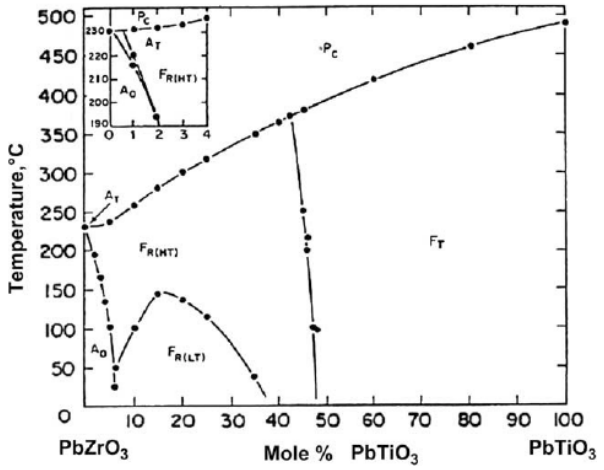

Fig. 2. Phase diagram of PZT.

Most of the piezoelectrically useful bodies have composition around MPB region.

2. Method of fabrication

The fabrication of most bulk piezoelectric ceramics starts with powder preparation. The powder is then pressed to the required shapes and sizes, and the green shapes are in turn processed to mechanically strong and dense ceramics. The more important processes that influence the product characteristics and properties are powder preparation, powder calcining and sintering. The next steps are machining, electroding and poling: application of a DC field to orient the dipoles and induce piezoelectricity.

The most common powder preparation is the mixed oxide route. In this process, powder is prepared from the appropriate stoichiometric mixture of the constituents oxides. In the case of lead zirconate titanate (PZT): lead oxide, titanium oxide, and zirconium oxide are the main compounds. Depending on application, various dopants are used to tailor the properties of interest. PZT ceramics are rarely utilized without the addition of dopants to modify some of their properties. A-site additives tend to lower the dissipation factor, which affects heat generation, but also lower the piezoelectric coefficients; for this reason they are mostly used in ultrasonic's and other high frequency applications. B-site dopants increase the piezoelectric coefficients but also increase the dielectric constant and loss.

They are utilized as actuators in vibration and noise control, benders, optical positioning application etc.

Mixing of the powders can be done by dry-ball milling or wet ball milling, both methods having advantages and disadvantages: wet ball-milling is faster than dry-milling; however, the disadvantage is the added step of liquid removal. The most common method for making PZT ceramics is through wet-ball milling; ethanol and stabilized zirconia media are added for a wet milling process. A vibratory mill may be used rather than a conventional ball mill; it was shown by Herner [8] that this process reduces the risk of contamination by the balls and the jar. Zirconia media are used to further reduce the contamination risks. The calcination step is a very crucial step in the processing of PZT ceramics; it is important that the crystallization be complete and that the perovskite phase forms during this step. The goals are to remove any organics, water or other volatiles left after mixing; to react the oxides to form the desired phase composition before the ceramic is processed to useful devices; and to reduce volume shrinkage and allow for better homogeneity during and after sintering.

After calcining, a binder is added to the powder, then the mixture is shaped usually by dry-pressing in a die for simple shapes, or extrusion, or casting for more complicated bodies. Next, the shapes are sintered: placed in an oven for binder burn-out and densification.

The major problem in the sintering of the PZT ceramic is the volatility of PbO at about 800°C. To minimize this problem, the PZT samples are sintered in the presence of a lead source, such as $PbZrO_3$, and placed in closed crucibles. The saturation of the sintering atmosphere with PbO minimizes lead loss from the PZT bodies.

Lead titanate zirconate oxide has been calcined at 1000^{o}C for one hour. The samples are sintered at a temperature of 1200 ^{o}C with heating rate 5 ^{o}C/min and a cooling rate 5 ^{o}C/min and a socking time held for three sets of specimens for a period of 3, 7 and 11 hour. Calcining and sintering process are made with a microprocessor controlled furnace model labotherm HT 04/17. The surface of five groups of specimens was polished and etched. In the chemical etching process, two factors are important. First is the kind of the etching material and the second is the time of etching. Etching process has been done with a 0.5% Hf Acid solution and 95% of HCL. This solution was composed with water with a rate of ten to one. After etching for 10 minutes by ultrasonic apparatus, the surface of specimen was cleaned. This process was done for removal of crashed grains which remained on surface from etching process. The scanning electron microscopy (SEM) observations were performed to inspect microstructures of PZT. In the SEM method, electrical charges are collected on surface, and so the photographs of the surface were destroyed. For this

reason, the surface was coated with a 2μm thick layer of gold.

After cutting and machining into desired shapes, electrodes are applied and a strong DC field is used to orient the domains in the polycrystalline ceramic. DC poling can be done at room temperature or at higher temperatures depending on the material and the composition. The poling process only partially aligns the dipoles in a polycrystalline ceramic, and the resulting polarization is lower than that for single crystals.

3. Results and discussion

The scanning electron micrographs of the samples of all groups have been taken at the room temperature. The grain size of a polished surface was determined from SEM photographs by using the linear intercept method. At least 100 PZT grains were included in the determination of grain size. Fig. 3 shows the surface of samples in group I which have been sintered for 3 hours at 1200 ^{o}C. The calculated grain size for this group is about 8.35 μm.

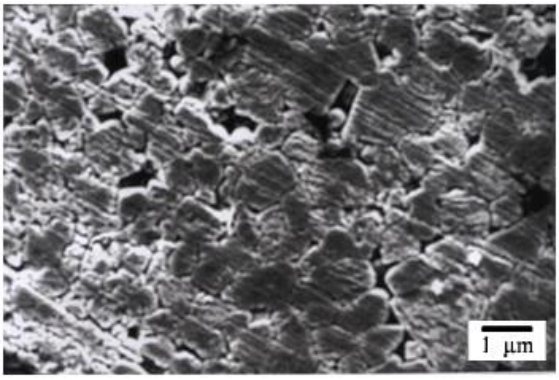

Fig. 3.scanning electron micrographs of sintered samples at 1200 ^{o}Cfor 3 hours.

Fig. 4 shows the surface of samples in group II which have been sintered for 7 hours. The calculated grain size for this group is about 13.13 μm. The grain size has increased with respect to samples that sintered for 3 hours.

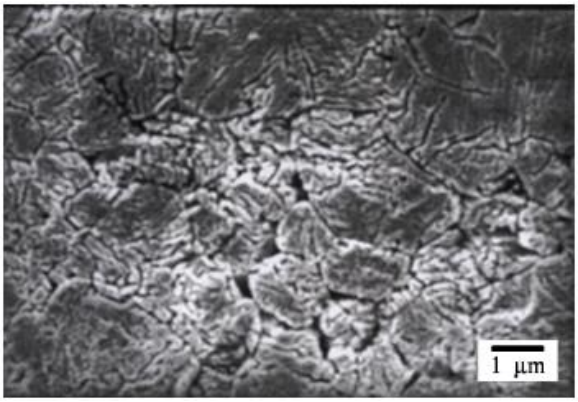

Fig. 4. Scanning electron micrographs of sintered samples for 7 hours.

Fig. 5 shows the surface of samples in group I which have been sintered for 11 hours. The calculated grain size for this group is about 16.29 μm. On the free-surface of the specimen a full densification has been observed. It is noted that some pull-outs shown in this figure were introduced in the preparation of polished surfaces because of soft PZT ceramics.

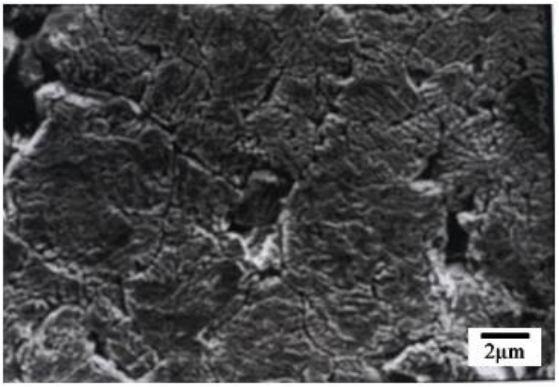

Fig. 5.scanning electron micrographs of sintered samples for 11 hours.

Table 1 shows the change of mean grain size with sintering time for three groups of samples. It is clear that grain size of specimens increases with increasing sintering time.

Table 1.The change of grain size with sintering time.

Sintering time (min)	180	420	660
Mean grain size (μm)	8.53	13.13	16.29

The capacitance and conductance of material are measured in a frequency range from 50Hz to 1MHz at various temperatures between 20 to 100 ^{o}C. Fig. 6 shows the change of dielectric function with temperature in range of 20 to 100 ^{o}C. It is clear that at low temperature the dielectric function is almost constant and the temperature range with constant dielectric function for group III is larger than the other groups. The value of dielectric function for group III is bigger than that of other groups. This means that the dielectric function have been increased with increasing sintering time.

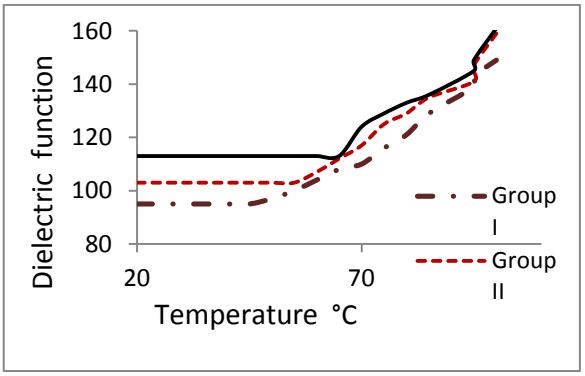

Fig. 6.The variation of dielectric function with temperature.

4. Conclusion

By powder mixing method, Lead zirconate titanate (PZT) ceramics were fabricated at three groups with different sintering time. The scanning electron micrograph (SEM) of the samples of all groups has been taken at the room temperature. The dielectric function of samples are measured in a frequency range from 50Hz to 1MHz at various temperatures between 20 to 100 ^{o}C microstructure and dielectric function exhibited obvious dependence on sintering time. The grain size of PZT ceramics plays critical roles in determining the magnitudes of dielectric function. With the increase of sintering time, the grain size increased which exerted direct influences on dielectric function.

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