SELCUK UNIVERSITY
FACULTY OF TECHNOLOGY

ICENTE'19

INTERNATIONAL CONFERENCE ON ENGINEERING TECHNOLOGIES

October 25-27, 2019
Konya/TURKEY

PROCEEDINGS

E-ISBN: 978-605-68537-9-1

Investigation on Dielectric Permittivity of PZT Manufactured by Electric Field Assisted Sintering

İ. ŞAVKLIYILDIZ[1] and Ç. OKUR[2]

[1] Konya Technical University, Konya/Turkey, isavkliyildiz@ktun.edu.tr
[2] Konya Technical, Konya/Turkey, cigdemokur@outlook.com

***Abstract* - By using submicron PZT(Pb[Zr_x,Ti_{1-x}]O_3 (0≤x≤1)) materials system, we provided electric field assisted sintering at 482–520 ºC temperature range in conjunction with 60 V/mm dc electric field on the specimen. The furnace temperature increased up to 520 ºC with 10 ºC/min increment. 0.3 amp current cut off was set by dc power supply to eliminate further temperature increase on specimen due to joule heating. The electric field assisted sintering system was prepared with sandwich type experimental setup. The specimen showing initially insulator behavior, revealed current leakage at 482 ºC. Maximum current draw of 0.3 amp was reached at 502 ºC with total power absorption of 5.27 watt/mm^3 during whole experiment. The power supply spontaneously decreased the electric field 20 V/cm due to variation conductivity behavior of specimen and maximum current cut off. Reaching 95 % theoretical density was verified with FESEM micrograph and there is almost no grain growth on specimen except very good grain boundary generation. The sintered PZT specimen showed appreciable dielectric permittivity (ε_r =273) on 1 kHz at room temperature comparing with other studies. Total power absorption of 5.27 watt/mm^3 in 180 seconds decreased sintering temperature from 1200 ºC to 500 ºC. Such an effect cannot be explained with joule heating in a short period of time with very low power supply. Therefore, we ascribe this behavior to electric field related polarization of atoms rested in lattice which increases mass transport triggered with impulse electron flux thorough electric field. Thermodiffusion (Soret effect) and electromigration are few theories could explain this phenomena. With this low temperature sintering techniques, lead emission could also be restricted during manufacturing process.**

***Keywords* – Electric field assisted, sintering, PZT ceramics, dielectric permittivity.**

I. INTRODUCTION

The sintering of ceramic materials, especially those that are covalently bonded, requires very high temperatures and very long times due to the low diffusivities in such materials [1-3]. For instance, piezoelectric ceramics such as PZT (Pb[Zr_x,Ti_{1-x}]O_3 (0≤x≤1)) are sintered at 1200 ºC for hours using conventional sintering to 99% density[4]. Sintering processes utilizing electrical current such as Spark Plasma Sintering (SPS) utilize a low voltage but ultrahigh current and in so doing is able to reduce the sintering time substantially to ~20 mins while the decrease in sintering temperature[4]. In SPS, Joule heating is the underlying mechanism that results sintering. In period 2010-2013, flash sintering was discovered which utilizes not only a low voltage but also a low current. The ceramic particulate system of interest can be sintered by sudden rise in current once a certain critical temperature is reached [6-10]. Typically, the current is limited to 10 A so as to prevent Joule heating by instantaneously switching to current control, followed by current cut off [11]. Sintering takes place at temperatures that are typically 30% of the melting temperature, whereas sintering times are drastically reduced to seconds to a few minutes. Such low sintering temperatures and times cannot be explained by classical diffusion kinetics. But the work by Akdogan and Savkliyildiz, which was published in 2013, has shown by in situ synchrotron x-ray diffraction that flash sintering is accompanied by an anelastic unit cell expansion in oxide, boride and carbide ceramics indiscriminately, which is believed to be the reason for enhanced diffusivity [12]. Although a series of articles appeared in the open literature speculating on a host of mechanisms, not clear understanding exists. What is common to all flash sintering studies is that one starts with particulate matter that involves particle to particle contacts [6-10]. As such, one is suspect that tunneling at particle-particle interfaces should have a correlation to enhanced diffusion kinetics. Power absorption during field assisted sintering study lead atomic level welding between particles so that proper grain boundary formation revealed with almost no grain growth [12].

Piezoelectric ceramics such as (PbTiO3, Pb [Zrx, Ti1-x] O3 (0≤x≤1) (PZT), is widely used in worldwide piezoelectric applications. However, lead emission at higher temperature production is a potential thread for human health [12]. With this presented study, a healthier production technique could be presented by sintering these materials at lower temperatures by electric field assisted sintering method.

II. EXPERIMENTS

The commercial sub-micron PZT (Pb[Zr_x,Ti_{1-x}]O_3 (0≤x≤1)) powder were prepared by uniaxial cold pressing into 12 mm diameter disks with 1.5 mm thickness. PEG was used as a binder media to get proper and compact green dense specimen fort his experiment. One hour annealing process was executed on as pressed specimen to eliminate the binder before electric field assisted sintering. MPB, morphotropic phase boundary (x=0,52) which is special composition showing higher piezoelectric and dielectric properties was chosen for this experiment. To measure density of final product, Archimedes method was used after electric field assisted sintering. FESEM (field emission scanning electron microscopy) investigation was done to assess microstructure as well as porosity. LCR meter was used to examine dielectric permittivity of sintered PZT specimen.

Figure 1 represents the electric field assisted sintering setup [12]. The specimen was positioned between ceramics insulators as sandwich type with silver electrodes on both surfaces. To provide ohmic contact on both surface, silver paste was spread properly. The electrodes was used to apply electric field on specimen during sintering. The applied electric field on specimen is set to 60 V/mm with 0.3 amp current cut off to avoid joule heating. Furnace temperature was rised 10 ºC/min intervals up to 520 ºC. Electric field with current draw through specimen and the furnace temperature was recorded during whole experiment.

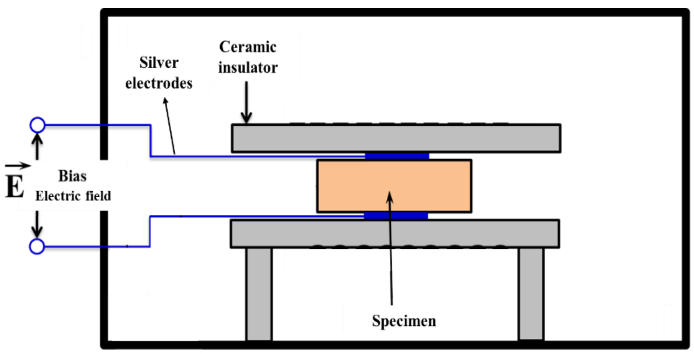

Figure 1: Schematic of sandwich model of experimental setup in furnace [12].

III. RESULTS AND DISCUSSION

Figure 2 shows history of electric field –current relation during field assisted sintering. Even though the specimen was exposed 60 V/mm electric field, no current transition was recorded up to 480 ºC which means specimen behaved as an insulator at the beginning due to the lack of particle contact. As increasing temperature, the conductivity of specimen was increased and particle-particle formation was appeared so that 0.1 amp current leakage was observed at 480 ºC. Further increase on temperature results increment on conductivity of specimen and current draw as well. Reaching 502 ºC as furnace temperature, specimen draw 0.3 amp max. current with 60 V/mm electric field. After this point, specimen conductivity kept increase so, power supply adjusted electric field down to 20 V/mm spontaneously to keep 0.3 amp current draw.

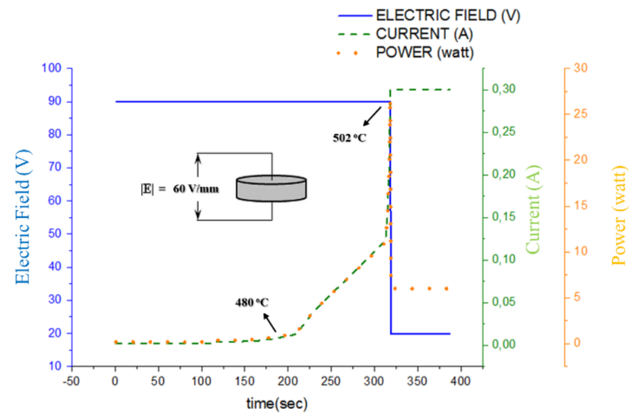

Figure 2: Electric field- current behavior of PZT as function of time

After 80 sec superimposed constant electric field with current draw was finalized to avoid joule heating of specimen. 95 % percent density was measured on sintered specimen by Archimedes method. Sintering PZT around 500 ºC (conventional sintering ~1200 ºC) groundbreaking outcome of this study. During experiment, specimen absorbed 5.27 watt/mm^3 power which results 10 ºC extra increase on furnace temperature. This much temperature increase is not enough to achieve 95 % density so there another mechanism underlying to explain this technique.

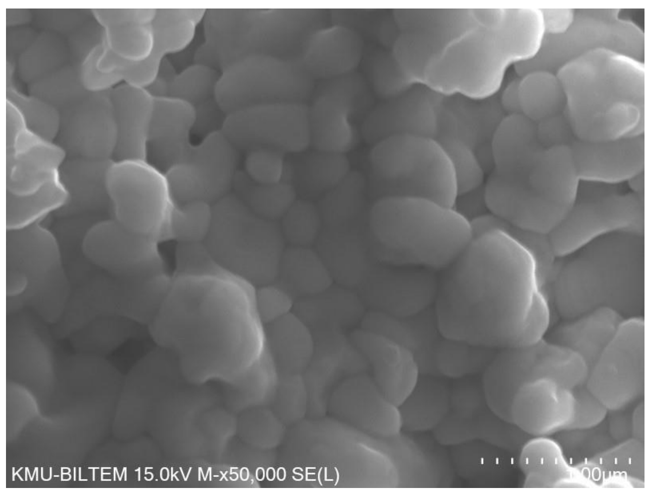

Figure 3: Microstructure of electric field assisted sintered of PZT

Figure 3 represents the microstructure of sintered specimen from fracture surface. A unimodal grain size distribution was observed with proper grain boundary formation. A closer look on microstructure suggest that sintering at low temperature limits grain growth (~700nm) beside very low porosity throughout the specimen. Starting with sub-micron powder results almost no grain growth but very good densification. Therefore, FESEM micrograph validate our density measurement.

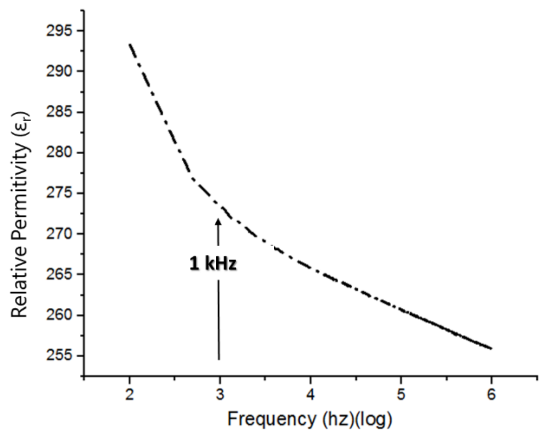

Figure 4: Dielectric permittivity behavior of PZT up to 1 MHz at room temperature

Dielectric permittivity of sintered specimen was illustrated in figure 4 up to 1 MHz at RT. Measuring 273 permittivity value is decent number comparing literature [14]. At higher frequency, specimen permittivity kept this number with little decrement. This behavior suggest that electric field assisted sintering is convenient method comparing other sintering techniques.

IV. Conclusion

Nonisothermal densification in sub- micron PZT powder was studied under 60 V/mm dc electric field and 10 ºC/min heating rate. Electric field assisted sintering occurred in the 482–516 ºC range, which resulted in 95 % of the theoretical density. No local melting due to current draw at particle-particle contacts was observed in scanning electron micrographs, suggesting densification was due to solid state mass transport processes. The maximum current draw at 502 ºC was 0.3 A, corresponding to instantaneous absorbed power density of 5.27 watt/mm^3. This much power absorption in short time period does not cause 95 % density according to literature, so we attribute this behavior to unit cell volume expansion with polarized atoms due to electric field increases mass. The electron flux during current gains enough momentum to migrate atoms which is called electromigration. Limitation of grain growth by using this technique results improvement on mechanical properties of final product according to hall-petch equation. Regarding dielectric permittivity of final product, specimen revealed 273 ε_r value which very acceptable results according to literature. Electric field assisted sintering technique decreases sintering temperature from 1200 ºC to 500 ºC which results very high energy saving and initial capital investment as well. Another outcome of this study is that eliminating lead emission arising at high temperature manufacturing process. Lead based piezoelectric materials is avoided due to lead emission problem at higher temperature, so our manufacture method could be a solution as a green processing technique.

Acknowledgment

The authors wish to express their gratitude for the financial support provided by the Scientific Research Projects Coordination Unit (SRPCU) of Selçuk University for the project (Contract # 18401032). The authors wish to thank Dr. E. Koray AKDOĞAN of Rutgers University for his valuable technical feedback and support of this work.

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