www.dergipark.gov.tr
ISSN:2148-3736
El-Cezerî Fen ve Mühendislik Dergisi
Cilt: 8, No: 2, 2021 (793-799)

El-Cezerî Journal of Science and Engineering
Vol: 8, No: 2, 2021 (793-799)
DOI :10.31202/ecjse.887859

ECJSE

Research Paper / Makale

Flash Sintering Effect on PMN-PT Ceramics

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Received/Geliş: 27.02.2021 **Accepted/Kabul:** 06.04.2021

Abstract: Densification of PMN-PT piezoelectric ceramic powder is carried out by electric field assisted/flash sintering method. The composition selected in PMN-PT materials system is $0.67[Pb(Mg_{1/3}Nb_{2/3})O_3]-0.33(PbTiO_3)$. During flash sintering experiment, 200 V/mm electric field is applied on sample with 0.1 amp current cutoff value. Flash sintering is accomplished in less than 90 sec at ~700 °C. Relative density for sintered sample is measured approximately 94 % which is reasonable value comparing with literature. SEM microstructure illustration exhibits proper consolidation morphology which is agreement with the relative density measurement. According to XRD analysis, the said materials system shows consistency in rhombohedral perovskite crystal structure and preserve its chemical and physical composition during whole experimental cycle. By electric field assisted/flash sintering technique, the sintering temperature is decreased from 1200 °C to 700 °C along with a decrement in sintering time from 2 hours to 90 seconds. PMN-PT is properly produced by flash sintering method for the first time with respect to open literature. Hence, this densification method will gain importance to reduce toxic Pb emission aroused at high temperature processes.

Keywords: PMN-PT, flash sintering, piezoelectric ceramics, electric field, ferroelectric

Flash Sinterlemenin PMN-PT Seramikleri Üzerine Etkisi

Öz: PMN-PT seramik tozların yoğunlaşması çalışması elektrik alan/flash sinterleme metoduyla uygulanmıştır. PMN-PT malzeme sisteminde seçilen kompozisyon $0.67[Pb(Mg_{1/3}Nb_{2/3})O_3]-0.33(PbTiO_3)$ olarak belirlenmiştir. Flash sinterleme deneyi sırasında numune üzerine 200 V/mm elektrik alan 0.1 amper akım kesme değeri ile uygulanmıştır. Flash sinterleme 90 saniyeden daha az bir sürede ve yaklaşık 700 °C tamamlanmıştır. Göreceli yoğunluk değeri yaklaşık 94 % olarak ölçülmüştür ve bu değer literatürdeki değerlere göre makul bir değerdir. SEM mikroyapı örneklemesi uygun katılaşma morfolojisi göstermekte ve göreceli yoğunluk ölçümüyle uyuşmaktadır. XRD analizine göre, bahsedilen malzeme sistemi romboedrik perovskit kristal yapısında devamlılık göstermiştir ve kimyasal ve fiziksel kompozisyonunu bütün deney süresince korumuştur. Elektrik alan yardımlı/flash sinterleme tekniği ile sinterleme sıcaklığı 1200 °C den 700 °C ve sinterleme süresini 2 saatten 90 saniyeye düşürmüştür. PMN-PT açık literatüre göre flash sinterleme metoduyla ilk defa üretilmiştir. Böylelikle bu yoğunlaşma metodu yüksek sıcaklık proseslerde ortaya çıkan toksik Pb salınımı azaltmasıyla önem kazanacaktır.

Anahtar Kelimeler: PMN-PT, flash sinterleme, piezoelektrik seramikler, elektrik alan, ferroelektrik

1. Introduction

Both $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $PbTiO_3$ (PT) ferroelectrics materials with perovskite-structure are employed for several applications such as actuators, capacitors, and MEMS [1-4]. PMN and PT are integrated with composition formula of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ - $xPbTiO_3$ to have improved piezoelectric properties for various usage area such as multilayer capacitors and sensors[5, 6]. Morphotropic phase boundary (MPB) composition is preferred due to interesting piezoelectric behaviors[6, 7]. Pure PMN-PT tend to exhibit many crystal structures such as tetragonal,

How to cite this article
Şavklıyıldız, İ., Demir, A., "*Flash Sintering Effect on PMN-PT Ceramics*" El-Cezerî Journal of Science and Engineering, 2021, 8 (2); 793-799.

Bu makaleye atıf yapmak için
Şavklıyıldız, İ., Demir, A., *"Flash Sinterlemenin PMN-PT Seramikleri Üzerine Etkisi"* El-Cezerî Fen ve Mühendislik Dergisi 2021, 8 (2); 793-799.
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rhombohedral and cubic variate with mixing ratio and temperature[8, 9]. The influence of impurity element on crystal structure of PMN-PT materials system has been also studied in literature[10, 11]. For instance. Sr addition in the said materials system make the rhombohedral phase dominant in MPB composition[11]. Bulk sample of PMN-PT is produced above 1000 °C with 2h sintering time [11, 12]. Such production methods cause high amount of toxic lead emission at elevated temperature[13].

Recently discovered electric field assisted/flash sintering method provides opportunity for rapid densification with lower processing temperature and time comparing other traditional methods [14-16]. In flash sintering process, specimen electrical conductivity is suddenly increase in conjunction with rapid mass transport in seconds which lead the rapid densification. This technique is suitable for densification of many materials system[15, 17]. Electric field assisted/flash sintering technique is expressed by several mechanism such as field-induced vacancy and Frenkel pairs generation and excessive joule heating formation at atomic level [18-20]. However, the most reliable explanation is offered by high resolution EDXRD study which suggests abnormal unit cell volume expansion during rapid current leakage through sample[16, 21]. Large amount of electron addition to system lead to polarization of each atom and change the interatomic distance in the lattice structure. Hence, the mass transport ratio and/or diffusivity of each atom is increased by selected electric field/temperature combination. In this study, we intend to produce high dense PMN-PT materials system with lower sintering temperature and time.

2. Experimental Methods

PMN-PT powder with $0.67[Pb(Mg_{1/3}Nb_{2/3})O_3]-0.33(PbTiO_3)$ composition is used for electric field assisted/flash sintering study. Regarding synthesis of PMN-PT, close to morphotropic phase boundary (MPB) composition of PMN-PT is produced by solid state reaction method. The detail of powder production is found elsewhere [11, 12]. PMN-PT ceramic powder with 3 μm average particulate size is mixed with 3 wt% of an aqueous solution and 5 wt % binder (PEG). Then, the powder is sieved before pressing process. To get green dense disc shape sample with 2mm thickness, the powder is pressed by using hardened stainless-steel die with 13 mm diameter under a pressure of 50 bar using a uniaxial press. Binder burnout process is carried out at 500 °C for 1 h with 1 °C/min heating rate. The disc shape PMN-PT specimen is positioned in parallel plate capacitor experimental setup for flash sintering[21]. Fig 1 illustrates the experimental setup located in the furnace. Both face of specimen is covered by platinum foils which are used for applying electric field and inducing a transient current draw by PMN-PT sample during whole experimental cycle.

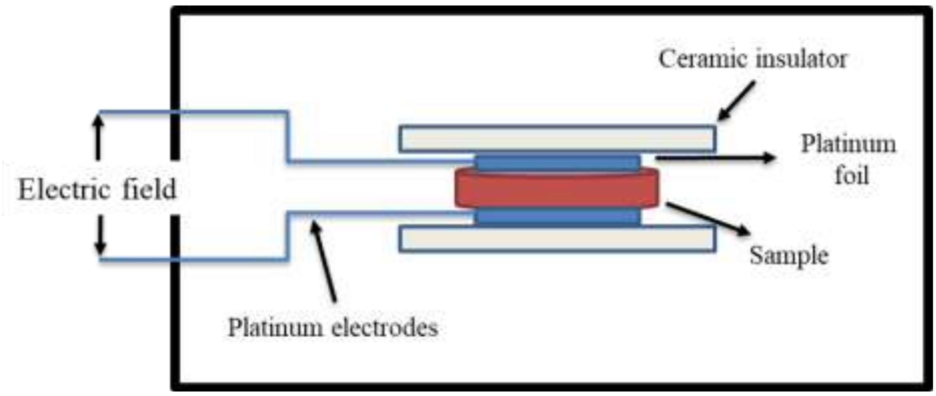

Figure 1 Parallel plate capacitor type of experimental setup which is used for flash sintering of PMN-PT ceramic

The main reason using platinum foil is creating proper and homogenous ohmic contact on surface of sample and applying uniform electric field on both faces of sample. The platinum foils are attached with platinum wires to power source which is positioned outside of the furnace. The platinum foils and wire have good electrical conductivity and inert behavior at high temperature, which makes platinum one of the best electrodes for flash sintering studies. The sample with foils is sandwiched by Al_2O_3 ceramic insulators to create tide contact. Because, it is possible losing contact between foils and sample during elevated temperature.

The furnace temperature is increased up to 750 °C with 12 °C/min heating rate. DC power source is used to apply electric field of 200 V/mm on the sample during flash sintering. The amount of applied electric field is determined with respect to materials' conductivity type (poloron, ionic etc.) band gap, and temperature dependent conductivity properties in conjunction with our previous work [18-25]. Current cutoff value is chosen as 0.1 amp to avoid joule heating. Voltage and current values are recorded as function time instead of temperature. Because current draw on sample could contribute extra temperature increase in furnace due to joule heating phenomena during flash sintering study. Both electric field and current cutoff values are determined our prejudice knowledge, preliminary studies and literature surveys. Archimedes' method is conducted to measure apparent density of the sample after flash sintering. Field emission scanning electron microscopy (FE-SEM, Hitachi SU5000) is used to assess microstructure as well as porosity on the surface of sintered sample. X-ray diffraction spectrometer (Rigaku ZSX Primus-II XRD) was employed to determine any changes in rhombohedral perovskite crystal structure during flash sintering process.

3. Results and Discussion

The power source is set to 400 V for 2mm PMN-PT to apply 200 V/mm electric field during whole experiment with 0.1 amp current cutoff value as shown fig 2. The whole electric field assisted sintering experiment could be divided into four section. The first section is defined where the specimen behaves like an insulator. Even though the furnace temperature is increased up to 683 °C with 12 °C/min heating rate and the sample is exposed 200 V/mm electric field, no current draw is observed through disc shape sample which suggests that specimen shows insulator structure due to lack of particle-particle contact in green dense sample and low electrical conductivity value. When the furnace temperature reach 683 °C, current leakage approximately 0.001 amp is observed through sample where the second section is initiated. After this point, the conductivity of sample tend to increase which leads to a monolithic increment in current draw recorded up to 0.02 amp. After reaching system temperature to 694 °C, PMN-PT ceramic spontaneously displays parabolic increase in conductivity which is considered as a nature of flash sintering[22]. This behavior is termed third section of flash sintering. In a very short period of time, the current draw through the said materials system is multiplied five times and achieves 0.1 amp which is read as current cutoff value at 697 °C. The reason determining a current cutoff value in flash sintering is to prevent current and electric field related joule heating. The uncertainty about flash sintering mechanism still exists and some studies in literature argue the huge contribution of joule heating in atomic level led to proper mass transport and grain boundary formation[18, 20]. However, our previously reported high resolution EDXRD study reveal the abnormal expansion in unit cell volume[16, 21]. Large amount of electron dumping in system with a very short time of period causes polarization of each atom settled in lattice. Considering such information along with conductivity behavior of specimen at high temperature, the maximum current value is determined as 0.1 amp. Further increment at temperature lead to increase in the conductivity of specimen or decrease in the resistivity. At this point, the power source automatically adjusts the electric field to preserve the selected current cutoff value according to $V = I \times R$ relationship. So, the electric field value goes down to 180 V/mm and stabilized at this number.

As a last section of this study, the current draw with 0.1 amp and the electric field with 180 V/mm is kept few more seconds to accomplish mass transport and sintering mechanism. The total power dissipation around 3.76 watt/mm^3 in specimen is observed thorough out the experiment. The value of power is important to understanding flash sintering method. Because it is claimed that joule heating originated temperature increase up to melting point conveys huge mass transport along with deterioration in porosity[23, 24].

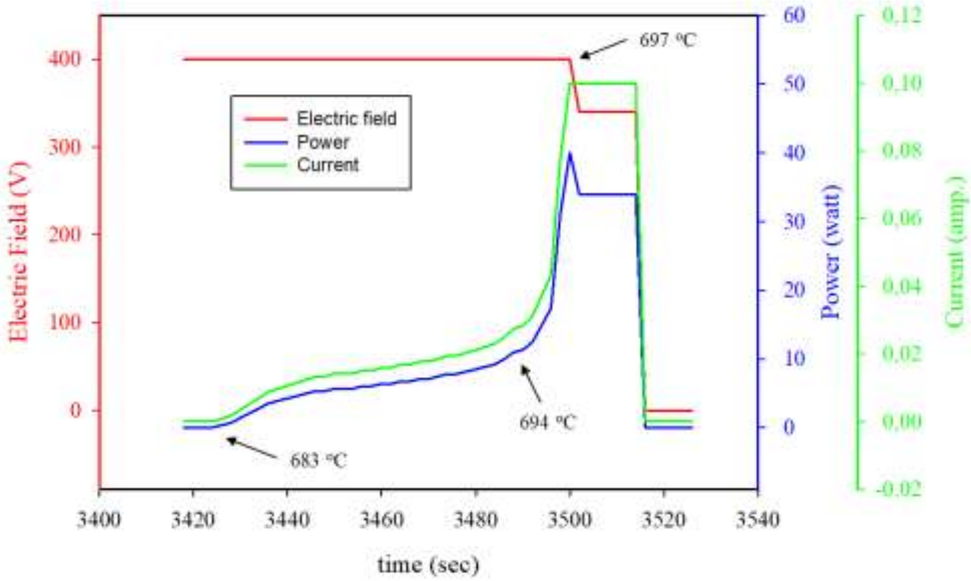

Figure 2. Current draw behavior of sample under 200 V/mm electric field

However this much power dissipation absorbed in less than 90 sec cannot increase temperature up to melting point according to joule heating calculations[25]. So, other mechanisms such as anomalous expansion in unit cell volume or electromigration involve to the flash sintering. The flash sintering is completed at approximately 700 °C which is very low temperature comparing with literature [10-12].

Figure 3. Microstructure of sample after flash sintering process

The sample cool down to room temperature and density measurement is carried out with Archimedes' method. The relative density is measured as 94% for flash sintered sample which is reasonable value comparing with literature data. The flash sintering experiment is completed in less 90 sec. In conventional sintering for PMN-PT, at least 2 h consolidation time is needed at 1000 - 1200 °C temperature range [10-12]. So, we are able to decrease sintering temperature to 700°C and sintering time to 90 sec with electric field assisted/flash sintering. Figure 3 represents microstructure morphology of sintered sample taken from fracture surface. The microstructure suggests high dense structure with less porosity on surface which verify the relative density measurement.

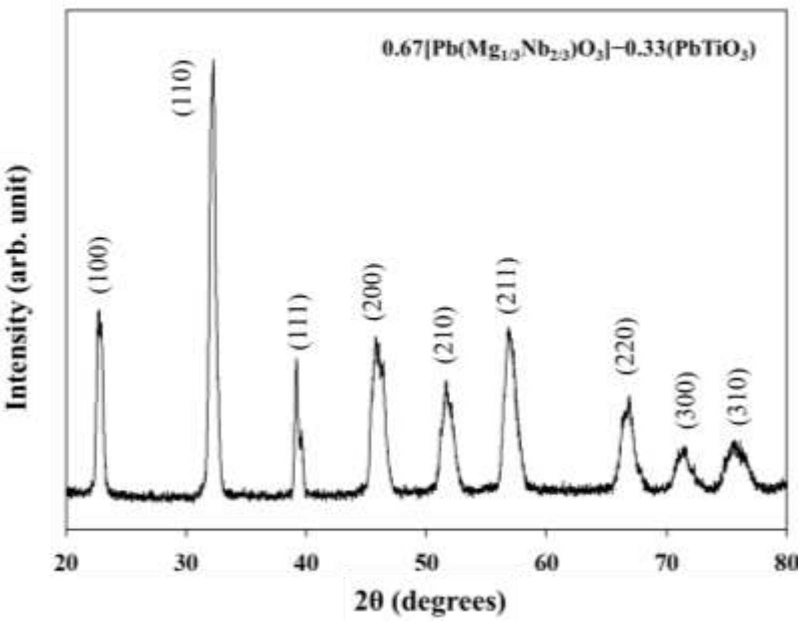

Figure 4. XRD spectrum of flash sintered sample with rhombohedral perovskite crystal structure

PMN-PT with morphotropic phase boundary composition could display tetragonal- rhombohedral phase transition depending on mixing amount and temperature[26]. To understand crystallographic evolution during flash sintering study, XRD experiment is employed. Figure 4 depicts XRD spectrum of sintered sample which reveals rhombohedral perovskite crystal structure. During flash sintering study, PMN-PT materials system preserve its initial crystal structure. Peak parameters acquired by peak fitting suggests that no residual lattice strain formation is observed by comparing the literature when the system is reached the ambient condition after flash sintering [2-12]. Some studies reported in literature suggest that materials system could exhibit allotropic phase transition or transient phase transformation during flash sintering[19, 27]. However, our materials system shows any changes regarding allotropic phase transition such as tetragonal- rhombohedral rather than proper consolidation at very low temperature and very short time period comparing conventional sintering methods[28].

4. Conclusions

In this study, electric field assisted/flash sintering technique is conducted to acquire highly dense PMN-PT piezoelectric ceramic. Initially, the sample is exposed 200 V/mm electric field with 0.1 amp current limit but there is no current draw recorded in experimental system. When the furnace temperature is measured as 683 °C, a small amount of current leakage is recorded with monolithic increase. The max current draw value is achieved at 697 °C and the power source spontaneously regulates itself by the electric field-current relation. Whole flash sintering is completed in less than 90 sec at ~700 °C. SEM micrograph reveals high dense materials system achieved by flash sintering and the density is determined as 94 % which confirms the SEM illustration. The chemical and physical variation is verified by XRD analysis which suggests stable rhombohedral perovskite crystal structure during flash sintering. Sintering temperature is decreased by at least 300 °C with 90 sec sintering process. This experimental procedure enable us to eliminate the lead emission in PMN-PT materials system which is confronted at high temperature lead based piezoelectric ceramics production.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the Scientific Research Projects Coordination Unit (SRPCU) of Selcuk University for the project (Contract # 18401032) and Scientific Research Projects at Konya Technical University for the project (Contract # 191019035). The authors wish to thank Dr. Volkan KALEM (Metallurgical and Materials Engineering Department at Konya Technical University) for providing PMN-PT powder.

Author Contributions

İŞ and AD conceived parallel plate capacitor flash sintering experimental setup. İŞ wrote the paper in conjunction with interpreting a major part of data. The flash sintering experiment along with data collection was carried out by both İŞ and AD. İŞ has 60% percent contribution where AD has 40% contribution on this work.

Competing Interests

The authors declare that they have no competing interests.

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