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Effect of Sintering on the Piezoelectric Properties and Microstructure of Lead Free ($Ba_{1-x}Ca_xZr_{0.1}Ti_{0.9}O_3$) (x = 0.065) Ceramics

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Abstract:

In this work, pellet samples of barium calcium zirconate titanate ($Ba_{1-x}Ca_xZr_{0.1}Ti_{0.9}O_3$, x=0.065) were prepared using solid state reaction route with double sintering. The structural and piezoelectric properties were measured. Further, SEM and EDAX analysis were observed. With different sintering temperature, the density and grain size of the prepared pellet samples were changed and further, their effect in piezoelectric properties has been observed. For the prepared samples, the converse piezoelectric constant (d_{33}^*) has been decreased with the increase in sintering temperature. The piezoelectric constant (d_{33}^*) was measured highest (153 pm/V) at 1300°C.

***Keywords**: Ferroelectrics; Piezoelectric constant; Perovskite; 2- step sintering.*

1. Introduction

Perovskite type materials are of huge interest because of their large piezoelectric and dielectric properties [1]. They are important due to their spontaneous polarization characteristics. Their contributions in the field of sensors and transducers are very important. The ABO_3 compounds also have the ferroelectric property [1]. Ferroelectric/ABO_3 type materials may generate voltage by applying pressure on it and produce stress due to applying electric field. Lead based compounds have been widely used because of its large electrical properties. One widely used compound is lead zirconate titanate (PZT). The PZT type compounds show a large piezoelectric value. It may be due to the coexistence of two phases (rhombohedral and tetragonal) at the MPB region [2-4]. But due to its toxic 'nature', PZT is prohibited and scientists are going for lead free piezoelectric materials [4]. Now, for the replacement of Lead- based compounds, lead free ABO_3 type compounds have been widely used. Their dielectric and piezoelectric properties aren't comparable with PZT, but these lead free ferroelectric/ABO_3 materials have been extensively used as a replacement. Further, lead free ABO_3 materials have been used in the various fields of sensors and transducers, etc.

Many researchers studied the PZT system. It has high piezoelectric properties near morphotropic phase boundary (MPB) [3]. It may be occurred because of the abrupt transformation of the polarization state leads to unstable state, at the MPB region. The ferroelectric domains may be altered or several ferroelectric domains may appear due to that reason, which results large piezoelectric properties [3].

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Several ferroelectric compounds such as $BaTiO_3$, KTN, KNN, NKN etc. have been studied [5]. But, they reflect the minimum value of piezoelectric coefficient as compared to PZT. One prominent lead free compound is (K, Na) NbO_3 or sodium potassium niobate based system, which has been reviewed as a good ferroelectric material for lead-based compounds [6]. They have good electrical properties, and further, their properties can be enhanced by using different technologies.

Another important lead free compound is the barium calcium zirconate titanate (BCZT) based system. It may have the significant potential to replace lead-based ceramics used in various dielectric and ferroelectric devices. Their electrical properties may be comparable to the PZT system. BCZT ceramics have been considered for various applications due to their large electrical properties [6]. With a variation in sintering temperature, the piezoelectric properties of BCZT ceramics significantly changed. Buatip et al. [7] reported that if the sintering temperature has been increased above 1300°C, then the piezoelectric coefficient of BCZT ceramics has been reduced. Villafuerte-Castrejón and Tian et al. [8, 9] reported about the piezoelectric coefficient of BCZT ($Ba_{1-x}Ca_xZr_{0.1}Ti_{0.9}O_3$) ceramics, which have a range from 160 pC/N - 600 pC/N.

Further, this research has been done to investigate the piezoelectric properties and grain size variation with the introduction of two - step sintering process. The pellet samples were sintered for 4 hrs with different sintering temperatures. The sintering temperatures were selected 1300, 1400, and 1450°C. Moreover, with variation in sintering temperature conditions, the structure, microstructure, and piezoelectric properties of the synthesized ($Ba_{0.935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_{3,}$ x = 0.065) pellet samples of BCZT ceramics were investigated. The composition x = 0.065 was selected to see and compare the piezoelectric properties, density and grain size. However, with composition x = 0.075, the sintering effect was already observed and their properties were compared in this study [7].

2. Materials and Experimental Procedures

The pellet samples of BCZT ($Ba_{0.935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics were prepared using solid-state reaction route with double sintering [10,11]. Raw materials of Barium carbonate ($BaCO_3$), Calcium carbonate ($CaCO_3$), Zirconium oxide (ZrO_2), and Titanium oxide (TiO_2) were taken with purity greater than 99.99 %. The materials were dried at 200°C for 2 h, to remove the absorbed moisture. A proper stoichiometric ratio has been maintained to prepare the compositions. An agate mullet mortar and pestle is used to ground. The powders were ground with acetone for 2 h and further, 'dry' for 4 h. After 6 hrs, the grinding cycle has been completed. The mixture was calcined in a crucible at 1100°C to remove all carbonate. The pre-sintered mixture was ground and pressed into the disk of 8 mm diameter and 2 mm thickness at 0.2 GPa. The ceramic pellet samples were sintered at 1100°C for 4 h. The sintered pellets were crushed and ground further into powder. This ground powder was further pressed into the disk of 8 mm diameter and 2 mm thickness, at 0.2 GPa. The ceramic pellet samples were sintered again with same conditions. The ceramic pellets were collected from the furnace and cooled it down to room temperature.

The X–ray diffraction patterns were observed at room temperature. For the prepared compositions, powder and pellet samples of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics were used. The XRD measurements were taken using PANalytical, X'PERT PRO with Cu$K_{\alpha1}$ radiation of wavelength 0.1541 nm. The 2θ angle has been selected from 20° to 70°, at a scan speed of 0.3 sec per step with step size 0.03°.

Scanning Electron Microscopy (SEM) has been used to view the microstructure and grain size of the prepared pellet samples, by ZEISS EVO 18 SEM equipped with energy dispersive X-ray Analyzer (EDAX) system.

For piezoelectric measurements, the sintered pellet samples were electrode, with air drying silver paste, in metal – insulator - metal (MIM) configuration. The piezoelectric constant ‘d_{33}^{*}’ was measured using the aixACCT system GMBH.

3. Results and Discussion

The XRD measurements were carried out for the powder and ‘pellet’ samples at different sintering temperatures as shown in Fig. 1 and Fig. 2, respectively. A pure perovskite structure has been observed for all the prepared pellet samples. No other phases were observed. The pellet samples have been shown polycrystalline behavior. They were found in good consistency with Inorganic Crystal Structure Database (ICSD) - (00-056-1033), with peaks corresponding to (111), (020), (221), etc. [12]. The RT - XRD of the pellet samples BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) show orthorhombic phase with matched ICSD file No. 00-056-1033 (Fig. 2).

The lattice parameters were calculated manually. The selected space group is ‘C’ type. For the prepared powder samples, the observed XRD data were matched with Inorganic Crystal Structure Database (ICSD). The ICSD data will give the information of the orthorhombic unit cell (a, b and c parameters) and volume. The manually calculated values (a, b and c parameters) must be in more close approximation to those values. At first, the positions of the observed x- ray peaks were identified. For a corresponding peak, the d-spacing and (hkl) has been noted from the ICSD data. The equation for an interplanar spacing for an orthorhombic unit cell was used to calculate the lattice parameters. To work with the above interplanar equation, the h, k, l, and d values were noted and further, the lattice parameters were calculated. The lattice parameters were shown in Table I.

Tab. I Lattice parameters of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics.

	a(Å)	**b(Å)**	**c(Å)**
BCZT Lattice parameters in (Å)	9.807	5.651	6.893

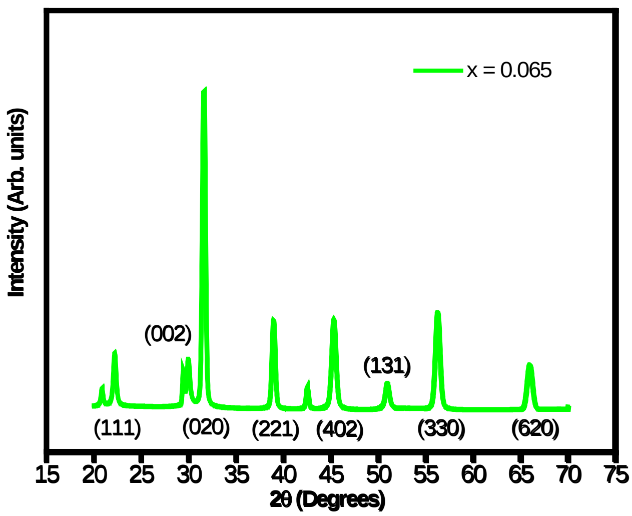

Fig. 1. XRD pattern of the powder sample of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$), at room temperature.

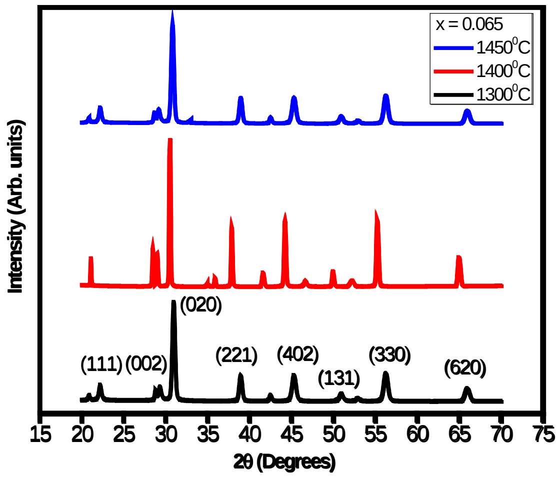

Fig. 2. XRD patterns of pellet samples of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$), at different sintering temperatures.

With the change in grain size, the piezoelectric properties of the prepared compositions were also altered. The SEM images of the sintered pellets were shown in Fig. 3-5. The influences of two-step sintering on the lead- free BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics with different sintering temperatures were analyzed. The density decreases as the sintering temperature increases (Table II). Further, if the sintering temperature has been increased then the grain size of the sintered pellet samples has been increased, leading to small grain boundary. Also, the porosity has been increased. The EDAX (Energy dispersive X-ray analyzer) measurements of the sintered pellet samples of BCZT ceramics has been shown in Tables III-V. From the EDAX results of the prepared compositions, the atomic percentage of barium and calcium has been observed. For an increase in sintering temperature, the atomic percentage of barium was decreased at 'A' site and further, the percentage of calcium has been increased at the 'B' site (Fig. 3-5). Calcium escaping has been reduced and escaping of barium was increased as the sintering temperature increased. For BCZT ceramics, grain growth has been seen with an inhomogeneous rate, due to the variation in the sintering temperature from 1300 to 1450°C. The reason is longer dwelling time and atoms of the pellet samples were getting more time to diffuse into adjoining grains, at the grain boundary, and the resulting in the grain growth of BCZT ceramics [13-15]. The measured grain size has been shown in Table II.

Tab. II Physical properties of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics sintered at various temperatures.

	Sintering temperature (°C)	Density (gm/cm^3)	Grain size (μm)
BCZT	1300	3.49	0.59-2.60
	1400	3.08	0.78-3.00
	1450	2.56	1.30-4.30

During the start of sintering, due to the low activation energy of the samples, extreme grain growth appears and grain coarsening has been introduced. So, the total surface area has been reduced due to an increase of the average size of the particles or grains. The driving force is basically changing surface area. Here, it is 'surface energy' and surface area both are changing. This is also another possibility, but in principle, this is not feasible because once these larger particles are there, the sintering itself becomes difficult and further, it may not reduce its pores so easily, until one may go to a very high temperature. Once that coarsening takes place, the pore removal becomes quite difficult and resulting in poor densification [16-18].

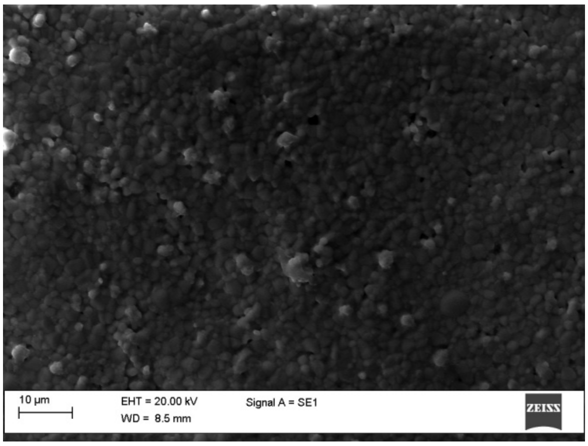

Fig. 3. SEM image of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1300$^oC$ temperature.

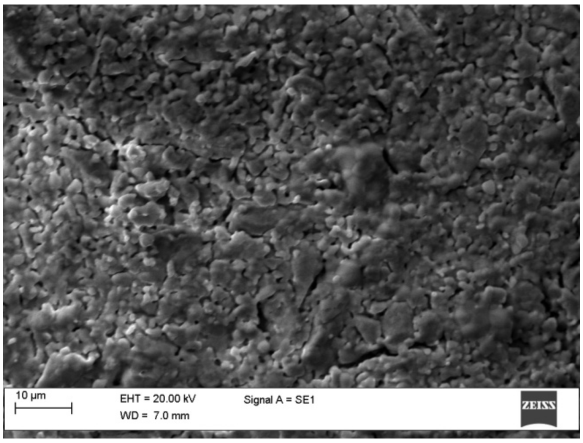

Fig. 4. SEM image of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1400$^oC$ temperature.

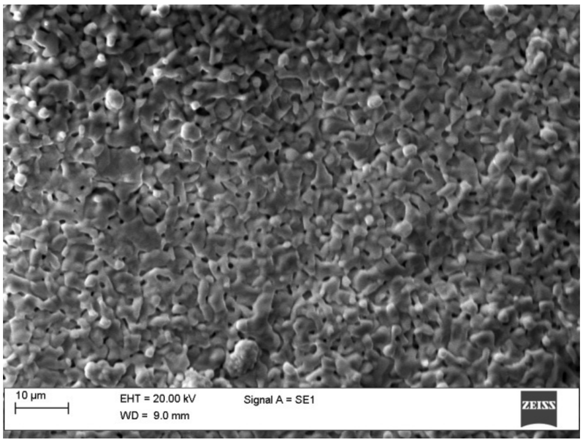

Fig. 5. SEM images of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1450$^oC$ temperature.

Tab. III EDAX result of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1300°C temperature.

Element	Weight %	Atomic %
O	25.51	64.23
Ca	4.22	3.23
Ti	18.53	15.50
Zr	0.62	0.24
Ba	51.65	15.32
Total	100.00	

Tab. IV EDAX result of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1400 °C temperature.

Element	Weight %	Atomic %
O	28.94	65.56
Ca	5.12	4.12
Ti	18.80	14.21
Zr	0.37	0.18
Ba	46.44	12.26
Total	100.00	

Tab. V EDAX result of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at 1450°C temperature.

Element	Weight %	Atomic %
O	30.75	66.11
Ca	6.45	5.75
Ti	18.95	15.78
Zr	0.27	0.12
Ba	43.58	11.04
Total	100.00	

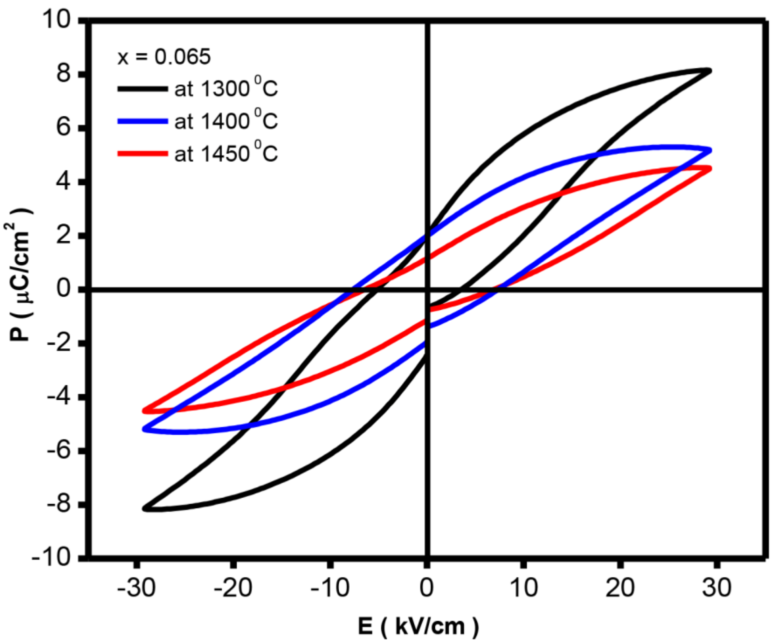

Fig. 6. P- E loops of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at different sintering temperature, at an applied field 14.73 (kV/cm).

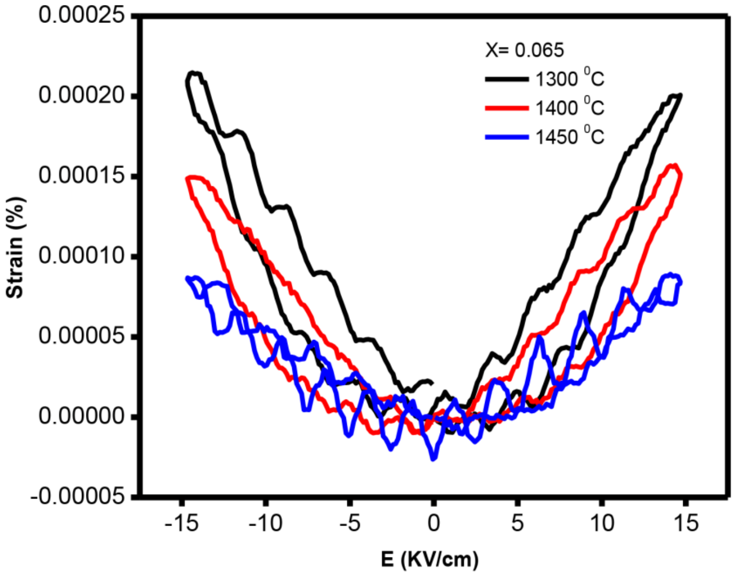

Fig. 7. Strain (%) with change in the electric field of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, at different sintering temperature, at an applied field 14.73 (kV/cm).

The P-E hysteresis loops of prepared BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics pellet samples were shown in Fig. 6. The piezoelectric measurements were carried out at room temperature (RT), and applied field 14.73 (kV/cm). For the prepared compositions, the hysteresis loops show a good ferroelectric nature. From P-E hysteresis loops, the value of the remnant polarization (P_r) was 2.074 μC/cm^2 and the corresponding coercive field was 3.63 kV/cm (E_C), with sample x = 0.065, sintered at 1300^{o}C. For the double sintering pellet samples, 'well saturated' loops were observed for the BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, with a temperature range from 1300 to 1450^{o}C. For the prepared pellet samples, 'well saturated' loops were measured due to high density and low porosity, at different sintering temperatures [7].

P-E strain% loops for the BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics pellet samples were shown in Fig. 7. The converse piezoelectric coefficient has been calculated for the BCZT pellet samples sintered at different temperatures, and has been shown in Table VI. They were observed at an electric field 14.73 (KV/cm). The effect of variation in sintering temperature has been observed, and found that the piezoelectric constant has been decreasing as the sintering temperature is increased beyond 1300^{o}C, and further, it may arise due to its low density which may be seen from the SEM images [7]. Also, at higher temperatures, grain size has been increased and further, grain boundary decreases. Further, porosity has been appeared at higher sintering temperature. For the pellet samples of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics sintered at different temperatures, the strain percentage was found maximum at 1300^{o}C. Buatip et al. [7] found similar results and said that with an increase in sintering temperature, the piezoelectric properties get minimized. Buatip et al. reported the various properties of BCZT ceramics, Table VII.

Tab. VI Converse piezoelectric properties of BCZT ($Ba_{0.0935}Ca_{0.065}Zr_{0.1}Ti_{0.9}O_3$) ceramics, for x = 0.065, at an applied field 14.73 (kV/cm).

	Sintering temperature (°C)	**Converse piezoelectric constant (d_{33}*) (pm/V)**
BCZT	1300	153
	1400	121
	1450	73

Therefore, from the observed data, the grain size and piezoelectric properties are more or less equal. However, remnant polarization and coercive field were found higher compared with the present study. The density was greater than the present data (3.49 gm/cm^3, sintered at 1300^{o}C, 4 h).

Tab. VII Piezoelectric properties and grain size of BCZT ($Ba_{0.0925}Ca_{0.075}Zr_{0.1}Ti_{0.9}O_3$) ceramics [7].

	$T_{sint.}$ (^{o}C)	Piezoelectric constant (d_{33}) (pC/N)	Grain size (μm)	Density (gm/cm^3)	Remnant polarization (μC/cm^2)	Coercive field (kV/cm)
($Ba_{0.0925}Ca_{0.075}Zr_{0.1}Ti_{0.9}O_3$)	1250	14	0.86 ± 0.41	5.48 ± 0.08	1.70	5.13
	1300	167	2.19 ± 0.87	5.62 ± 0.02	5.84	4.22
	1350	16	0.68 ± 0.19	5.52 ± 0.08	1.43	4.32

4. Conclusion

For the prepared compositions, the value of the converse piezoelectric properties has been decreased as the sintering temperature has been increased. The XRD patterns show that BCZT ceramics have a perovskite structure for all sintering conditions. The grain size tends to increase and further, density decreases for the prepared pellet samples with an increase in sintering temperature. The sintering conditions greatly alter the piezoelectric properties and microstructure of the BCZT ceramics. This may be due to its density and grain size effect on the domain switch ability and alignment. BCZT ceramics sintered at 1300^{o}C for 4 h, exhibited an optimum density (3.49 g/cm^3, ~72 % of theoretical density), grain size (average 2.01 ± 0.59 μm) and piezoelectric properties (2.074 μC/cm^2 and d_{33}* = 153 pC/N).

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Сажетак: *У овом раду, припремљени су узорци титаната ($Ba_{1-x}Ca_xZr_{0.1}Ti_{0.9}O_3$, x = 0.065) реакцијом у чврстом стању двостепеним синтеровањем. Одређена су структурна и пиезоелектрична својства. Примењене су и методе SEM и EDAX анализе. Са различитим температурама синтеровања, густина и величина зрна су се мењале, и посматран је њихов утицај на пиезоелектрична својства. Конверзна пиезоелетрична константа (d_{33}^*) је опадала са порастом температуре синтеровања. Највиша вредност од 153 pm/V је измерена на 1300°C.*

Кључне речи: *фероелектрици; пиезоелектрична константа; перовскит; двостепено синтеровање.*