The Cold Sintering Process of ZnO and BaTiO$_3$ ceramics under the electric current influence

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Abstract. The paper presents the preliminary study results of the influence of the electric current (direct or alternating), the values of voltage and current, the presence or absence of activating additives, and external heating of the mold on the process of cold sintering of ZnO and BaTiO$_3$ powders. The microstructures of the obtained samples are analyzed. Approaches to further research are proposed. The article substantiates the prospects for using electric current in the process of cold sintering of ceramics.

1. Introduction

Traditionally, approaches to producing ceramic materials are based on high-temperature sintering (temperature above 1000°C, long exposure time from 1 hour to several tens of hours). Currently, new approaches to sintering based on the Cold Sintering Process (CSP) are being developed [1]. This process is carried out as follows (Figure 1, a): a mixture of powders (usually oxide ceramics) in combination with the liquid phase (usually water) is pressed uniaxially (50–500 MPa) in a mold at a temperature usually below $\approx$350 °C [2]. CSP development is at an early stage, with the most detailed data available only for ZnO-based ceramics. Significant progress has been made in obtaining samples of high-density ZnO ceramics in an aqueous medium at temperatures below 300°C and a pressure of less than 100 MPa [3-5]. Simultaneously, for a large number of ceramic materials, such as ferroelectric ceramics based on BaTiO$_3$, there are no known and scientifically-based approaches that allow stable production of high-density ceramics with proper properties as a result of CSP [6,7].

A possible way to reduce the sintering temperature of ferroelectric ceramic materials can be electric current. Dense ceramics made of perovskite-like ferroelectrics were successfully obtained using the FLASH-sintering process – ultrafast sintering in the presence of a high-intensity electromagnetic field [8]. The FLASH effect was observed when the pressings were heated to 600–900°C, and an AC or DC voltage of more than 100 V/cm was applied. As a result, the dense ceramic was sintered within a few tens of seconds. This process, despite its high efficiency, has several disadvantages – the need to heat the billet in the furnace to significant temperatures, and, as a result, the presence of significant energy...
costs, as well as pronounced structural inhomogeneities and restrictions on the shape and size of the sintered workpieces.

A recent paper [9], using the example of ZnO shows the fundamental possibility of combining the advantages of CSP and FLASH sintering. Using a liquid medium made it possible to reduce simultaneously the electric field strength, the external heating temperature, and the mechanical pressing pressure. The use of a direct current with a voltage of only 20 V at CSP ZnO made it possible to achieve a relative density of ceramic samples of over 96% in 1 minute without additional heating, at a pressing pressure of only 20 MPa. Based on these results, a hypothesis was proposed that the combination of CSP and electric current can be extended to a wide range of ceramic materials. To test this hypothesis, detailed parametric studies on various compositions of ceramic materials are required, as well as the study of the regularities of the influence of the characteristics of the electric field, the composition and amount of the liquid medium, the additional heating temperature, and the pressing pressure on the result of CSP with an electric current.

The article presents the first results of studying the effect of electric current on the microstructure of ZnO and BaTiO$_3$ CSP samples.

2. Materials and methods

The following raw materials were used: ZnO powder (purity 99%) with an average particle size of 0.2 microns, BaTiO$_3$ powder (purity 99%, LLC "Aril," Russia) with an average particle size of d50 of 21 microns. The size distribution of the ZnO powder crystals was determined by analyzing images [10] obtained with a scanning electron microscope JSM-6390 LA (JEOL Ltd, Japan). The particle sizes of BaTiO$_3$ powder were determined by laser diffraction using the LS 13320 MW particle size analyzer (Beckman Coulter, USA). Typical images of powder particles obtained with a scanning electron microscope are shown in Figure 2.

The experimental conditions are presented in Table 1. For the experiments, the initial powders were mixed with distilled water in 20, 30, and 50 wt.% For the two experiments (samples ZS1 and ZS2), the ZnO powder was mixed with the activating additive zinc acetate Zn(CH$_3$COO)$_2$·2H$_2$O-HC in the amount of 5% of the mass of ZnO, following the results of the work [3,4,11–16]. For this purpose, 20 g of the powder was mixed in an ultrasonic bath with 30 ml of a solution of 0.5 g of zinc acetate in distilled water. The suspension was dried at a temperature not exceeding 70 °C for 12 hours. Then the dried mass was crushed in an agate mortar and sifted through a sieve with holes of 300 microns.
Table 1. Experimental conditions.

| Sample | Composition | Water content, % | Current Type | Voltage, V | Current, A | Pressure, MPa | External Heating | Max temp, °C |
|--------|-------------|-----------------|--------------|-----------|------------|--------------|-----------------|-------------|
| ZS1    | ZnO:5%Zn(Ac) 20 | DC 3           | -            | 390       |            | Yes          | 92              |
| ZS2    | ZnO:5%Zn(Ac) 20 | AC 30          | 180          | 80        | No         |              | 31              |
| ZS3    | ZnO 30        | DC 3           | 30           | 80        | No         |              | 108             |
| ZS4    | ZnO 30        | DC 3           | 30           | 80        | No         |              | 170             |

The experiments were carried out on a specially assembled laboratory unit for CSP, mounted on a hydraulic press with a maximum force of up to 50 tons. The device of the laboratory installation is described in detail in previous publications [11, 12]. An ATTEN KPS3050DA (30 V, 50 A) pulsed DC power source was used to supply a direct electric current to the working area of the mold with a polymer matrix. The welding inverter FUBAG IRTIG 200 AC/DC Pulse (FUBAG GmbH, Germany) was used to supply alternating current. The electrical resistance, voltage, and current in the circuit were measured with a T6-600 electrical tester (Fluke, USA). The choice of both direct and alternating current for ZnO and only alternating current for BaTiO₃ is due to the difference in the electrical conductivity of powder mixtures with an aqueous medium. ZnO is a semiconductor, and when water and, in particular, the activating additive of zinc acetate are added, the mold resistance is on the order of 1 Ω, which allows the use of both direct and alternating current. BaTiO₃ ferroelectric powder mixed with water has a high resistance (from 0.5 to 8 mΩ depending on the pressing pressure), which allows the use of only alternating current and high pressing pressures (390 MPa).

Figure 2. The starting powder is ZnO (a) and BaTiO₃ (b).

3. Results

Four experiments with ZnO powder and three experiments with BaTiO₃ powder were performed. ZnO and BaTiO₃ powders have different electrical resistances. The mixture of ZnO powder with water has a low electrical resistance in the mold: at a pressing pressure of 390 MPa, about 0.1 Ω, at a pressure of 80 MPa, about 1 Ω. As a result, when using voltage-stabilized power supplies, the current quickly reaches more than 150 A values, which leads to overheating of the power supply, and the process has to be
interrupted. When receiving the ZN1 sample, the current reached the limit values within a second, and its value could not be recorded.

In contrast, a mold with a mixture of BaTiO₃ powder and water has a high electrical resistance. At a pressing pressure of 80 MPa, the resistance is about 8 mΩ. When the pressing pressure increases to 390 MPa, the resistance decreases to 0.5 mOhm.

The microstructure of the ZnO samples: ZS1, ZS2, ZS3, ZS4 is shown in Figures 3-6. The microstructures of the BaTiO₃ samples are shown in Figure 7. The results showed that in both types of powders, the structure was inhomogeneous, and the strength was insufficient to measure the density. The ZnO samples consisted of separate dense pieces (Figure 3. a) and compressed unsealed powder. The BaTiO₃ samples had no dense regions and were a compressed powder.

![Figure 3](image3.png)

**Figure 3.** Microstructure of the ZnO ZS1 sample: general view (a) and fracture surface (b).

![Figure 4](image4.png)

**Figure 4.** Microstructure of the ZnO sample ZS2 (a) and the ZnO sample with a similar composition and of the activating additive concentration obtained by CSP at a temperature of about 250 °C and a pressure of 80 MPa (b) (reprinted from [11] under the Creative Commons Attribution License, MDPI).
Figure 5. Microstructure of the ZnO ZS3 sample: samples central region (a) peripheral region (b).

Figure 6. Microstructure of the ZnO ZS4.

Figure 7. Microstructures of BaTiO₃ samples: BTS1 (a), BTS2 (b), BTS3 (c).

4. Discussion
The microstructures of the samples Z1, Z2, Z3 indicate the presence of a pronounced positive effect of the electric current on the CSP of the ZnO powder. However, when studying the activation by an electric current of cold sintering of ZnO and BaTiO₃ powders in the experiments carried out, it was impossible to obtain a homogeneous sample of dense ceramics and reproduce the results of the work [9]. Perhaps this is due to the difference between the sintering conditions and the work [9], in which both the voltage and the current were controlled simultaneously.

The microstructure of the ZS1 sample (Figure 3) demonstrates the formation of dense grain boundaries and a change in their morphology towards the formation of rounded grains (compared to the original powder (Figure 2. a). Time and temperature were not enough for further grain growth, since the
electric current was turned on after preheating the mold to 90 °C and its action lasted less than 1 second, since the power source instantly overheated due to a rapid voltage drop and an increase in current strength, and the process had to be stopped. The use of an activating additive of zinc acetate dramatically reduces the electrical resistance of the entire system. With such a high conductivity, it is impossible to use the high pressing pressure (390 MPa) that is usually used for CSP ZnO. The resistance in the circuit before switching on the current was 0.5 Ω, and after switching on, it instantly fell below 0.1 Ω.

To increase the electrical resistance of the ZS2 sample, the mechanical pressure was lowered to 80 MPa. The composition of the source material was identical to the ZS1 sample as the system resistance was 1 Ω. An AC power source was used. When the voltage was stabilized at 30 V, the average current in the circuit was 180 A. Voltages below and above 30 V did not provide stable current values. The mold temperature reached 31 °C due to Joule heating (no external heater was used) in 5 minutes, after which the resistance fell below 0.1 ohms, and the process had to be stopped. The microstructure of the dense regions of the ZS2 sample is shown in Figure 4, compared with the microstructure of the ZnO dense ceramic sample (Figure 4, b), obtained as a result of CSP from an identical powder with the addition of zinc acetate 5 wt. % at a temperature of 250 °C, and pressure of 80 MPa with an exposure time of 1 hour [11]. It can be seen that in the ZS2 sample, there was a comparable growth of grains with traces of forced cutting, but a dense packing of smaller grains was not formed.

When using the initial ZnO powder without activating additives (only distilled water), the system resistance at 80 MPa pressure was 1.5-2 Ω. When the ZS3 sample was obtained, 30 wt. % water was added to the initial powder. When using a DC power supply and 1.5 V voltage stabilization, the average current was 180 A (as in the ZS2 sample). No external heating was used. Due to the Joule heating, the mold was heated to 108 °C in about 20 minutes. Then the system resistance dropped sharply below 0.1 Ω, and the process was stopped. As a result, a sample was obtained, where a dense piece of material was formed in the central region and the peripheral region – separate compacted pieces and non-sintered powder. The microstructures of the regions are very different. The microstructure of the ZS3 sample sintered in the absence of the activating additive Zn (Ac) 2 (Table. 1) contains a local region of densely packed large crystals of anisotropic growth (Fig. 5a). Outside this region, the morphology and size of the pressed crystals remained similar to the original powder (Fig. 5b, fig. 2a). A constant electric current flowed in the central region of the sample, coaxially with the direction of pressing the punches-the electrodes. The formation of a dense structure of abnormally large grains is probably due to the intense Joule heat heating of small volumes of powder in the central region of the sample. To obtain a uniform microstructure over the entire sample cross-section, current stabilization is required to avoid overheating the sample’s local areas.

The ZS4 sample was obtained at a lower water content (20 wt. %), which was done to increase the electrical resistance of the system. It was possible to achieve a maximum electrical resistance of 2 Ω, in the entire series of experiments with ZnO. The DC power supply has been current-stabilized. The current was maintained at 30 A, with an average voltage of 3 V. Without external heating, the mold temperature reached 170 °C in 1 hour. The process proceeded stably, without power surges. However, the ZS4 sample was a compressed, un-baked powder without dense chunks. The microstructure of the ZS4 sample compressed with a low current load also in the absence of an activating additive (Table. 1), consists of submicron crystals (Fig. 6), as well as the peripheral region of the ZS3 sample (Fig. 5b). The value of the electric voltage was insufficient, and the temperature did not reach 250-300 °C, at which dense samples of ZnO ceramics were obtained in work [9].

Changing the heating conditions and the pressing temperature of the BaTiO₃ powder with different water content without the addition of an activator did not lead to an increase in the size of the crystals and their compaction (Fig. 7). In all three samples BTS1, BTS2, and BTS3, grain growth and densification were not observed. This may be due to the use of alternating current instead of direct current. The high electrical resistance of the powder pressing (about 0.5 MΩ at 390 MPa pressure), even with 50 wt % water and external heating up to 200 °C, did not achieve sufficient alternating current. It is necessary to select the activating additive to increase the electrical conductivity of the medium and
activate the mobility of the structure. The additive selection can be performed using thermocouple treatment of the material in an autoclave [11].

5. Conclusions
The influence of the type and modes of electric current, the presence or absence of activating additives, and external heating of the mold on the CSP process of ZnO and BaTiO$_3$ powders was investigated. The microstructures of the ZnO samples ZS1, ZS2, ZS3 indicate the presence of a pronounced positive effect of the electric current on the CSP of the ZnO powder. Zinc acetate additive 5 wt. % leads to the formation of microstructures similar to the microstructures of CSP samples. An AC voltage of 30 V without external heating of the mold gives the most pronounced effect (sample ZS2).

A mixture of ZnO powder with distilled water when using DC voltage-stabilized leads to a more stable process flow. The high electrical resistance of BaTiO$_3$ powder pressing under alternating current conditions requires selecting the activating additive to increase the electrical conductivity of the medium.

To successfully implement the CSP of ZnO and BaTiO$_3$ powders, it is necessary to create conditions for an electric current uniform flow through the powder layer along the axis of pressing force. Identifying the specifics of the action of DC or AC voltage requires more extensive research.

6. References
[1] Guo J, Guo H, Baker A L, Lanagan M T, Kupp E R, Messing G L and Randall C A 2016 Angew. Chemie - Int. Ed. 55 11457–61
[2] Maria J P, Kang X, Floyd R D, Dickey E C, Guo H, Guo J, Baker A, Funihashi S and Randall C A 2017 J. Mater. Res. 32 3205–18
[3] Jiang X, Zhu G, Xu H, Dong L, Song J, Zhang X, Zhao Y, Yan D and Yu 2019 Ceram. Int. 45 17382–86
[4] Gonzalez-Julian J, Neuhaus K, Bernemann M, Pereira da Silva J, Laptev A, Bram M and Guillon O 2018 Acta Mater. 144 116–28
[5] Funahashi S, Guo J, Guo H, Wang K, Baker A L, Shiratsuyu K and Randall C A 2017 J. Am. Ceram. Soc. 100 546–53
[6] Sada T, Tsuji K, Ndayishimiye A, Fan Z, Fujioka Y and Randall C A 2020 J. Appl. Phys. 128 084103
[7] Tsuji K, Ndayishimiye A, Lowum S, Floyd R, Wang K, Wetherington M, Maria J P and Randall C A 2020 J. Eur. Ceram. Soc. 40 1280–4
[8] Biesuz M, Sgulavo V M 2020 Scr. Mater. 187 49–56
[9] Kermani M, Biesuz M, Dong J, Deng H, Bortolotti M, Chiappini A, Reece M J, Sgulavo V M, Hu C, Grasso S 2020 J. Eur. Ceram. Soc. 40 6266–71
[10] Ivakin Y D, Danchevskaya M N 2018 Russ. J. Phys. Chem. B. 12 1205-1211
[11] Ivakin Y, Smirnov A, Kholodkova A, Vasin A, Kormilicin M, Kornyushin M and Stolyarov V 2021 Crystals 11 71
[12] Ivakin Y D, Smirnov A V, Tarasovskii V P, Rybal'chenko V V, Vasin A A, Kholodkova A A and Kormilitsin M N 2019 Glas. Ceram. 76 210–5
[13] Jing Y, Luo N, Wu S, Han K, Wang X, Miao L and Wei Y 2018 Ceram. Int. 44 20570–20574
[14] Dargatz B, Gonzalez-Julian J, Guillon O 2015 J. Cryst. Growth. 419 69–78
[15] Dargatz B, Gonzalez-Julian J, Bram M, Shinoda Y, Wakai F and Guillon O 2016 J. Eur. Ceram. Soc. 36 1221–32
[16] Ivakin Y D, Danchevskaya M N, Muravieva G P 2019 Russ. J. Phys. Chem. B. 13 1189–1200

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