

UTILIZATION DC METHOD DURING ZIRCONIA CERAMICS PROCESSING

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Dispersion of temperature dependencies of direct electrical conductivity values of samples prepared from ultrafine powders of zirconia ceramics (ZrO_2 : 11 mol % CaO) was found as a function of powders time storage. The significance of the powders homogeneity reached by the additional grinding before the samples preparation for obtaining of reproducible values of direct electrical conductivity is presented. There is shown that temperature dependencies of absolute values of direct electrical conductivity are depended on the phase composition of the ceramic sample. There was found on the base of measurements the heating temperature 1400 °C as a sufficient for searched powders.

INTRODUCTION

The utilization of new materials in industry requires a knowledge of the functional dependence of material properties on the preparation and treatment conditions (in the case of ceramic materials, especially on the quality and treatment of the initial powders, the pressing pressure, the firing temperature and temperature range, the firing atmosphere, etc.). Solid phase physics provides various experimental methods to assist in this task.

Among the traditional approaches, the measurement of bulk density, X-ray diffraction, optical metallography and scanning electron microscopy are the most frequently used [1, 2]. On the other hand, the measurements of electrical properties assist to evaluate the quality and to optimize the processing of ceramics have not been utilized until now.

Electrical methods are employed in the experimental research of ceramic materials while the direct following of the electrical conductivity changes as the resulting functional properties of the ceramic material is the research works output [e.g.3,4].

Numerous preferences of electrical methods (the simplicity, the accuracy and the reproducibility belong among them) give the assumptions to utilize them profitably also in the technological research or in the results evaluation of the individual technological steps. It is even possible to employ them in such a case when the changes of electrical properties are not decisive in ceramic materials applications. It seems the above mentioned preferences of electrical methods are not familiar generally. It confirms only a few papers employing them which we found formerly.

Electrical methods together with conventional ones (but separately also) can give the more complete picture about ceramic materials and processes occurring during

the treatment process inside them. It is possible by means of the electrical methods also to appreciate the such specific properties as e.g. the phase composition of ceramics, the reached quality of powders for the chosen technology and the purpose of processing or the reached level of calcination of ceramic powders.

The presented advantage of the electrical methods utilization in the evaluation of the technological process quality was confirmed in our experiments by measuring direct electrical conductivity of zirconia powders specified below.

EXPERIMENTAL MATERIAL

Powders for the preparation of zirconia ceramics were produced by the method of coprecipitation from secondary sources of raw materials where oxides of rare-earth elements were occurred, too. The calculated amounts of $ZrOCl_2$ and $CaCl_2$ (or YCl_3) were dissolved in water. The coagulating of $ZrOCl_2$ by aqueous ammonia solution from the mentioned mixtures is the principle of the coprecipitation method. The obtained voluminous coagulation was washed until the absence of Cl^- ions was proven, further dried in air and calcined at a temperature of 650 °C. The resultant powders had specific surface in the range 85 - 95 $m^2 g^{-1}$ and tap densities in the range 0.9 - 1.1 $g cm^{-3}$.

Two types of ceramics were prepared from the powders:

- A. stabilized zirconia ceramics (11 Ca - SZ): ZrO_2 with 11 mol % of CaO,
- B. stabilized zirconia ceramics (3 Y - SZ): ZrO_2 with 3 mol % of Y_2O_3 .

Discs of diameter 8 mm and thickness 1 mm were cold pressed at pressures of 50, 91 and 125 MPa from powders. The input powders used in experiments were

ground in the ball-shaped mill (Netsch) which had grinding vessel of smelted ZrO_2 . Powders were treated by grinding by means of wet balls of ZrO_2 diameters of 10, 20 and 30 mm. The samples were fired in the air at a temperature of 1400 °C, with 20 minutes at maximum temperature in a controlled heating rate furnace. The samples were furnace - cooled at zero furnace power to ambient temperature.

METHODS OF MEASUREMENTS

All measurements were made on fired discs. Direct conductivity dc was measured by the standard two-electrodes method in a vacuum of 1 Pa by means of a vibration electrometer (Va-J - 51, RFT) in the temperature range 20 to 800 °C. Contacts prepared by burning Pt paste onto samples at 1000 °C are usually used for the measurements of electrical and dielectric properties of ceramics. However, the preparation of such contacts is slow and the creation of suitable contacts is not always guaranteed.

Therefore, contacts prepared by application of colloidal graphite (Dag 580) to samples before every measurement were used.

EXPERIMENTAL

Conventional Methods

Optimization of the preparation of zirconia ceramic is closely dependent upon the determination of suitable methods of preparation, grinding, pressing and firing of the starting powders. The chemical composition, purity and distribution of particles are the basic input parameters of ceramic powders and are decisive to their technological quality. Chemical analysis proved the high purity of our powders containing, besides zirconium oxide and the stabilizing oxide, only trace amount (≤ 0.001 %) of Si, Fe, Mg, Al, Ti and (≤ 0.01 %) of Mn, Pb, Ni, Cu, Co were found.

X - ray diffraction (XRD) on samples made from powders type (A) showed the coexistence of both cubic (70 %) and monoclinic phases (30%) (Figure 1a). Fully stabilized tetragonal phase plus some excess Y_2O_3 was identified in samples from powder (B) (Figure 1b). XRD analysis also showed that the phase composition of 11 Ca - SZ depended slightly on the pressing pressure and the firing time. This dependence was not found in the case of 3 Y - SZ [5].

Our powder samples after grinding were characterized by a high fractions of ultrafine particles ($<1 \mu m$) with a high surface area and so had high reactivity during sintering (Figures 2a, b). A general feature of ultrafine powders is the tendency for individual crystallites to be bound into aggregates which cluster into

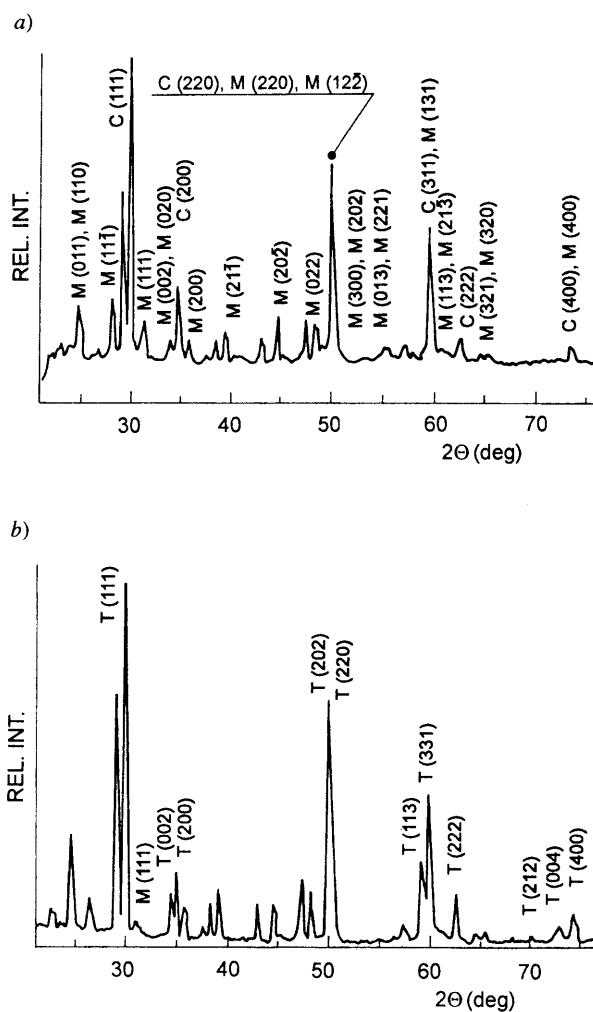


Figure 1. a) Diffraction pattern of sample of sample of 11 Ca-SZ, b) Diffraction pattern of sample of 3 Y - SZ.

large porous agglomerates [6]. Both aggregates and agglomerates have an important influence on the sintering process, and hence on the final bulk density of the ceramics [7]. For example, agglomerates with an open configuration can result in large residual pores while tightly bound agglomerates can result in inter - aggregate sintering, again creating closed pores.

This assumption is proved also by measurements of the dependence of the porosity of sintered ceramics on the grinding time of powder (Figures 3a, b). The porosity of samples after the firing increased with the longer time of grinding while the pressing pressure was constant. This result agrees with the assumption on the increasing of the number of ultrafine particles by the grinding. It also agrees with the increasing of the porosity unfired samples with longer time of the grinding at the same pressure (Figure 3a).

The grain size of the resulting ceramics is dependent on the temperature of firing. The rate of grain growth of granules is most significant in the temperature intervals

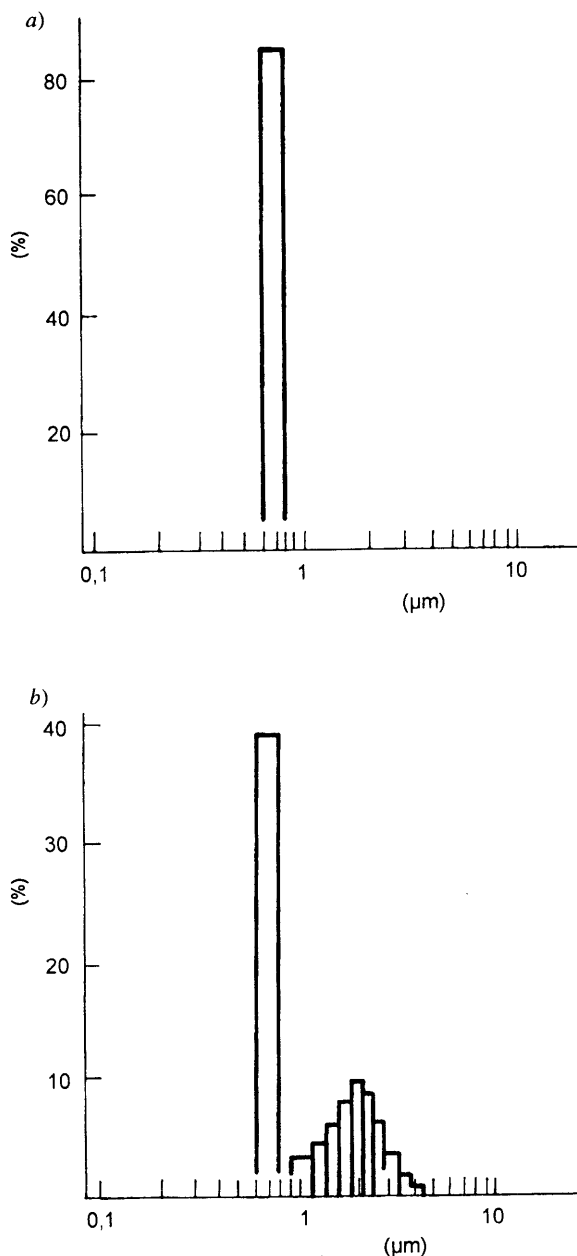


Figure 2. a) Distribution of particle sizes of 11 Ca - SZ, b) Distribution of particle sizes of 3 Y - SZ.

1000 - 1200 °C and 1500 - 1600 °C [6]. Accordingly, the temperature interval 1000 - 1200 °C was overstepped the maximum rate allowed by the laboratory furnace (approximately 1.6 °C min⁻¹) during the firing of our experimental samples. After the first exploratory measurements of the electric conductivity of fired samples, during which the maximum temperature of firing was varied in the range 1000 - 1600 °C, the maximum temperature was fixed at 1400 °C. This temperature was found to be optimum for producing samples with fine grain size and high density.

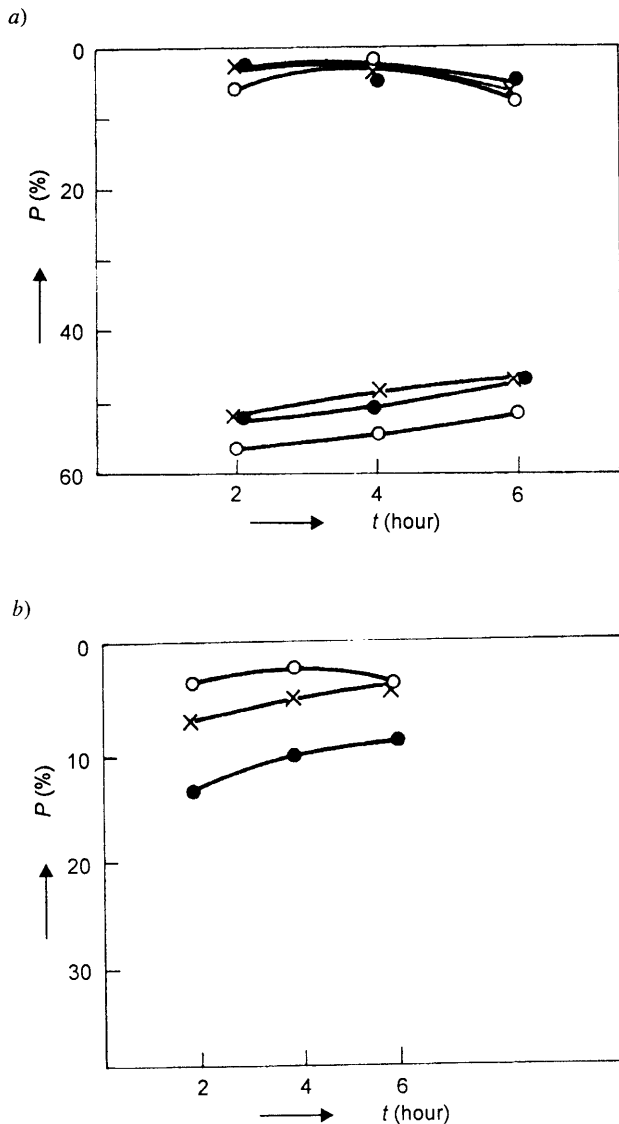


Figure 3. Porosity plot of the sintered ceramics in the dependence on the grinding time (firing at 1400 °C / holding temperature 6 hours), diameter of grinding balls 20 mm. (x) - 50 MPa; (o) - 91 MPa; (●) - 125 MPa. a) Samples of 3 Y - SZ, b) Samples of 11 Ca-Sz.

Direct Electric Conductivity

The influence of the way and period of grinding the powder, pressing pressure and time of firing on the quality of the ceramics was observed by the measurement of direct electrical conductivity d_c of fired ceramics up to a temperature of 800 °C in the air atmosphere.

Cold pressing pressure in the range 50 - 125 MPa had no significant effect on d_c of 11 Ca - SZ and Y - SZ samples (Figures 4, 5). This result is in agreement with the results of a previous paper [6], according to which

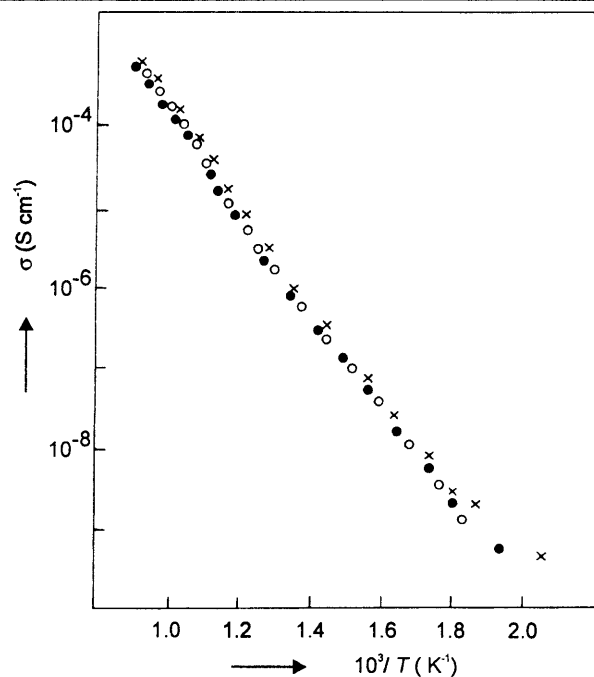


Figure 4. Temperature dependence of the dc of 11 Ca - SZ ceramics on the pressure (6 hours grinding, firing at 1 400 °C / holding temperature 4 hours). (x) - 50 MPa; (●) - 91 MPa; (○) - 125 MPa.

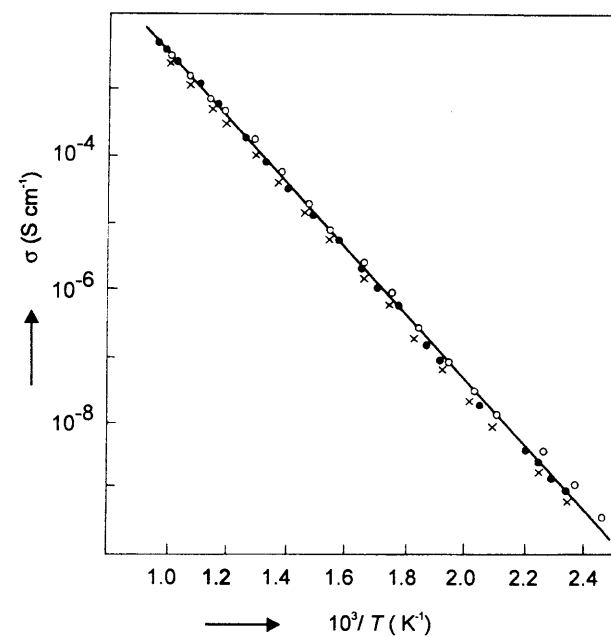
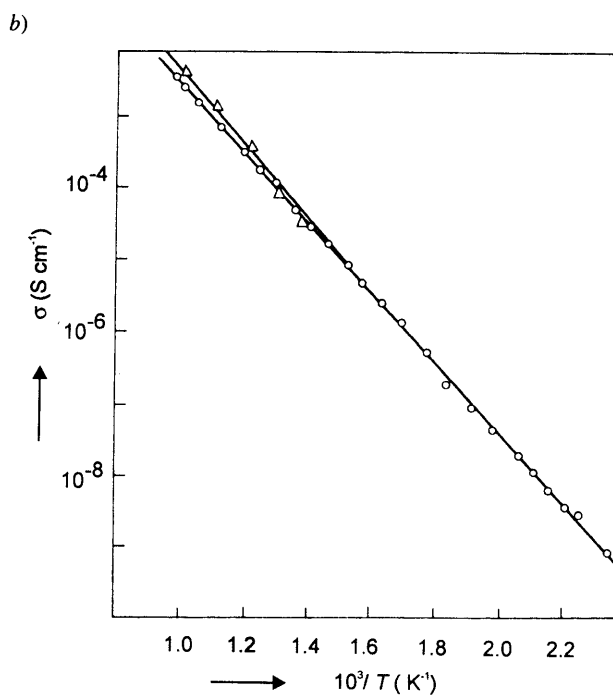
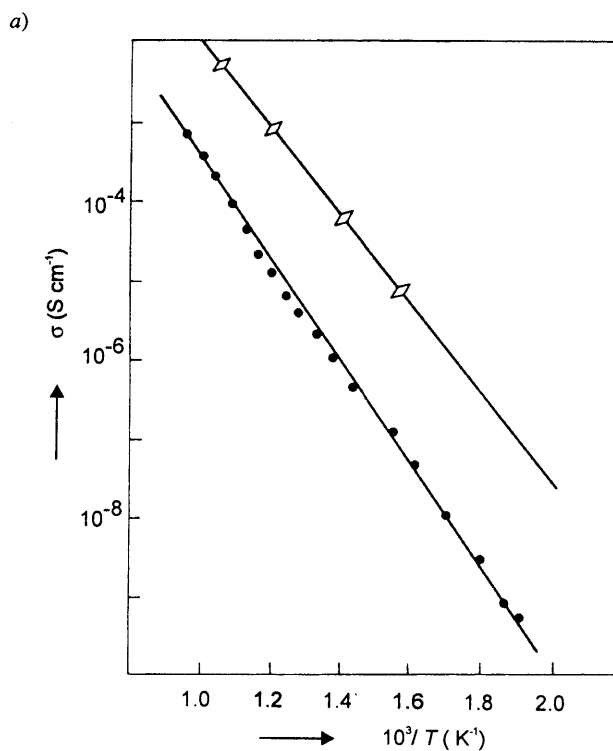


Figure 5. Temperature dependence of the dc of 3 Y - SZ ceramics on the pressure (6 hours grinding, firing at 1400 °C / holding temperature 6 hours). (○) - 50 MPa; (●) - 91 MPa; (x) - 125 MPa.

Figure 6. a) The comparison of the temperature dependence of the dc 11 Ca - SZ (●) with that one of FSZ with CaO (◇) given in [2]. b) The comparison of the temperature dependence of the dc of 3 Y - SZ (○) with that one of PSZ with Y_2O_3 (Δ) given in [5].

for efficient pressing the deformation of large aggregates is necessary. But this effect appears at pressures above the value of 40 MPa, while our pressing was above this level.

After thermal treatment zirconium oxide can exist in various crystalline modifications: monoclinic, tetragonal and cubic [6]. The electrical conductivity of the cubic phase is significantly higher than that of the monoclinic phase. Therefore dc of a zirconia ceramic sample is sensitive to the presence of monoclinic phase - the more monoclinic phase is present, the lower must be dc of the ceramics.

The measurements of dc suggested the presence of less conductive monoclinic phase in the experimental Ca - SZ samples fired at 1400 °C, their dc being considerably lower than the value of single phase cubic samples from a previous paper [8] (Figure 6a). This result from measurements of dc was consistent with the XRD results showing the presence of around 30 % monoclinic along with the cubic phase [5].

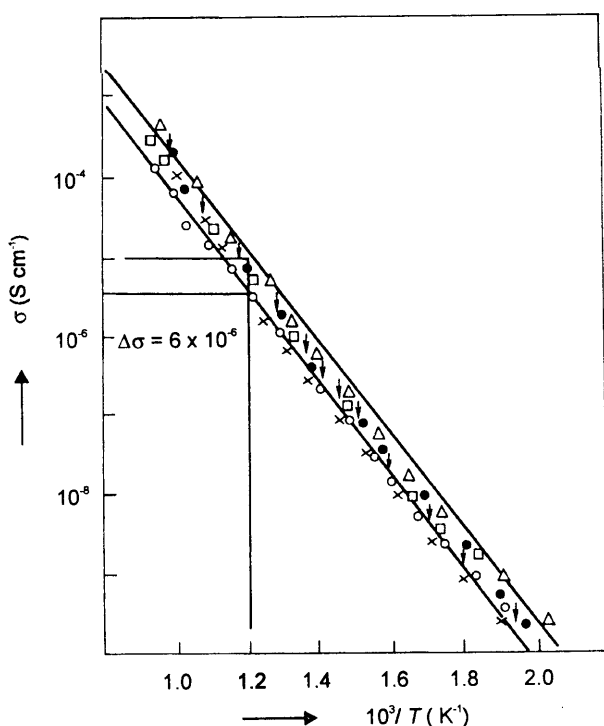


Figure 7. Temperature dependence of the dc of 11 Ca - SZ ceramics. (6 hours grinding, firing at 1400 °C / holding temperature 4 hours). Powders had a different long time stored. (○) - without storage, (×), (▼), (●), (□), (Δ) - stored 2, 4, 6, 8, 10 months, respectively.

This result proved clearly the possibility of using dc conductivity measurements for the differentiation of ceramic materials with different phase contents, including in the case of zirconia the extent of departure from a single phase state.

The results of our samples of the ceramic 3Y - SZ proved again this point. Measured values of dc were in agreement with the values published in reference [10], which were for samples of single phase tetragonal zirconia (Figure 6b), suggesting that was also single phase tetragonal. This conclusion was consistent with the XRD results [5].

We also evaluated the effect on dc of the storage time of the powder from which the samples had been prepared. We found a significant scatter of the conductivity values ($\Delta\sigma = 6 \times 10^{-6} \text{ S.cm}^{-1}$ at temperature 560 °C - Figure 7) for the samples prepared from the same powder but stored for different times (from 0 to 10 months) in the laboratorial atmosphere. The stored powder was not additionally homogenized or re-ground before the samples were prepared.

We speculate that this scattering of dc values versus temperature is related in some way to an increase of the powder aggregation during the relatively long storage times. We could observe such an effect with the naked eye while pouring the stored powder. On the basis of these findings the powders were homogenized by additional grinding before use in our experiments. We believe that attention to this likely macroscopic effect of powder storage would also be important in production technology.

CONCLUSION

The results described above show that it is possible to employ with advantages dc temperature dependencies measurements of ceramic powders ($\text{ZrO}_2 + 11 \text{ mol\% CaO}$ and $\text{ZrO}_2 + 3 \text{ mol\% Y}_2\text{O}_3$) for:

- the determination of optimal parameters of the technological processing powders (duration and the way of grinding, pressing conditions and the firing regime),
- the appreciation of the ending level of the prescribed technological processes in the powders preparation (e.g. calcination, stabilization, etc.),
- the appreciation the powders structural changes after treatment (e.g. the phase composition, etc.).

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VYUŽITIE DC METÓDY
PRI SPRACOVANÍ ZIRKONOVÝCH KERAMÍK

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Rozptyl hodnôt v teplotných závislostiach jednosmernej elektrickej vodivosti vzoriek pripravených z ultrajemných práškov pre zirkónové keramiky (ZrO_2 :11 mol % CaO) bol nájdený v závislosti od doby skladovania práškov. Prezentovaný je význam homogenity práškov, dosiahnutej dodatočným mletím pred prípravou vzoriek, na dosiahnutie reprodukovateľných hodnôt jednosmernej elektrickej vodivosti. Je ukázané, že teplotné závislosti absolútnych hodnôt jednosmernej elektrickej vodivosti závisia od fázového zloženia keramickej vzorky. Na základe meraní sa zistilo, že 1400 °C je dostatočná vypalovacia teplota pre skúmané prášky.