

Synthesis-characteristics and sintering behavior of PZT-powder

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In the $\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$ system, two powders were produced by chemical co-precipitation and mechanical mixing of $\text{Pb}(\text{NO}_3)_2$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$ and $\text{Ti}(\text{OC}_3\text{H}_7)_4$. The powders were characterized with regard to their specific surface area, particle size distribution, phases present and the pore size distribution of the pressed powder tablets. The co-precipitated powder was sintered already at 750 °C to 99% of its theoretical density. The mechanically-mixed powders reached only 62.5% of the theoretical density at 900 °C sintering temperature, although they had a higher specific surface area and finer particle size than the co-precipitated powder. The better sintering behavior of the co-precipitated powder can be explained by a narrow pore size distribution and small pore size in its pressed powder tablets. This is further proof that a determination of the pore size distribution of pressed powder tablets gives reliable indications about the sintering behavior.

Keywords: Sintering, PZT-Powder, Piezoelectric.

Introduction

Piezoelectric-ceramics are sintered materials with piezo-electrical properties due to their composition and crystal structure. These materials have the property of generating an electric force when placed under pressure, and conversely, of changing dimensions when an electric field is applied. Piezoelectric-ceramics were also called as "Ferroelektrika" in the German literature.

Piezo-ceramics show, especially in the vicinity of the curie point, a remarkable temperature dependency of their dielectrical and electromagnetical properties. At the curie point, a crystallographic phase change occurs. Below the curie point, the piezoelectrical behavior of the ceramic is expected, above that it disappears due to changes in the crystal-structure.

Piezo-ceramics are statistically isotropic due to their polycrystalline structure. At first, they show any piezo-effect. If such a ceramic is put under an electrical field using electrodes, an orientation of dipole-areas, so called domains, occurs due to polarization in the direction of the polar axis. So, the conditions for the piezoelectricity are fulfilled.

It is important that polarized ceramics should keep their orientation even when the electrical field is cut off, in other words the remnant polarization is held. Piezo-ceramics are used for transforming mechanical energy into electrical (e.g. spark generation) or conversely (e.g. in production of ultrasonic sound and vibrations) [1-4].

Piezoelectric-ceramics are derived from oxide systems

such as BaO-TiO_2 , PbO-BaO-TiO_2 , $\text{PbO-ZrO}_2\text{-TiO}_2$ (PZT ceramic) and $\text{PbO-La}_2\text{O}_3\text{-ZrO}_2\text{-TiO}_2$ (PLZT ceramic). The crystal-chemical properties of piezoelectric ceramics are based on the property of perovskite crystals which show polarization under an electric force. However, it should be noted that not only the mineral perovskite but other oxide compounds with similar structures find application as piezoelectric ceramics due to their enhanced properties. Polycrystalline piezoelectric ceramics compared to single crystals such as quartz have the advantage that they can be manufactured in any shape and size. The piezoelectrical properties of piezo-ceramics depend on their composition and their porosity.

In the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ system the high sintering temperature effects the stoichiometry of the material due to the high partial pressure of Pb vapour. One tries to sinter this type of ceramic to the highest possible density at sintering temperatures below 1000 °C.

The aim of the present study was to produce and characterize a sinter-active powder in the system $\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$. The sintering behavior of this powder was compared with another powder which was made by mechanical mixing of its components.

Experimental

In the experiments, $\text{Pb}(\text{NO}_3)_2$ (Merck), $\text{Zr}(\text{OC}_3\text{H}_7)_4$ (Alfa Products) and $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (Alfa Products) were used as basic materials.

The sinter-active powder was prepared according to the following procedure:

For production of about 75 g $\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$, 82.80 g $\text{Pb}(\text{NO}_3)_2$ was dissolved in 500 ml de-ionized water and diluted with 4.5 l water. $\text{Pb}(\text{OH})_2$ was precipitated out of this solution by adding 100 ml 25%-

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ammonia solution. The precipitate was separated from the water and nitrate ions with the help of a centrifuge.

42.98 g $\text{Zr}(\text{OC}_3\text{H}_7)_4$ and 33.76 g $\text{Ti}(\text{OC}_3\text{H}_7)_4$ were first stirred with a magnetic mixer and homogeneously dissolved in 500 ml isopropyl alcohol. Then, this solution was mixed intensively with the $\text{Pb}(\text{OH})_2$ -precipitate using an Ultra Turrax mixer. During mixing, Ti and Zr- hydroxides as well as oxyhydrates were precipitated.

The homogenous suspension was fed directly into liquid nitrogen to be frozen. The frozen precipitate was dried. The dried powder was very fine and homogenous and showed a very low bulk density. Afterwards, the hydroxides were calcined for about 3 hours at a temperature of 600 °C.

The powder was then pressed in to cylindrical tablets (10 mm dia, 5 mm height) at 80 MPa uniaxially and then at 300 MPa isostatically using an hydraulic pres. The tablets were sintered in covered Al_2O_3 -crucibles at sinter temperatures 700-900 °C. The temperature gradient was 200 K h^{-1} and the sintering time at the final temperature was 3 hours.

From the oxides of Pb, Zr and Ti a mechanically mixed powder was produced (powder B) and this was investigated in the same manner as the sinter-active powder (powder A) with regard to its sintering behavior.

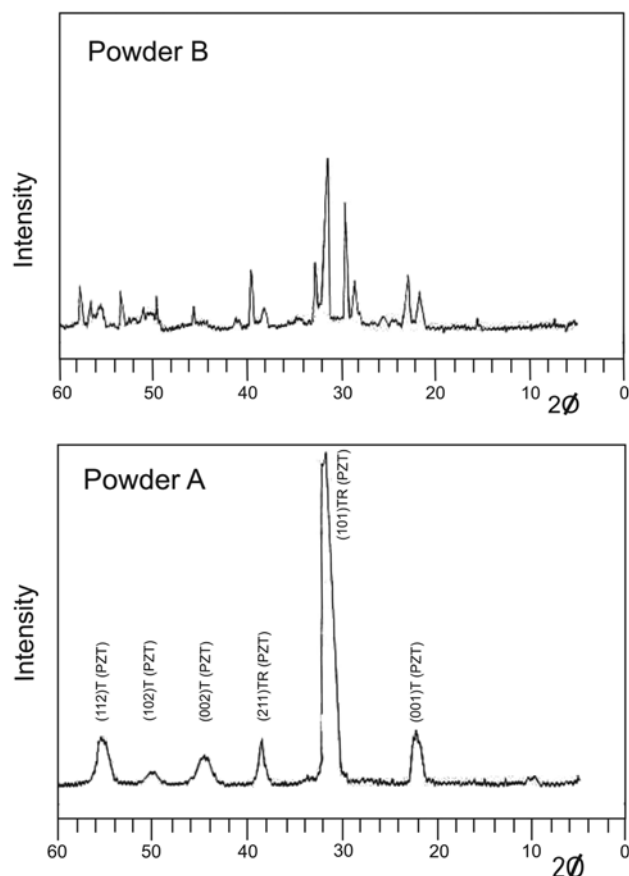


Fig. 1. X-Ray diffraction patterns of powders A and B.

Results and Discussion

XRD analyses were performed with the calcination products of powders A and B in order to determine the components. Powder B did not show any peaks indicating $\text{Pb}(\text{Zr}_{0.525}\text{Ti}_{0.475})\text{O}_3$ at a calcination temperature of 600 °C. Individual oxide- and mixed oxide phases could be identified (Fig. 1). Whereas, the powder A calcined at 600 °C showed clear peaks indicating the formation of PZT which confirmed the results of Lucuta et al. [2]. This can be attributed to the homogeneity and the sinter-active properties of the co-precipitated powders in comparison to the mixture of individual oxides.

The specific surface area of powder A was measured as $42 \text{ m}^2/\text{g}$. Powder B showed a specific surface area of $107 \text{ m}^2/\text{g}$. Since powder A has a lower specific surface area than powder B it would be expected that powder B would have a better sintering behavior. However, this is not the case as seen from the sintering results (Fig. 2).

The particle size distributions of both powders are shown in Fig. 3. Figure 3 illustrates clearly that the particle size distribution of powder A is monomodal whereas that of powder B is bimodal. The average particle sizes of powder A and powder B were found to be 7 and 2 micrometres respectively. Furthermore, it was shown that both powders consist of micro-agglomerates. The size distribution of the pores in the pressed powders are given in Fig. 4. As seen from Fig. 4 powder A shows a narrower pore size distribution compared to powder B. The highest pore concentration is found to be at 18 nm for powder A. Powder B showed two maxima namely at 9 and 35 nm. There is a clear relation between the pore size distribution and

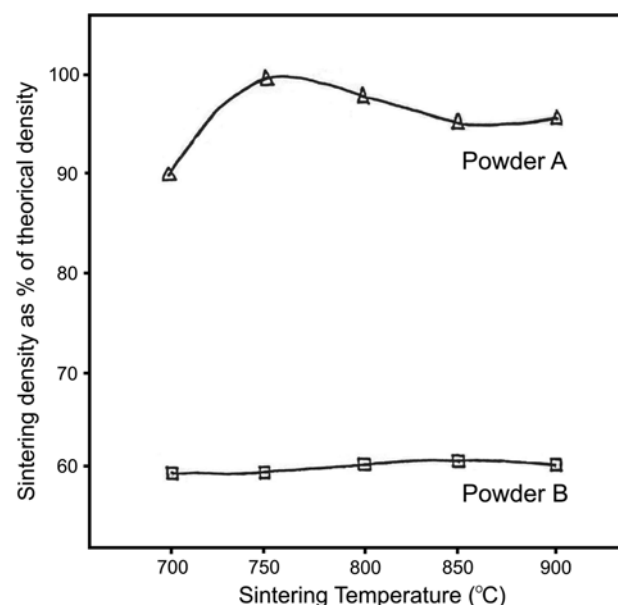


Fig. 2. Sintering results of the powders.

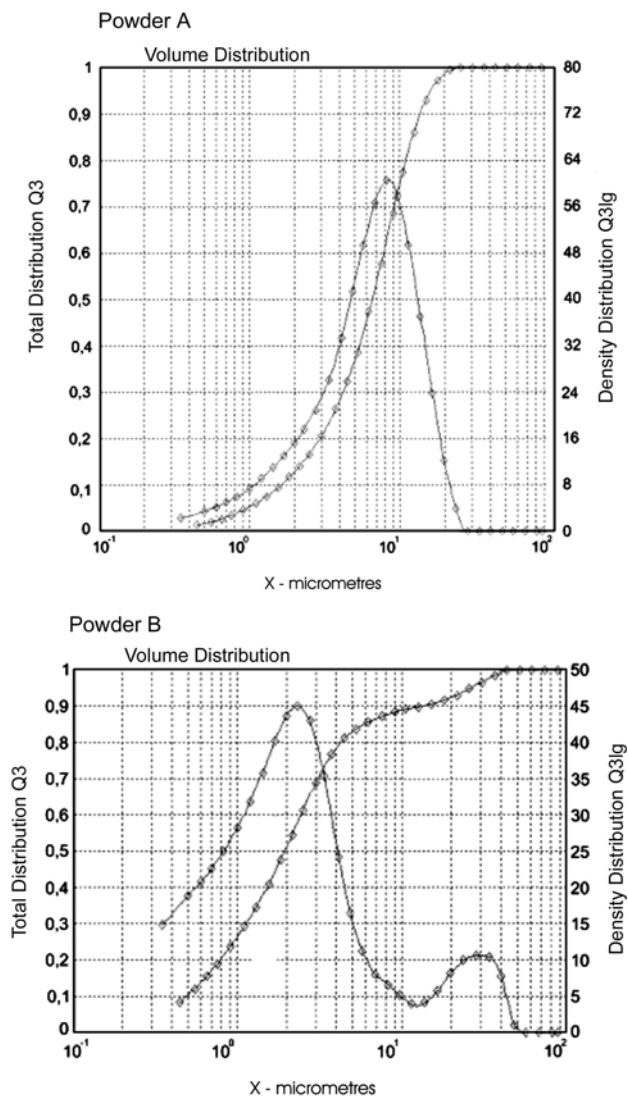


Fig. 3. Particle size distributions of Powders A and B.

sintering results.

The results of sintering tests are illustrated in Fig. 2. As seen from Fig. 2 powder A shows a better sintering behavior compared to powder B. Powder A was sintered at 750 °C to 99% of its theoretical density. This is also the maximum sintering density, which decreases with increasing sintering temperature thereafter. This can be attributed to the evaporation of Pb and hence to the increased porosity of the sinter product. Powder B shows only 62.5% theoretical density at 900 °C sintering temperature. Figures 5-7 show micrographs of the sinter products obtained from powder B which were taken with a light optical microscope. It can be seen clearly that the porosity of the sinter product increases with increasing sintering temperature. The phases are separated by pores and cavities. The large pores are dark colored. Micrographs of the sinter products made from powder A (Figs. 8-11) indicate that sample A shows a homogeneous structure with homogeneously distributed small pores. However, towards

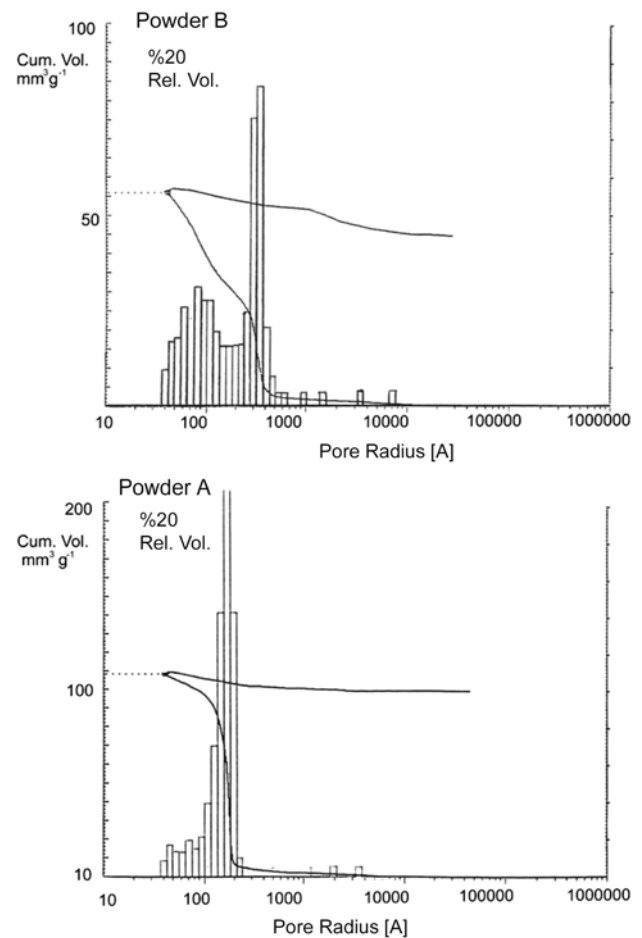


Fig. 4. Pore size distributions of the pressed powders A and B.

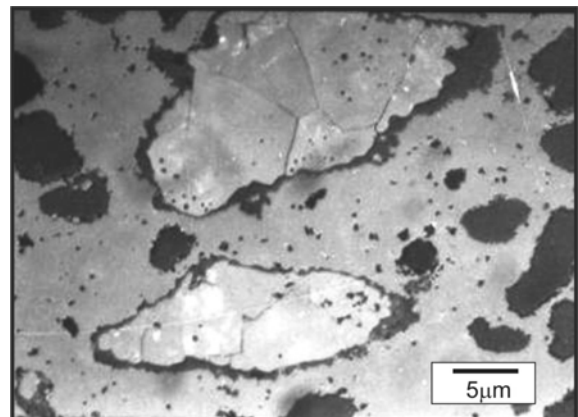


Fig. 5. Structure of powder B, Sintering temp.: 800 °C.

higher sintering temperatures an increase of pore size is noted.

Conclusions and Recommendations

It can be concluded that the sintering behavior of the powders investigated can not be interpreted by the determination of their specific surface areas and particle size distributions. It is often thought that a high

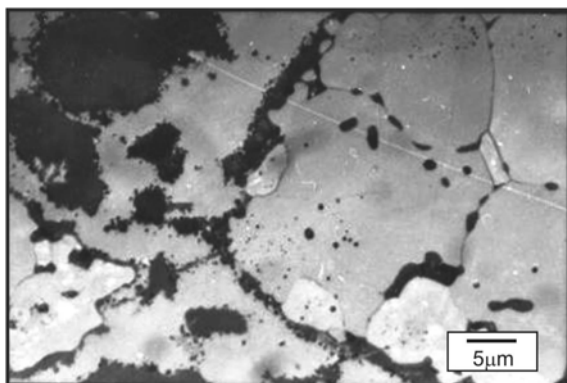


Fig. 6. Structure of powder B, Sintering temp.: 850 °C.

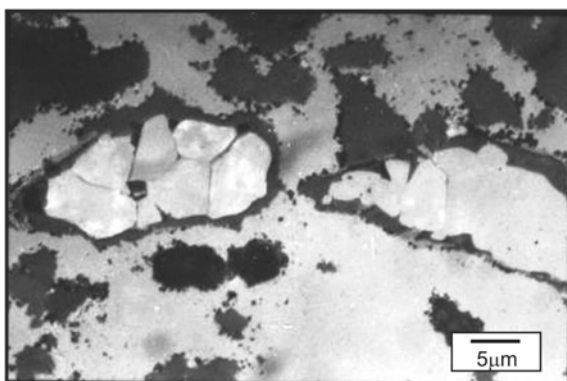


Fig. 7. Structure of powder B, Sintering temp.: 900 °C.

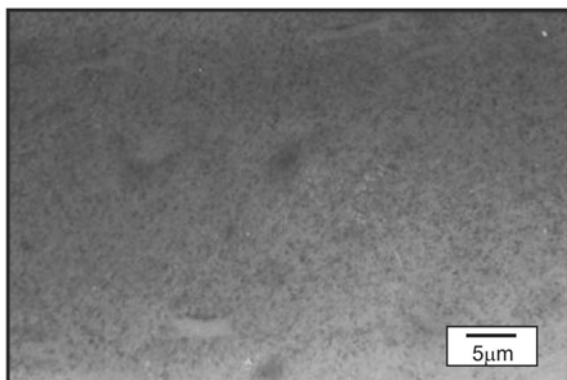


Fig. 8. Structure of powder A, Sintering temp.: 700 °C.

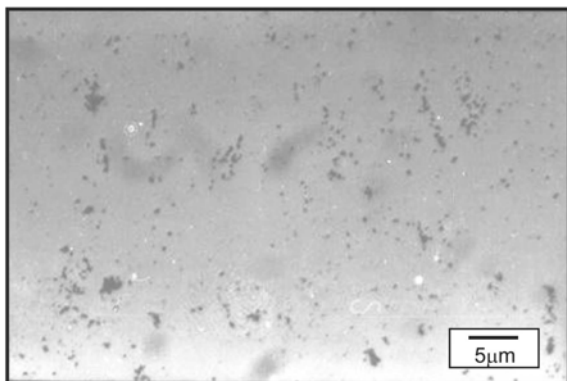


Fig. 9. Structure of powder A, Sintering temp.: 750 °C.

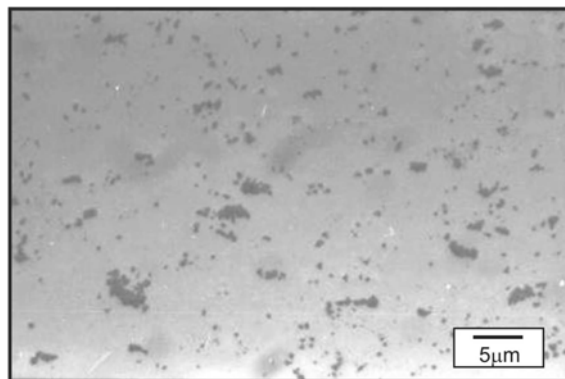


Fig. 10. Structure of powder A, Sintering temp.: 800 °C.

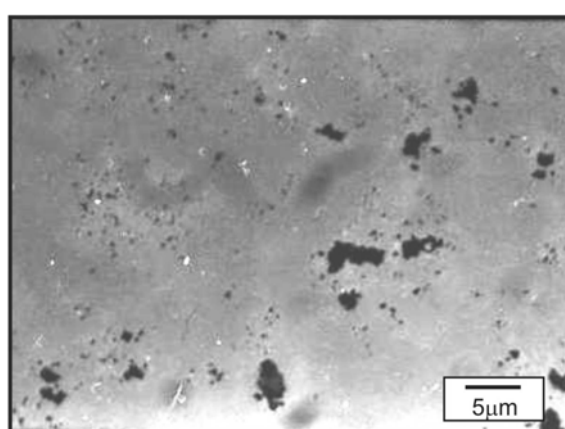


Fig. 11. Structure of powder A, Sintering temp.: 900 °C.

specific surface area and small particle size lead to better sintering results. This was, however, not the case for the powders investigated in this study. However, if the pore size distribution of the powders are compared, it is found that, a narrow pore size distribution leads to a denser sinter product at lower sintering temperatures [5-8].

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