



Sintering and grain growth kinetics in undoped and silica doped zinc oxide ceramics

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Abstract

Dilatometric sintering and grain growth kinetics of undoped and silica doped (2, 4, 6 wt% respectively) zinc oxide samples were systematically investigated. Silica (SiO₂) as a dopant retards the densification and changes the sintering behavior of zinc oxide (ZnO) ceramics by increasing the apparent activation energy of sintering and changing densification mechanism at the initial stage. At the same time, SiO₂ addition restricts the grain growth of ZnO compacts by influencing the mechanism and activation energy of the process. It is observed that the increase in temperature of sintering was more crucial for grain growth than the isothermal holding time. These effects were pronounced up to 4 wt% SiO₂ doping, and beyond this level, there was a tendency of saturation (marginal change) regarding the shrinkage behavior as well as grain growth of the compacts. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Zinc oxide (ZnO) is an n-type semi-conducting material, which have widespread applications in optoelectronic instruments such as photo detectors, light-emitting diodes, thin film transistors, solar cells, piezo-electric devices [1]. ZnO varistors are used as surge protection devices in different electrical and electronic circuits. They are fabricated by sintering ZnO powders with additives, such as Bi₂O₃, Pr₆O₁₁, CoO, Cr₂O₃ etc. [2,3]. The non-linear voltage–current characteristics of these varistors arise because of electronic phenomena occurring near the grain boundaries. Thus, the microstructures of the dense ceramics play a major role in the final properties depending upon its applications. The microstructural development in ceramics can be efficiently controlled by tuning the dopants and sintering conditions [4].

The material transport that occurs during sintering is essentially a diffusion controlled process and is well explained in literature [5–7]. However, the practical approach to understand

these processes in ceramics have been still a challenge. It is necessary to determine various rates controlling parameters of sintering in order to understand the sintering mechanism of a particular system. The densification process for this ceramic system can then be efficiently controlled with the thorough knowledge of the sintering mechanism. In most of the cases, a number of diffusion mechanisms exist simultaneously at an elevated temperature during sintering. The data analyses and interpretation may be erroneous due to the co-existence of more than one process at a time. Thus, data analysis is restricted within the initial stage of sintering, i.e. within 5% linear shrinkage with the assumption that only one predominant sintering mechanism is operative at this stage. The kinetics of initial-stage of sintering has been expressed with various rate equations; data, mostly available from isothermal sintering experiments (ISE) [8–10]. Reproducibility in experimental data is poor in case of ISE for the ceramics because of their bad thermal conductivity, which leads to shrinkage in the sample before reaching a steady-state temperature during firing. At the same time, several experimentations are required to find out the sintering kinetics viz. activation energy (Q) and mechanism of sintering (n) from ISE. The other approach is to

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study the sintering kinetics in the ceramic system under constant rate of heating (CRH) which does not have the drawbacks of ISE methods. Woolfrey and Bannister [11] have proposed one such non-isothermal CRH method which permits the accurate determination of all the sintering parameters. The general difficulty with CRH method is to determine both the sintering parameters, n and Q , simultaneously from a single experiment. Hence, to determine the values of n and Q both, either several CRH experiments should be carried out at different rate of heating or a single CRH experiment should be combined with another technique. This would enable to determine the value of one of these parameters which could be further used to get the value of other one. In this respect, Modified Dorn method [12] is a very effective technique to determine the activation energy of sintering from a single experiment. In this, the instantaneous effect of change in temperature in a small step from one isothermal region to other on the shrinkage rate is harnessed to determine the Q value of sintering directly.

The discussion in the above paragraph shows that the study of sintering kinetics needs an elaborate approach to reach into a final conclusion. Different non-isothermal models [11,13,14] available in the literature are used for sintering of different ceramic systems using CRH techniques. Although, there are few publications on sintering of ZnO ceramics using master sintering curves [15–17], the dilatometric shrinkage and sintering kinetics of this multi functional ceramic has not been well studied. In the present investigation, the detailed sintering kinetics of undoped as well as SiO₂ doped ZnO ceramics has been carried out using both Woolfrey and Bannister model [11] and modified Dorn method [12] to determine the apparent activation energy of sintering, Q and the sintering parameter, n . This, in turn, would enable the researchers to understand the sintering mechanism of these systems.

The grain growth behavior of ZnO based ceramics can be intensely affected by dopants. ZnO based varistors are well studied with addition of either single metal oxide or combination of various oxides, e.g. Bi₂O₃, Sb₂O₃, MnO₂, CoO, Nb₂O₅, V₂O₅, Y₂O₃, Pr₆O₁₁, Er₂O₃ [18–22] etc. Addition of V₂O₅ [20] as the dopant induces grain growth and early sintering in ZnO whereas addition of Sb₂O₃ [21], Er₂O₃ [22] delays sintering and arrest grain growth. Our previous study [23] showed that SiO₂ doping in ZnO hinders the grain growth by affecting the rate of this process. Hence, to explore the detailed kinetics of grain growth for the ZnO–SiO₂ ceramics; the activation energy values are determined from the grain growth kinetic equations at different stages of non-isothermal sintering in the present study. The results are compared against the activation energy values obtained for undoped ZnO ceramics.

2. Experimental

2.1. Powder characterization

High purity (> 99.99%) commercial ZnO and SiO₂ powders (make: Alpha Aesar, Johnson Matthey, Germany) were used as starting material in this study. As received ZnO powder

(0.1–0.15 μm) was ground in a planetary ball mill grinder (Fritsch Pulverisette 5) with agate pots and balls (ball: charge ratio equals to 15:1) for 30 h. The speed of rotation of the mill was set at 200 rpm during grinding operation. The crystallite sizes of the powder samples were determined from the diffraction pattern obtained using Cu Kα radiation in an x-ray diffractometer (PW1710, Philips) with a Ni filter ($\lambda=1.5418$ Å). Scanning rate was maintained at 0.02° step with a 3 s holding at each step. The particle size and morphology of the powder samples were characterized using transmission electron microscopy (TEM). To do the analysis, powder particles were dispersed in isopropyl alcohol using a high-power ultrasonic vibrator. The specific surface area of the ZnO powder was determined by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption in a surface area analyzer (Sorptometric-1990, CE Instruments, Italy). The powder sample was initially dried in an oven at ~373 K and degassed at 1×10^{-4} Pa vacuum overnight.

2.2. Compaction and sintering

In case of SiO₂ addition, ground ZnO powder was mixed thoroughly with the required amount of SiO₂ powder (2, 4 and 6 wt%) in the ball mill for sufficient time. Green compacts for sintering study were made by pelletization of powder samples to ~10 mm diameter and 3–4 mm height in a hydraulic press at 400 MPa pressure. These compacts were heated in an air furnace within the range of 1273–1573 K for different duration of holding. Relative densities of the sintered specimens (dispersion ~ ± 1%) were determined by Archimedes's liquid immersion technique [24] and expressed in terms of percentage theoretical density. Microstructures of the polished and fractured surfaces were taken in a Scanning Electron Microscope, SEM (EVO 50, Carl Zeiss, UK) after coating with a thin layer of Au–Pd alloy. The grain size was measured by linear intercept method [25]. Average grain size was calculated by multiplying the average grain boundary intercept length by 1.56. The average grain boundary intercept-length was obtained by drawing four random lines on two different micrographs of each sample.

2.3. Dilatometric study

Dilatometric linear shrinkage measurement under constant rate of heating (5 K/min) was carried out in a double push rod dilatometer (TD5000SMAC Science, Japan) up to 1500 K. The samples used were made by compaction to a cylindrical shape of 6 mm diameter, 8 mm length and green density ~60% TD (theoretical density). To determine activation energy of sintering by modified Dorn's method, a special heating schedule was maintained. In this, the compact mass was hold isothermally at some predetermined temperature, mostly for a period of 30 min for thermal stability and the sample was ramped from one isotherm to the next higher one with a heating rate of 10 K/min.

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