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Sintering studies of nano-crystalline zinc oxide

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Abstract

Sintering and grain growth of nano-crystalline undoped ZnO has been studied in detail over a wide range of temperature and holding time. Below 800 °C, sintering of over 70% theoretical density is not observed, irrespective of particle size. At 900 °C for 6 h, the nano-crystalline sample sinters to 99% of theoretical density whereas the density for as received sample is 93% of theoretical density. However, at 1300 °C or higher, the densification is found to be much faster and after a few hours becomes independent of holding time. Grain growth studies reveal a similar feature of attaining saturation over holding time. The average saturated grain size is found to be ~1.5 and ~2.2 μm at 800 and 900 °C, respectively, while at 1300 °C or higher, it is in between 12 and 13 μm.

Keywords: A. Sintering; Grain growth; B. Electron microscopy; D. ZnO; RIB

1. Introduction

Studies of different nano-phase ceramics have already gained much attention because of their interesting electrical, optical, mechanical and chemical properties. Apart from these, such studies are also important for the design and development of thick targets [1] for the production of Radioactive Ion Beam (RIB).

An Isotope Separation On Line (ISOL) type RIB facility is presently under construction at Variable Energy Cyclotron Centre, Kolkata. In an ISOL type RIB, radioactive atoms are produced inside thick targets by compound nucleus type nuclear reaction of the projectile beam with the target material. Diffusion is the underlying process by which the radioactive atoms come out of the target. The grain size is usually chosen to be a few micrometer [1] so that the radioactive atoms can diffuse out from inside the grain in a time not exceeding a few seconds, which is roughly equal to the half-lives of the radioactive atoms of interest. Since a typical experiment using RIB lasts for about a week, it is important that the grain size remains below the acceptable limit despite heating and consequent temperature rise in the target caused by long hours of beam irradiation.

Thus, to examine a compound suitability for use as a target material for RIB production, one needs to study all the aspects, such as, sintering temperature as a function of particle size, extent of densification as a function of temperature and time, grain growth as a function of temperature, time and initial particle size. These studies determine the ultimate grain size and porosity, which in turn, decides the efficiency of release of radioactive atoms from the thick target.

Since, diffusion constant is directly proportional to temperature, it is always desirable that the target be heated at elevated temperature in order to have maximum extraction efficiency. Refractory compounds, in general, have high melting temperatures (mostly carbides or oxides) and therefore are used as target materials. An earlier study [2] on boron carbide (B_4C) pellets has revealed that heating at 2375 °C [T_m = 2723 K] results in ultimate grain sizes of 50–60 and 100–120 μm when the initial particle sizes are 0.5 and 0.8 μm, respectively. It is interesting to see whether this trend is a general one for all other or most of the refractory compounds. If so, this property can be made use of in target design. To be more specific, it might be advantageous to fabricate thick targets with nano-sized grains as compared to grains of bigger sizes. Not only grain growth, but also porosity determines the release efficiency of the radioactive atoms. It is therefore necessary to study densification as well as grain growth as a function of temperature.

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Densification and grain growth of undoped ZnO has been studied by a number of workers [3–6]. Qin et al. [3] recently studied the sintering and grain growth behavior of undoped ZnO powder (mean particle size of 20 nm) in the temperature range of 700–900 °C. Hynes et al. [4] sintered undoped ZnO to 95–98% of theoretical density at 650–700 °C starting with 5–10 nm powder. Han et al. [5] studied the grain growth in Mn doped ZnO. They observed a maximum densification of around 96% theoretical density when heated undoped ZnO at 1300 °C for 2 h. Tsai and Wu [6] studied the microstructure and nonohmic properties in $ZnO–V_2O_5$ system sintered at 900 °C.

However, in the present study, we have systematically studied the densification of undoped ZnO pellets over a much wider range of temperature as compared to earlier studies (450–1500 °C) in order to have an estimate of percent porosity in our samples and compared some of them with measurements done by earlier groups [3–6]. We have also studied the grain growth behavior of ZnO over a much wider range of sintering temperatures and heating durations. The upper limit of temperature is estimated to be 1300 °C in order to keep the vapor pressure below 10^{-4} Torr according to our specific requirement [1]. Furthermore, our observations of densification and grain growth at 800, 900 and 1300 °C have been substantiated by microstructural studies. The data have been found to be consistent with the observed microstructure at all the temperatures.

2. Experimental procedure

2.1. Materials

Zinc oxide powder (purity > 99.99%, particle size ~ 0.1 μm) used in this study was procured from M/S Aldrich Chemical Co., Inc. This powder was ground to a size of 30 nm in a commercial ball mill grinder (Fritsch- Pulverisette 5) with ball: charge weight ratio 16:1 in 20 h. The speed of rotation was fixed at 200 rpm during this process.

2.2. Compaction

Cylindrical pellets of approximately 10 mm diameter and 3–4 mm height were prepared by uniaxial pressing in a hydraulic press at 350 MPa. Green pellets were observed to have relative density of 62 ± 1%.

2.3. Sintering

Green pellets of both as received (AR) and nano-sized powders (NS) were examined as a function of either time or temperature for sintering study. A few samples were heated in air for 1 h at successively higher temperatures from 450 to 1500 °C. The same exercise was repeated for 2 h. Densification study as a function of time was conducted by heating the samples in air at fixed temperatures of 800, 900 and 1300 °C up to 6 h. A constant heating rate of ~10 °C/min was maintained during heating and cooling cycle.

2.4. Sample characterization

2.4.1. X-ray analysis

X-ray diffraction study was conducted for both AR and NS powder samples using Philips automatic diffractometer (PW1710) with Cu Kα radiation. Phase composition analyses, for both AR and NS samples, confirmed the peaks of ZnO.

Particle size was estimated from the intercept (=0.9λ/d) of the plot $B_s \cos\theta$ versus $\sin\theta$ considering the X-ray line broadening due to both strain and particle size as:

$$B_s = 2\varepsilon \tan\theta + \frac{0.9\lambda}{d\cos\theta}, \quad (1)$$

where ε is the strain, d the grain size, λ the wave length of Cu Kα and θ is the diffraction angle. B_s is the broadening due to the sample. Instrument broadening (B_{Si}) was subtracted from the full width at half maxima for the peaks (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) according to Eq. (2).

$$B_s^2 = B_t^2 - B_{Si}^2, \quad (2)$$

where B_t is the measured total broadening.

2.4.2. Density measurements

Densities of the sintered samples were measured by the Archimedes method with distilled water. Values were found to be consistent with those obtained from the ratio of weight to volume.

2.4.3. Microscopic observations

For micro-structural characterization, sintered pellets were fractured and observed under JEOL scanning electron microscope (JSM 6700F, JSM 5510). Grain sizes of the sintered pellets were calculated from the image analysis software. Both AR and NS powders were dispersed in isopropyl alcohol and examined by transmission electron microscope (Hitachi, H600) to observe the size distributions of the powdered samples (Fig. 1).

3. Results and discussion

3.1. Density

The need for densification study has already been mentioned earlier. Elimination of pores inhibits diffusion. Therefore, one needs to find out the sintering temperature and time for which the sample gets maximally dense and reaches saturation. The experiments have been done in two steps:

1. To start with, we have sintered both AR and NS samples from 700 to 1400 °C, restricting the sintering time for 1 and 2 h only for the study of densification.
2. We have further extended the study for sintering time up to 6 h, but for discrete temperatures at 800, 900 and 1300 °C for both AR and NS samples.

Fig. 2(a) shows the variation of density of ZnO pellets with different sintering temperatures for 1 h heating. Pellets treated

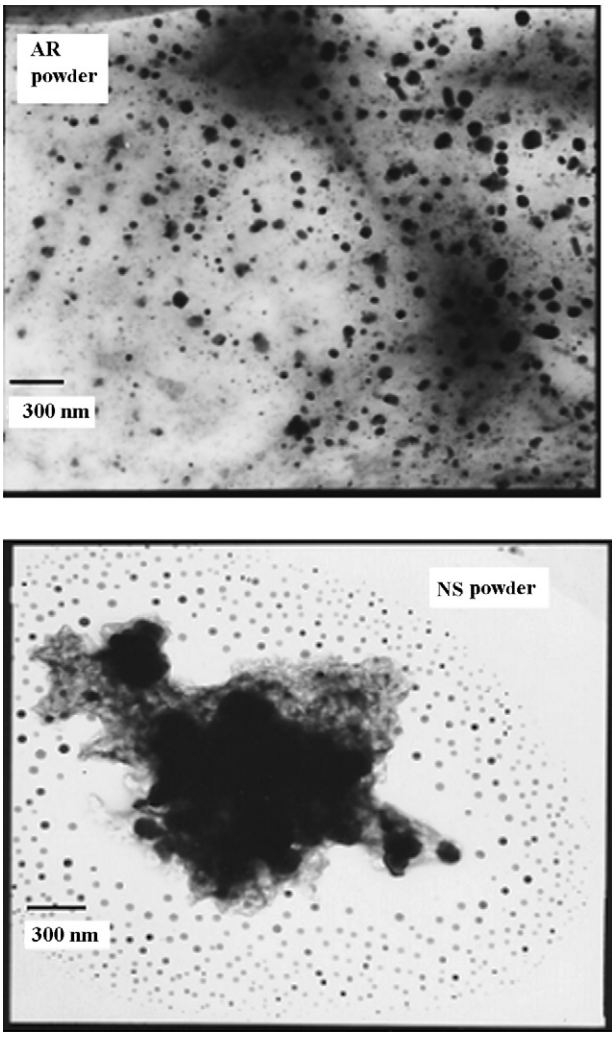


Fig. 1. TEM picture of ZnO powder (both AR and NS powders).

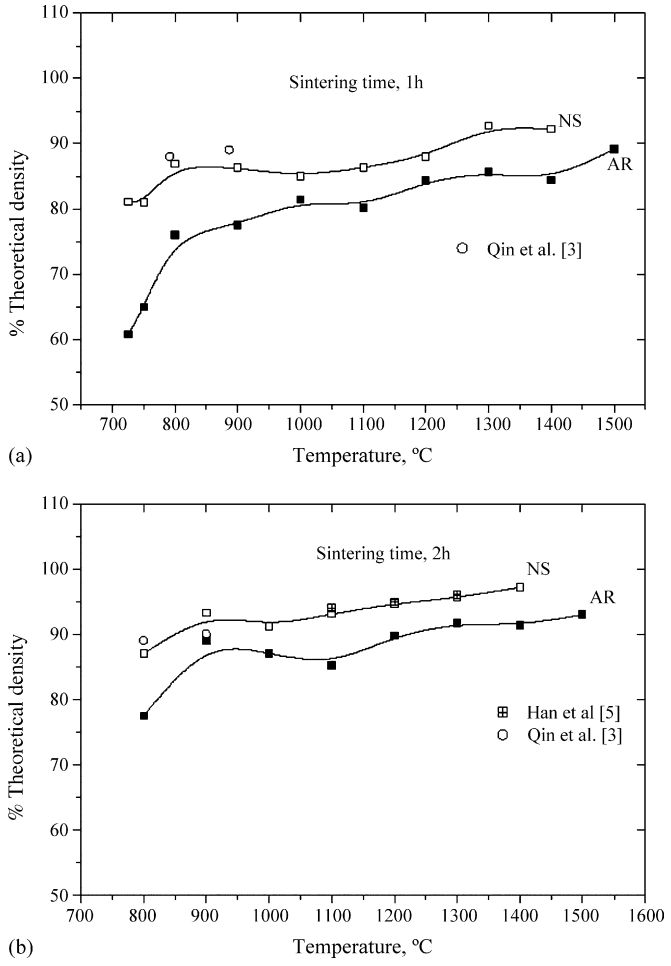


Fig. 2. Densification behavior of ZnO pellets with temperature for: (a) 1 h and (b) 2 h holding.

below 700 °C show densities less than 70% ρ_{theo} (theoretical density) irrespective of the particle size of the starting powder. Sintered pellets prepared from AR powder shows a maximum density of 89% ρ_{theo} when treated at 1500 °C. Pellets prepared from NS powder show density of 80% ρ_{theo} in the temperature range of 700–750 °C and increases to 87% ρ_{theo} at 800 °C. Density increases significantly when heated beyond 1100 °C and reaches around 92% ρ_{theo} at 1300–1400 °C. Above results show that sintering becomes more favorable as particle size reduces. This is expected as a decrease in particle size causes an increase in surface area and surface energy, which is a driving force for sintering. In the temperature range of 700–900 °C where earlier data [3] are available our results are in good agreement. However, the results obtained by Hyne et al. [4] are little different. They have observed a density $\geq$95% ρ_{theo} when heated at 700 °C for 40 min. This may be due to the much lower (5–10 nm) particle size of the starting powder in their experiment.

In Fig. 2(b), sintering results for 2 h holding are shown. In case of AR samples, density varies from 89% ρ_{theo} at 900 °C to 95% ρ_{theo} at 1300 °C and almost reaches a plateau thereafter when heated up to a temperature of 1500 °C. For NS pellets, variation of density is in the range of 93–97% ρ_{theo} when heated from 900 to 1400 °C. Therefore, it is clear that heating for longer time leads to better densification. Our data are in good agreement with Qin et al. [3] in the lower temperature regime of 700–900 °C and also with the results of Han et al. [5] who studied undoped ZnO in the intermediate range of 1000–1200 °C for 2 h heating, although their main aim was to study ZnO doped with Mn.

In order to understand the variation of density with time, pellets made from both AR and NS powders were heated at temperatures 800, 900 and 1300 °C for duration up to 6 h. Density increases strongly with sintering time, as shown clearly in Fig. 3(a–c).

At 800 °C, density achieved for NS pellets is less than 90% ρ_{theo} when heated up to 3 h. It further improves to 96% ρ_{theo} for 4 h of heating. Finally, it has been saturated (~99% ρ_{theo}) for continuous heating for more than 5 h. Comparing our data with recent observation of Qin et al. [3], it can be seen that density matches with their results up to 3 h of heating. Beyond 3 h, the density observed by us is higher than that observed by them.

At 900 °C, for both AR and NS samples, the density changes substantially from ~78 to ~89 and ~86 to ~93% ρ_{theo},

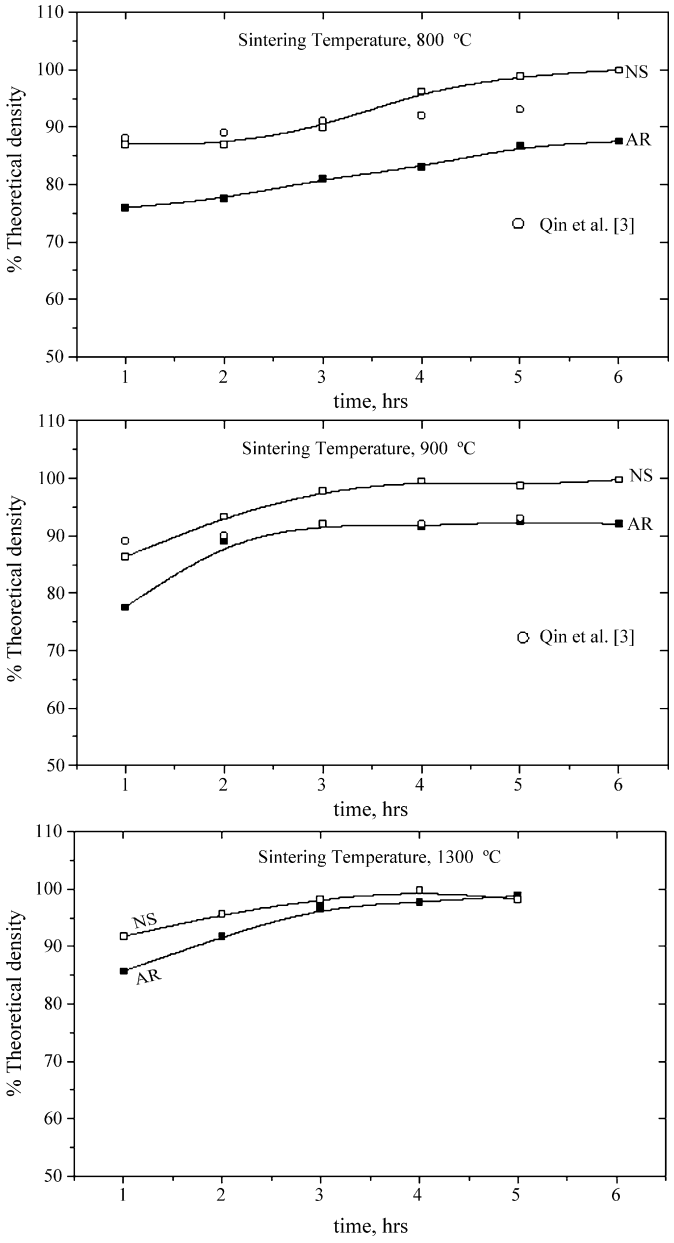


Fig. 3. Densification behavior of ZnO pellets with time at: (a) 800 °C, (b) 900 °C and (c) 1300 °C.

respectively, during holding for 1–2 h. Density of NS samples becomes 98% ρ_{theo} for 3 h of heating at 900 °C, which saturates to 99% ρ_{theo} when heated for more than 3 h. In the case of AR sample, the nature of the curve is similar but the saturation density is less (93% ρ_{theo}) even after 6 h of heating at 900 °C. Tsai and Wu [6] studied ZnO–V_2O_5 system and obtained a density of 97% ρ_{theo} when they heated undoped ZnO pellet for 4 h at 900 °C. Density data of Qin et al. [3] are of lower value than ours as can be seen in Fig. 3(b). However, interestingly we find the densities for both AR and NS samples become 99% ρ_{theo} when heated at 1300 °C for more than 4 h.

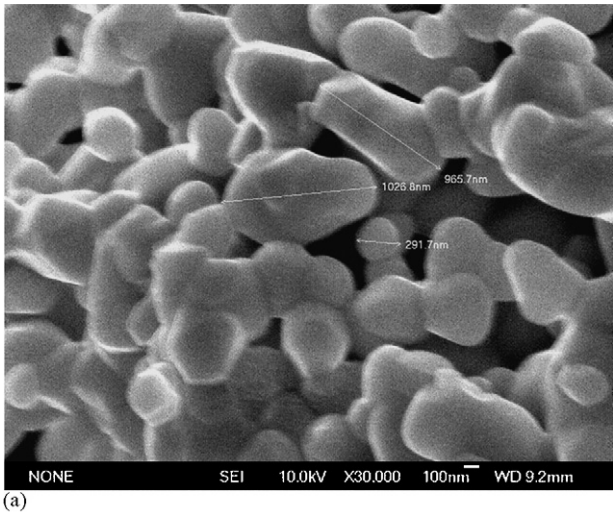
The nature of densification curve is quite different at the three temperatures. The densification is clearly faster at higher temperature. Also the density difference between AR and NS pellets decreases as the temperature increases from 800 to 900 °C and finally vanishes at 1300 °C after 4 h of heating.

3.2. Microscopic examinations

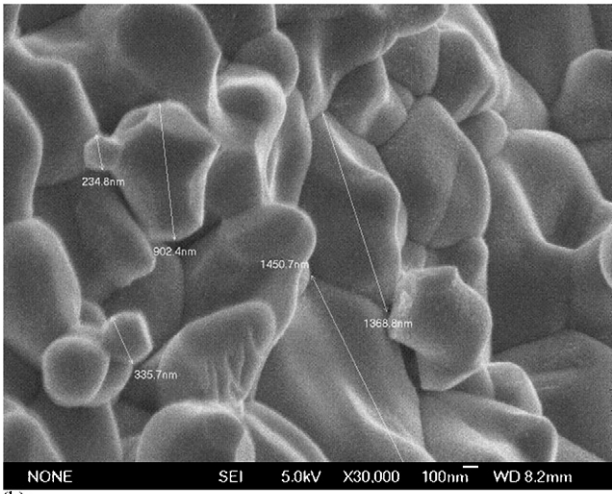
3.2.1. Micrographs

SEM micrographs of a few samples are presented in Figs. 4–7. Fig. 4(a) presents the NS sample sintered at 800 °C for 4 h. It can be observed in this sample that though particles have joined with each other, well-defined grains have not formed. Porosity of about 4–5% ρ_{theo} is also visible. On further heating for 5 h at 800 °C, well-defined grains are visible with almost negligible porosity, as evident in Fig. 4(b).

Fig. 5(a) presents the micrograph of the NS sample heated for 1 h at 900 °C. It is clearly visible from the picture that the sintering process has initiated. Particles have joined together forming a few necks. Small particles of 200–300 nm are visible. Heating the same sample for 2 h reveals more joining and less porosity as seen in Fig. 5(b). In case of 3 h heating of this sample, density improves to ~98% ρ_{theo} as reflected in SEM micrograph (Fig. 5(c)). Prominent features observed in this case



(a)



(b)

Fig. 4. SEM micrographs of ZnO pellets sintered at 800 °C: (a) 4 h and (b) 5 h.

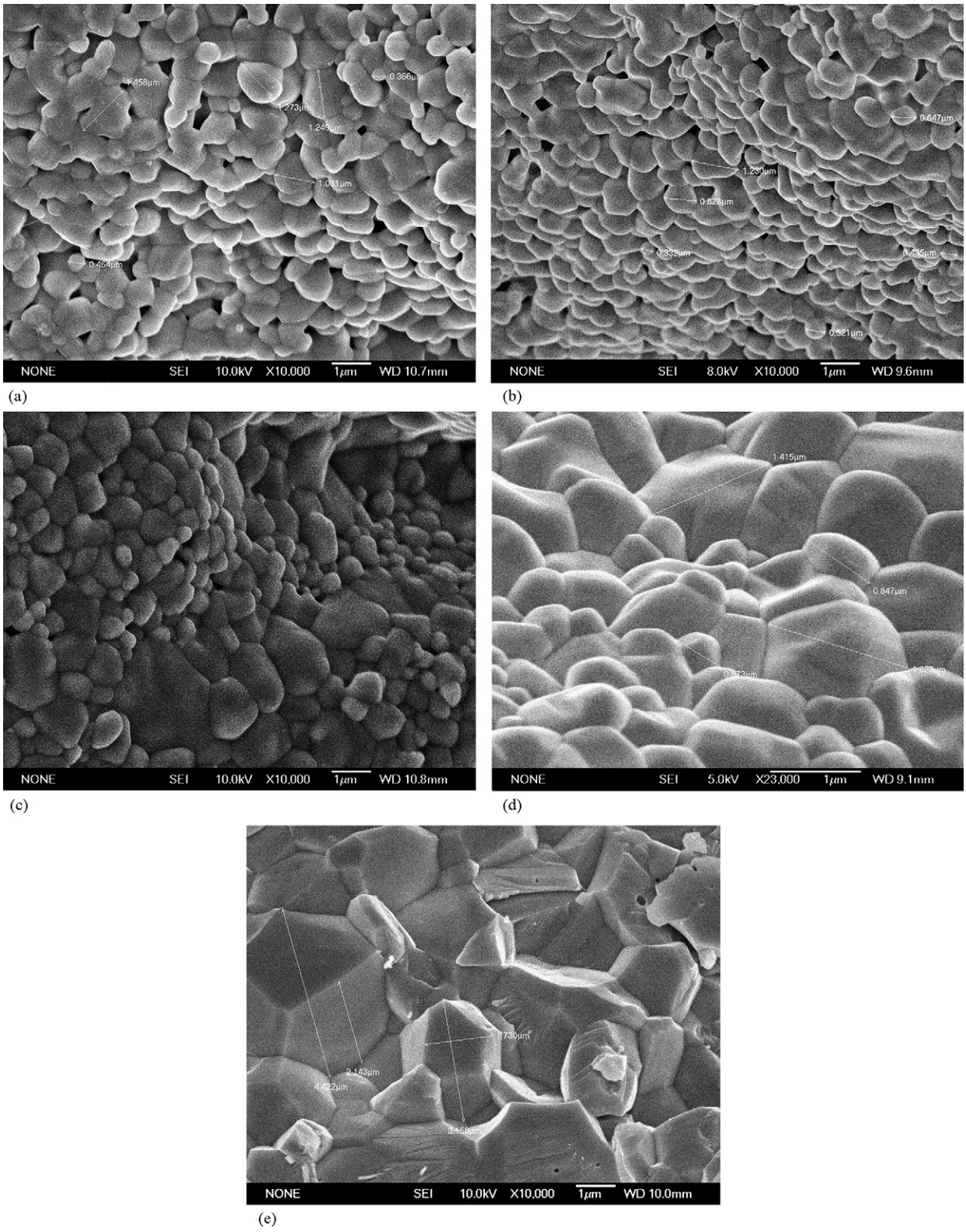
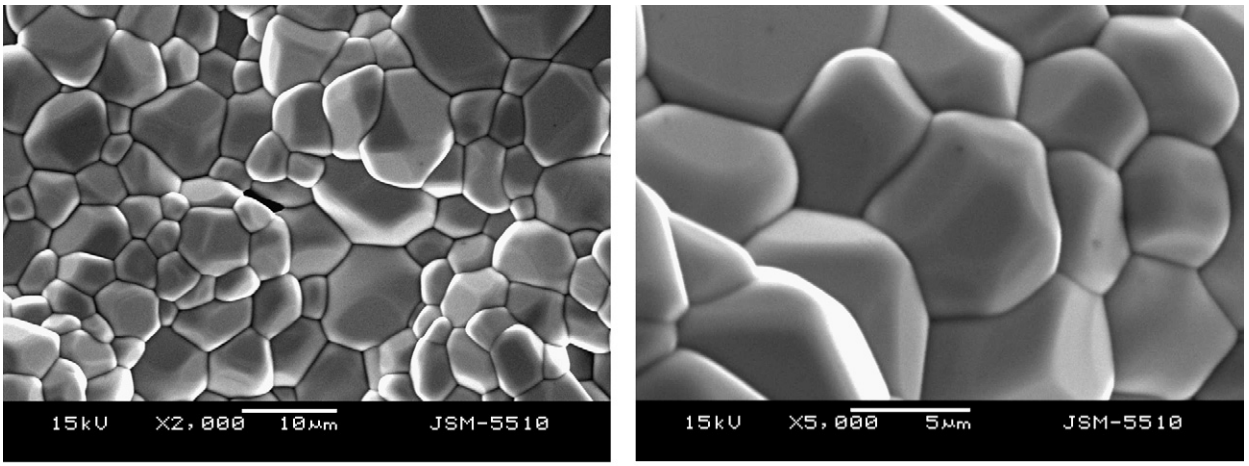


Fig. 5. SEM micrographs of ZnO pellets sintered at 900 °C: (a) 1 h, (b) 2 h, (c) 3 h, (d) 5 h and (e) 6 h.

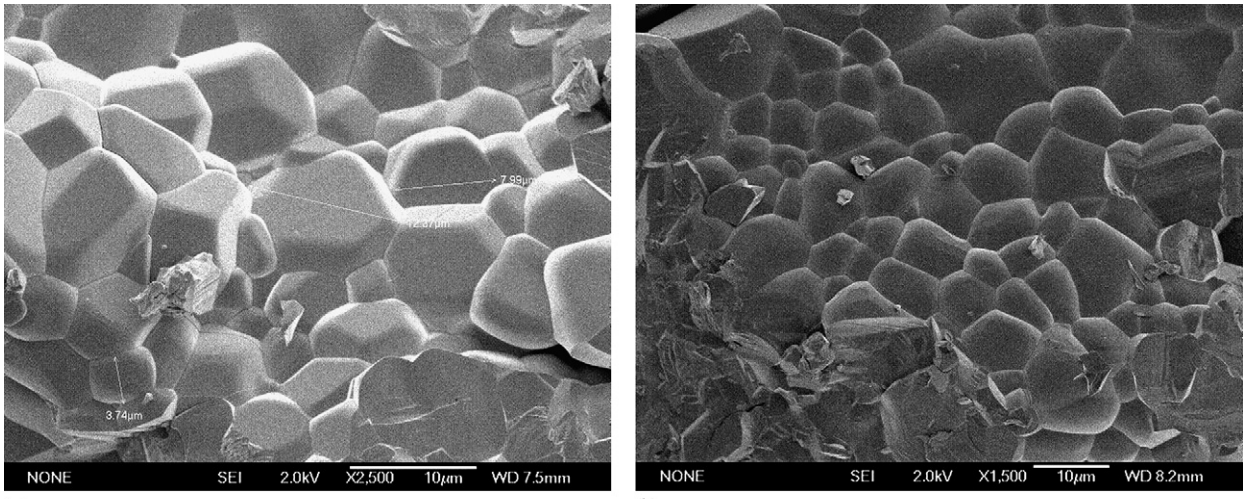
are presence of well-defined grains, less porosity and a few big grains giving impression of grain growth. On further heating, as the density improves to >99% ρ_{theo}, more number of big grains of diameter ~1.6–2 μm are visible in Fig. 5(d and e).

Micrographs of the samples sintered at 1300 °C are presented in Figs. 6(a and b) and 7(a and b). The micrograph of NS sample sintered for 2 h, as observed in Fig. 6(a), shows a perfectly bonded grain structure with a combination of small



(a) (b)

Fig. 6. SEM micrographs of ZnO pellets sintered at 1300 °C for 2 h at: (a) 2000× and (b) 5000×.



(a) (b)

Fig. 7. SEM micrographs of ZnO pellets sintered at 1300 °C for: (a) 3 h and (b) 5 h.

and large grains. Very few pores are visible. In higher magnification (Fig. 6(b)) these features are much more clear. Similar nature with almost no porosity prevails for the samples under heat treatment for longer duration as in Fig. 7(a and b).

3.2.2. Grain growth

Maximum grain size of sintered ZnO pellets of NS samples have been studied systematically as a function of sintering temperature and time. The measured grain sizes from SEM images of fractured pellets sintered at 800, 900 and 1300 °C for different holding time of 1–6 h are shown in Figs. 8 and 9.

Samples heated at 800 °C for up to 3 h holding does not have density >90% ρ_{theo}, therefore, are not observed under SEM. Maximum grain size obtained for 4–6 h of heating at 800 °C is in the range of 1–1.5 μm. At 900 °C, maximum grain size for 6 h heating is observed to be ∼2.3 μm. Therefore, higher the temperature more rapid is the grain growth with respect to sintering time. In addition, saturation in grain growth almost sets in after 3 h of heating. In fact after 1 h of heating at 1300 °C size of a big grain becomes 8 μm. This increases to 10 μm for

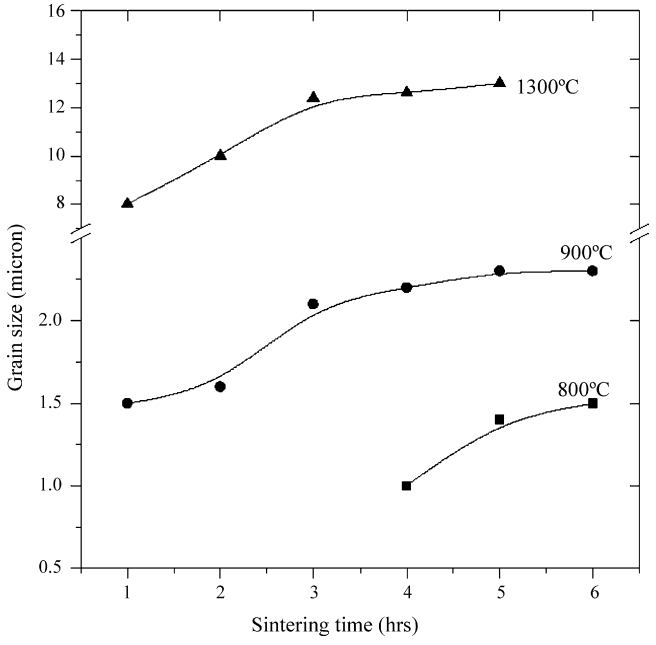


Fig. 8. Grain growth variation with sintering time at T = 800, 900 and 1300 °C.

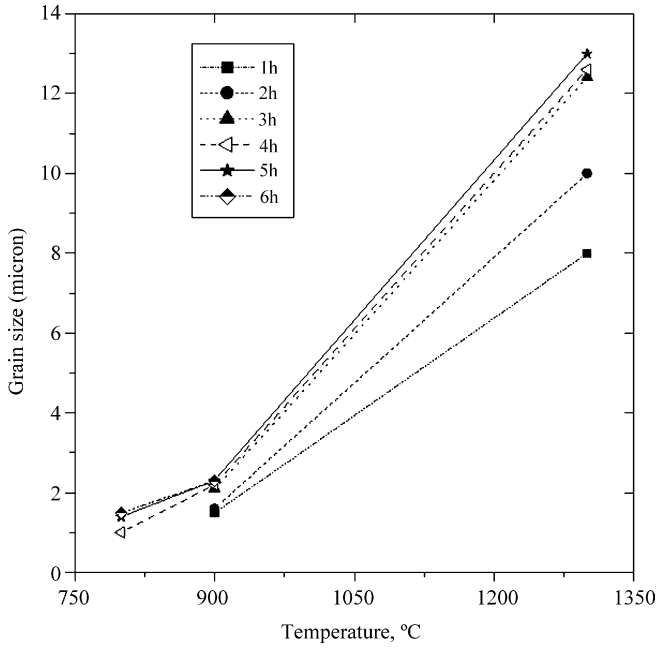


Fig. 9. Grain growth variation with temperature for different sintering times (1–6 h).

2 h of heating and to 12.3 μm for 3 h. Afterwards, for duration of 4 and 5 h the change is not much, as visible from Fig. 8, although Fig. 9 clearly shows that up to 2 h there is a change in slope of the grain growth curves. By uniform heating for 5 h from 800 to 1300 °C, it is found that the rate of change of grain growth is almost the same (Fig. 9). Our grain growth data match quite well with the study of Tsai and Wu [6] at 900 °C, but slightly differ from the results of Qin et al. [3]. In fact, Qin et al. [3] have studied the grain growth of nano-crystalline undoped ZnO in the temperature range of 700–900 °C for a maximum of 2.5 h heating time without exploring the saturation region.

4. Conclusions

The isothermal sintering of undoped nano-crystalline ZnO has been studied in the temperature range from 450 to 1400 °C in air. This study differs from the earlier studies [3–6] in that it is done over a much wider range of temperature and for long enough holding time (up to 6 h) to observe the saturation in density and grain growth. Also the correspondence between the data and the microstructure, as revealed by SEM micrographs, has been established in each case at temperatures 800, 900 and 1300 °C. ZnO pellets are observed to have ∼70% ρ_{theo} when sintered below 700 °C irrespective of particle size. Effect of particle size and sintering time are best manifested when sintered at 800 °C. Densification is found to be much faster as temperature is increased from 800 to 1300 °C and eventually becomes independent on sintering time. Pellets made from AR powder attain maximum 88% ρ_{theo} after holding of 6 h whereas NS pellets attain 99% ρ_{theo} after 5 h holding at 800 °C. However, at 1300 °C, after 4 h of heating, there was no difference so far the densities of AR and NS samples are concerned.

Grain growth reveals similar feature of attaining saturation over sintering time, but only after 900 °C for 3 h of heating. The maximum saturated grain size is found to be ∼1.5 and ∼2.2 μm at 800 and 900 °C, respectively, while it is in between 12 and 13 μm at 1300 °C.

Thus, it is clear that if ZnO nano-particles are to be used as a target for RIB production, we would need to ensure that the target temperature remains much below 1400 °C. This is because at around 1400 °C one looses the advantage of using nano-particles (smaller ultimate grain size). However, it might be possible to control the grain growth effectively by adding some suitable dopants. Alternately, one can hope to control both grain growth and porosity by dispersing the nano-particles on some suitable substrate. Such studies are being undertaken at present.

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