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## A positron study of sintering processes in ZnO-based ceramics

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**Abstract.** Positron annihilation spectroscopy has been used to study the sintering processes in pure and Bi-doped ZnO. The lifetime measurements in the as-pressed specimens reveal the presence of a long component, this being ascribed to pores. By following the evolution of the annihilation parameters as a function of the annealing temperature between 673 and 1573 K it is suggested that a satisfactory sintering occurs above 1373 and 1173 K for pure and Bi-doped ZnO, respectively.

From the lifetime measurements, the activation energy for the sintering processes in pure ZnO is found to be  $Q_R = (360 \pm 10) \text{ kJ mol}^{-1}$ , which is in agreement with previous values obtained from densification measurements.

### 1. Introduction

The potential use of ZnO-based ceramics in practical applications such as varistors, acoustic and optoelectronic devices demands close control of the microstructure developed during sintering. Thus, the use of sensitive techniques to monitor the sintering processes is highly desirable.

The positron annihilation technique has been widely used to detect vacancies and other defects involving a decrease of the electronic density in comparison with the perfect lattice and for this reason it is expected to detect the presence of pores in compacted ceramics and to be able to follow the evolution of sintering. The microstructure of compacted metals and semiconductors powders has been recently investigated by means of this technique (Dekhtyar *et al* 1981, Semenov 1985, Schaefer and Würschum 1987, Schaefer *et al* 1987, Würschum *et al* 1987).

In the present work we have studied the sintering of pure and Bi-doped ZnO ceramics by using the positron annihilation technique. New sintering parameters have been used that correlate satisfactorily with some traditional ones available in the literature. From the experimental data the activation energy for the sintering process in pure ZnO has been obtained.

### 2. Experimental procedure

The pure ZnO samples were prepared from Merck reagent powder. The particle size was made homogeneous by milling the powder in an agatha mortar for one hour.

**Table 1.** Results of two-term analyses of positron annihilation spectra from sintered ZnO powders.

Sample	$\tau_1$ (ps)	$\tau_2$ (ps)	$I_2$ (%)	$\bar{\tau}$ (ps)
As-pressed	221 $\pm$ 5	434 $\pm$ 15	24 $\pm$ 3	272 $\pm$ 3
Annealed at 673 K for 3 h	209 $\pm$ 5	426 $\pm$ 15	30 $\pm$ 4	274 $\pm$ 3
Annealed at 873 K for 3 h	224 $\pm$ 5	447 $\pm$ 18	21 $\pm$ 3	272 $\pm$ 3

Afterwards the powders were pressed into discs at pressures of about 0.9 GPa and subjected to different thermal treatments.

In the case of the Bi-doped samples, a mixture of ZnO and Bi<sub>2</sub>O<sub>3</sub> powders from Merck was prepared. Two different concentrations of Bi<sub>2</sub>O<sub>3</sub> were used, i.e., 0.2 and 1.0 wt%. In both cases the mixture was prepared by milling the powders in an agatha mortar. After mixing the two components, the preparation procedure was identical to the one followed for the pure samples.

The time evolution of sintering for a fixed temperature was followed by performing lifetime measurements in pure ZnO samples treated at 873, 1073, 1173, 1273, and 1473 K for periods of 1, 2, 3 and 6 hours for every temperature.

To monitor the sintering process with temperature in both pure and Bi-doped samples, lifetime and Doppler-broadening measurements were made. The isochronal treatment was fixed at 3 hours at temperatures ranging from 873 to 1573 K in 100 K steps. Additional treatments of 2 hours at the corresponding temperature were also given to the pure samples.

In all cases, the specimens were cooled slowly in order to avoid damage from thermal shock and consequent crack nucleation.

The lifetime spectra with  $7 \times 10^5$  counts were recorded at room temperature by using a fast-fast spectrometer with a time resolution of 290 ps (FWHM); the Doppler-broadening measurements were made with a stabilised Ge(Li) detector having an energy resolution of 1.5 keV at 511 keV; as a positron source a <sup>22</sup>NaCl aqueous solution evaporated onto a thin nickel foil (0.4 mg cm<sup>-2</sup>) was used. The lifetime spectra were analysed with one- or two-component fits, after subtracting the Ni foil and salt contributions. The *S*-parameter was calculated as the relative area of a fixed region taken around the annihilation peak.

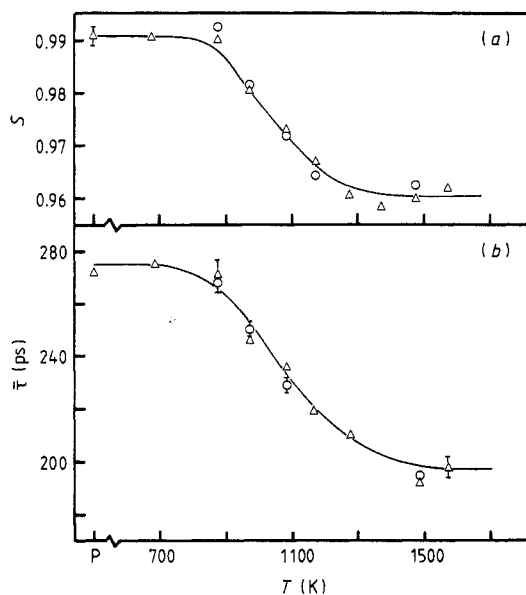
### 3. Results and discussion

#### 3.1. Pure ZnO

The as-pressed samples were analysed by using two terms and the fit was satisfactory. For the samples annealed at 673 and 873 K a two-component fit was also possible; for the samples annealed between 1073 and 1273 K the two-components analysis improved the variance of the fit but the statistical uncertainties associated with the lifetime and the relative intensities were too high to consider the analyses reliable; thus, one-component fits were used. For the specimens annealed above 1273 K, decomposition into two components was not possible, indicating the presence of only one lifetime.

The results obtained for the two-term analyses have been summarised in table 1.

For the as-pressed specimen, the long component with a value  $\tau_2 \approx 430$  ps and an intensity  $I_2 \approx 24\%$  is characteristic of large three-dimensional vacancy clusters (Puska



**Figure 1.** (a) The evolution of the  $S$ -parameter, and (b) the average positron lifetime  $\bar{\tau}$ , as a function of annealing temperature for a pressed ZnO sample. The point P denotes the values for the as-pressed sample.  $\Delta$ , annealed for 3 hours;  $\circ$ , annealed for 3 + 2 hours (cumulative treatment).

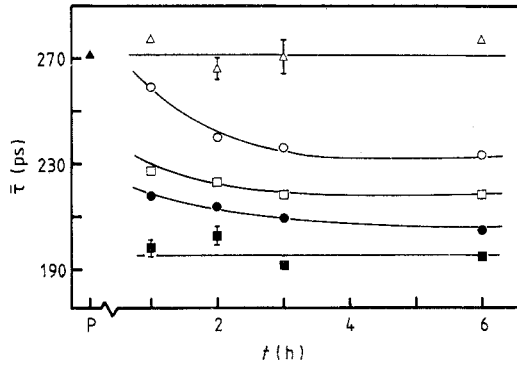
and Nieminen 1983). We ascribe this component to positron trapping at pores and the  $\tau_2$  value obtained is related to the pore size distribution present in the sample. Thus, the average lifetime  $\bar{\tau} = \tau_1 I_1 + \tau_2 I_2$  contains information on the presence of pores in the samples and can be used as a useful parameter to follow the evolution of the pore structure in the pressed ZnO samples. It can be seen from the table that the pore structure does not change noticeably in the temperature range shown.

In figure 1 the  $S$ -parameter and the average lifetime as a function of the annealing temperature have been plotted. In the same figure the as-pressed value has been also represented as a reference (point marked P in the figure). A drop in both parameters is observed at about 800 K for the samples heated for 3 hours (open triangles); the decrease continues up to 1300 K, where a constant value is achieved. The average grain size in the temperature interval 1373–1473 K ranges between 5 and 8  $\mu\text{m}$ ; thus, positron trapping at grain boundaries can be excluded. It is worth noting that the constant value reached by the lifetime  $\tau = 195$  ps is characteristic of pure, defect-free monocrystalline ZnO (Pareja 1988). As can be seen in figure 1, further heat treatment for two hours does not modify the results (open circles).

We have interpreted the changes in the annihilation parameters as a modification in the pore structure of the samples. The decrease observed from 800 K in both the  $S$ -parameter and the average lifetime  $\bar{\tau}$  indicates that the pores start to disappear at this temperature and that satisfactory sintering is obtained above 1300 K, where the bulk value is achieved. It has been also found that pre-annealing hampers the sintering process. These measurements reproduce previous results on shrinkage and densification in sintered ZnO (Gupta and Coble 1968, Baumgartner 1983).

In figure 2 the evolution of the average lifetime  $\bar{\tau}$  as a function of the annealing time is shown for five fixed temperatures: 873, 1073, 1173, 1273 and 1473 K. For the specimens treated at 873 K,  $\bar{\tau}$  is roughly constant for the whole time range studied. Its value of 270 ps, is the same as the one found for the as-pressed sample, indicating that no noticeable changes in the pore distribution take place at this temperature.

In the samples annealed at 1073 K for between 1 and 3 hours the average lifetime decreases. However, no further decrease is observed when the treatment time increases



**Figure 2.** The average lifetime  $\bar{\tau}$  for pressed ZnO samples as a function of annealing time at various temperatures:  $\Delta$ , 873 K;  $\circ$ , 1073 K;  $\square$ , 1173 K;  $\bullet$ , 1273 K;  $\blacksquare$ , 1473 K.

and  $\bar{\tau}$  stays constant at 230 ps, higher than the bulk lifetime, suggesting that sintering has reached its maximum extent at this temperature after a heating period of 3 hours.

The average lifetime for the sample heat treated at 1473 K remains constant independent of the annealing time and has a value of 195 ps characteristic of monocrystalline ZnO. These results suggest that complete sintering is obtained by heating the specimens at 1473 K, even for short periods.

To obtain the activation energy for the sintering processes, we have used reasoning similar to that of Dlubek and Brümmer (1976) for studying the recrystallisation processes from positron data.

In a partially sintered sample we can assume that porous regions coexist with totally sintered zones. By denoting the lifetimes characteristic of the sintered and porous regions  $\tau_b$  and  $\tau_p$ , respectively, we can write the average lifetime  $\tau(t)$  for a heating period  $t$  as a function of the fraction of sintered material  $X(t)$  in the form

$$\tau(t) = X(t)\tau_b + [1 - X(t)]\tau_p. \quad (1)$$

If it is assumed that the fraction of sintered material can be described through an Avrami equation (Detert and Dressler 1965), it can be written as

$$X(t) = [\tau_p - \tau(t)]/(\tau_p - \tau_b) = 1 - \exp[-(t/\mu)^n]. \quad (2)$$

The value of the constant  $n$  can be obtained by plotting  $\log\{\ln[1/(1 - X(t))]\}$  versus  $\log t$ ;  $\mu$  is also a constant which is related to the activation energy for the sintering process  $Q_R$  through the expression:

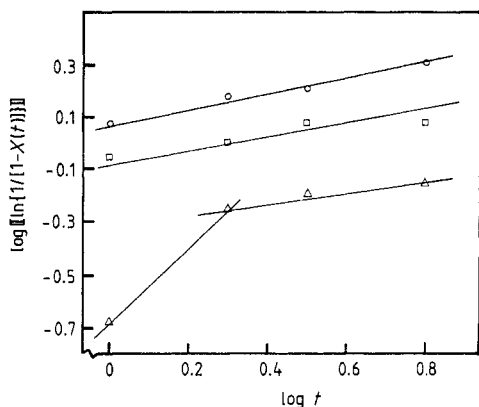
$$1/\mu = A \exp[-Q_R/RT] \quad (3)$$

where  $A$  is a constant,  $R$  the universal gas constant and  $T$  the absolute temperature.

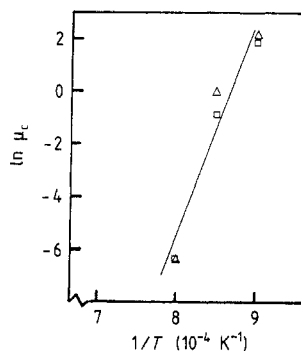
In figure 2 it is seen that the lifetime values for 873 and 1473 K do not change as the treatment time increases, thus we have taken as  $\tau_p$  and  $\tau_b$  the lifetime values at 873 and 1473 K, respectively.

The plot of  $\log\{\ln[1/(1 - X(t))]\}$  versus  $\log t$  is shown in figure 3. The change in the slope observed at 1073 K can be attributed to a change in the driving force for the sintering process, indicating that the dominant mechanism responsible for sintering is changing.

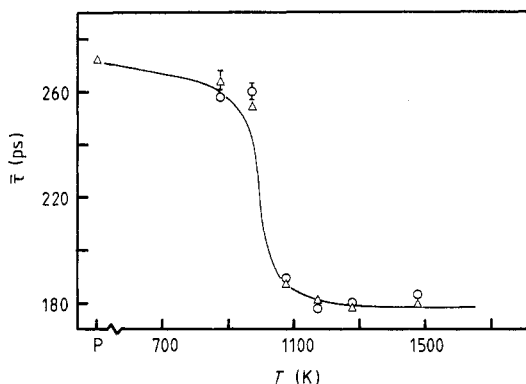
By defining a characteristic time  $\mu_c$  as the time necessary for achieving a certain constant fraction  $X(t)$ , the activation energy can be obtained from (3) by plotting  $\ln \mu_c$  as a function of  $1/T$ . In figure 4 the plots are shown for  $X(t) = 0.5$  and  $X(t) = 0.6$ . The points can be aligned to a straight line from which  $Q_R = (360 \pm 10)$  kJ mol $^{-1}$ , which is in agreement with the value  $Q_R = (376 \pm 30)$  kJ mol $^{-1}$  obtained by Baumgartner (1983) from densification measurements.



**Figure 3.** Avrami plot for several annealing temperatures.  $X(t)$  represents the fraction of sintered material and  $t$  is the annealing time.  $\Delta$ , 1073 K;  $\square$ , 1173 K;  $\circ$ , 1273 K.



**Figure 4.** The characteristic time  $\mu_c$  as a function of the inverse temperature for two different fractions  $X(t)$  (see § 3.1 for explanation):  $\square$ ,  $X(t) = 0.5$ ;  $\Delta$ ,  $X(t) = 0.6$ .



**Figure 5.** The evolution of the average lifetime  $\bar{\tau}$  as a function of the annealing temperature for Bi-doped samples (annealing time 3 hours):  $\circ$ , 0.2 wt% Bi;  $\Delta$ , 1.0 wt% Bi.

### 3.2. Bi-doped ZnO

The evolution of the average lifetime  $\bar{\tau}$  as a function of the annealing temperature has been plotted for 1 wt% Bi- and 0.2 wt% Bi-doped ZnO in figure 5. The value marked as P in the figure corresponds to the measurement in the as-pressed 1 wt% Bi-doped sample; this value of 270 ps is the same, within experimental error, as the one obtained for the as-pressed ZnO sample. In this case only the spectra for the as-pressed samples could be decomposed in two terms, the longer component having a characteristic value of  $\tau_2 = 410$  ps and an intensity  $I_2 = 26\%$ . For the samples annealed in the temperature range 800–1100 K the two-component fit gave statistical uncertainties which were too high. Above 1200 K only one-term analyses gave satisfactory fits.

Since the values for the as-pressed Bi-doped sample are, within experimental error, close to the ones obtained for the as-pressed pure sample, we conclude that the addition of 1 wt% Bi does not change the as-pressed state of the specimens. However, there is a striking difference when one compares the annealing behaviour of the doped and undoped samples. The decrease of the average lifetime  $\bar{\tau}$  starts at about 873 K for the doped sample;  $\bar{\tau}$  drops drastically up to about 1173 K, where a constant value of 180 ps is achieved. Note that in the range 1073–1473 K one-term analysis gives satisfactory

fits, indicating that no longer lifetime components are present. The different sintering behaviour in comparison with the pure samples is attributed to the presence of a liquid phase, which would enhance the transport processes. Figure 5 shows no noticeable differences between the two Bi concentrations studied.

#### 4. Conclusions

It has been demonstrated that the positron annihilation technique can be used to monitor sintering processes in ZnO. For pure ZnO these processes take place between 873 and 1373 K, and that satisfactory sintering is obtained by annealing above 1500 K. The addition of Bi retards the beginning of the process and lowers the temperature at which complete sintering is achieved, this being in agreement with previous results based on traditional techniques.

From the lifetime measurements the activation energy for the sintering process in pure ZnO has been calculated to be  $Q_R = (360 \pm 10) \text{ kJ mol}^{-1}$ , again in agreement with previous calculations.

It has also been found that pre-annealing hampers the sintering process in pure ZnO.

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