Grain growth kinetics and magnetic properties of a vanadium-doped ZnO dilute magnetic oxide

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Abstract

Zn_{0.95}V_{0.05}O ceramics, elaborated from milled ZnO and V₂O₅ nanopowders, were sintered at 900, 1000 and 1100 °C for 1, 2, 4, 6, 10 and 14 h. The growth kinetics was studied identifying the grain growth exponent, the activation energy and the pre-exponential factor. The high V₂O₅ concentration allowed a rapid grain growth at 900 °C only at the very first stages ($t < 1$ h). Meanwhile, at temperatures of 1000 and 1100 °C, the grain growth was extremely fast with a growth exponent of 0.72. The magnetic properties of the samples indicate that ferromagnetism exist in all samples in different magnitudes depending on the sintering conditions. In particular, the maximum magnetization was obtained on the sample sintered at 1100 °C for 14 h, despite the reduction of V concentration. Additionally, secondary paramagnetic phases were detected in the samples sintered at lower temperatures and shorter sintering times.

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1. Introduction

The elaboration of ZnO-based ceramics has a wide variety of technological applications in optoelectronics [1,2] photoluminescence [3,4], varistor fabrication [5], magnetism [6,7] and transparent conductive contacts [8,9]. The V₂O₅-doped ZnO system is of interest in its bulk form as it exhibits varistor behavior, i.e., a non-linear voltage dependence on the current, due to the segregation of the dopants at the grain boundaries forming an electric barrier. The varistor behavior depends on the microstructure, grain size and secondary-phase distribution in particular at the grain boundaries [10]. These characteristics can be tuned by sintering at different temperatures, time, and dopant concentration. One of the advantages of the V₂O₅-doped ZnO system is that sintering does not require high temperatures [11].

On the other hand, dilute magnetic oxides (DMO) are a fascinating family of materials that have attracted much attention due to their high Curie temperature (T_C) and their semiconductor or insulating behavior. These materials consist on wide-bandgap oxides as In₂O₃, SnO₂, TiO₂ and ZnO doped with a small amount of 3d-transition metals. These DMOs exhibit ferromagnetic (FM) ordering at room temperature even when the concentration of magnetic ions lies below the percolation limit [12]. The ZnO:V system is of particular interest as none of its original components is FM, neither ZnO and V₂O₅ nor the secondary phases formed by their reaction. However, room temperature ferromagnetism has been observed in Zn_{0.95}V_{0.05}O nanoparticles [13], thin films [14] and bulk samples [15,16]. Secondary phases that appear during the synthesis of V-doped ZnO samples are paramagnetic, thus interfering on the pure FM behavior of the samples. In our samples, FM ordering is located at the grain boundaries of undoped ZnO grains. It is important to know the conditions at which bulk ceramic samples should be synthesized in order to control the formation of secondary phases and their magnetic behavior.

In this work, Zn_{0.95}V_{0.05}O ceramics were elaborated by sintering ZnO and V₂O₅ nanopowders. We have combined the analysis of the grain growth kinetics and X-ray diffraction (XRD), to identify the grain growth exponents and the formation of secondary phases dependent on the sintering conditions. Furthermore, the role of paramagnetic

phases and the formation of a perfect DMO at the grain boundaries has been examined and measured. According to our results, it seems that ZnO grains remain undoped.

2. Experimental

Bulk $\text{Zn}_{0.95}\text{V}_{0.05}\text{O}$ ceramics were prepared from high purity ZnO and V_2O_5 powders (Sigma Aldrich) in a stoichiometric relation in order to obtain the desired composition. Powders were milled with ethanol for 1 h in a high-energy mill (SPEX D8000) using a Nylamid jar and yttrium-stabilized zirconia beads as the milling media. The average size of the **crystallites** was 42 nm (obtained from the XRD **patterns**). Powders were compressed in pellets of 10 mm of diameter with a pressure of 1.2 MPa. The pellets were sintered in air at 900, 1000, and 1100 °C for 1, 2, 4, 6, 10, and 14 h. Heating and cooling processes were achieved at a rate of 3 °C per minute. The preparation of the ceramics surface for observation by scanning electron microscopy (SEM) includes a final polishing with 0.3 µm size alumina powders and a chemical attack with Nital (98% ethanol - 2% nitric acid) for a few seconds in order to reveal the grain boundaries. Phase identification has been performed by XRD using a PanAlytical equipment with Cu-K α radiation. SEM micrographs and **energy dispersive spectroscopy (EDS) microanalysis** were obtained using a Jeol JSM 5800-LV microscope and **an EDAX detector**. Grain size was measured using the intercept method, which consist on drawing random lines over the micrographs. The length of the intersection of the line with two grain-boundaries is L [17]. The average $\bar{L}$, **calculated from over 300 measurements** for each sintering condition, is multiplied by 1.56 to obtain the real (diameter) grain size, G . The magnetization dependence on the applied magnetic field and temperature curves were obtained using a superconductor quantum interference device (SQUID) from Quantum Design.

3. Results and discussion

3.1. Grain growth kinetics

Figure 1 shows the XRD patterns of samples sintered at 900, 1000 and 1100 °C for 1 and

14 h. The most intense peaks correspond to the wurtzite structure of ZnO, JCPDS No. 36-1451. However, on the XRD patterns of the samples sintered for short sintering time and/or temperature there are low intensity peaks, which are identified to be secondary phases formed by the solid reaction between ZnO and V_2O_5 . These phases are ZnV_2O_4 , JCPDS No. 75-0318 and $\gamma\text{-Zn}_3(\text{VO}_4)_2$, JCPDS No. 71-0021. The XRD pattern of the milled and dried powders exhibits only ZnO peaks, and from Scherrer analysis, the crystallite size is of 42 nm after 1 h milling (not shown). Further milling for 8 h reduces the crystallite size to 28 nm, but zirconia contaminations were found on the powder samples. Analysis by EDS reveals that ZnO grains in the pellets do not contain V, indicating that only grain boundary diffusion takes place and that the formation energy of the secondary phases is lower than that required to dissociate the V_2O_5 nanocrystals. As a consequence, no lattice diffusion of V into ZnO was observed.

Figure 1. XRD patterns of samples sintered at 900, 1000 and 1100 °C for 1 and 14 h.

Furthermore, the V concentration is not the same at the surface and in the middle of the ceramic. V-based secondary phases diffuse towards the outer faces of the pellet due to the low melting point of V_2O_5 of 690 °C. The diffusion coefficients of this decarburization-like diffusion process are reported in Ref. 16. It is important to remark that long sintering time (14 h) with a combination of high sintering temperature (1000 and 1100 °C) lead to a reduction of the formation of secondary phases, at least upon the detection limit of the XRD diffractometer.

In Fig. 2 are shown the SEM micrographs of the polished surface of samples sintered at

900, 1000 and 1100 °C for 1 and 14 h. The darker zones correspond to ZnO:V grains that have been detached from the surface. The Zn-V-O secondary phases nucleate at the interstitial sites between three or more grains. The grains have oblate shape typical of an abnormal (no faceting) growth observed in doped ZnO samples [18].

Figure 2. SEM micrographs and EDS mapping of the polished surface of ZnO:V ceramics sintered at 900 °C for (a) 1 h and (d) 14 h; at 1000 °C for (b) 1 h and (e) 14 h and; at 1100 °C for (c) 1 h and (f) 14 h. The green (left) panels correspond to the Zn mapping and the purple maps (right) the V distribution. The scale bar is 10 μ m.

This behavior is due to the liquid phase sintering process that takes place in the ZnO- V_2O_5 system as the melting point of V_2O_5 is 690 °C and the eutectic point in the ZnO- V_2O_5 phase diagram appear at 600 °C [19]. The liquid phase sintering promoter is $Zn_3(VO_4)_2$, which diffuses along the grain boundaries at the same time that induces the ZnO grain growth [20]. For each panel (a) – (f) in Fig. 2 are shown the EDS mapping of Zn and V demonstrating that secondary phases exist at the grain boundaries of well defined ZnO grains. The green panels (left) correspond to Zn mapping following the $L-\alpha_{1-2}$ transition of Zn atoms, while the purple panels (right) show the V mapping obtained from the $K-\alpha_1$ radiation of V.

An example of the evolution of the grain growth morphology for the sintering temperature of 1100 °C for 1, 2, 4, 6, 10 and 14 h is shown in Figs. 3(a) – 3(f). As 1100 °C is the highest used temperature, the amount of secondary phases is too small to be

seen by XRD patterns but EDS mapping in Fig. 2(f) depicts the existence of secondary phases at the grain boundaries.

Figure 4(a) shows the plot of the evolution of the grain growth for different sintering time and each temperature. The grain growth kinetics obeys to the phenomenological model [21]:

$$G^n = K_0 t \exp(-Q/RT) \quad (1)$$

Figure 3. An example of the grain growth evolution for ZnO:V ceramics at 1100 °C, for (a) 1, (b) 2, (c) 4, (d) 6, (e) 10 and (f) 14 h. The scale bar is 10 μm.

where n is the grain growth exponent, K_0 is the pre-exponential factor related to the experiment conditions, t is the sintering time, Q is the apparent activation energy, T is the absolute temperature, and R is the universal gas constant. This equation is reduced to the following expression for each temperature:

$$G = c \sqrt[n]{t} \quad (2)$$

which is used to fit the experimental data and to provide a first approximation and a guide to the eye of the measured grain size shown in Fig. 4(a). For a better accuracy on the calculation of n , the $\ln$ function is applied to Eq. (1) leading to the following

rearrangement:

$$\ln G = \frac{1}{n} \ln t + \frac{1}{n} \ln K_0 - \frac{Q}{nRT} \quad (3)$$

The logarithmic manipulation of the G and t axes is shown in Fig. 4(b). The fits were calculated using Eq. (3). The values of the slopes of the fitted lines are the inverse of n . Thus, the values of n are 5.6, 0.72, and 0.56 for sintering temperatures of 900, 1000 and 1100 °C, respectively. High values of n imply slow grain growth, even smaller than that of pure ZnO, which is $n = 3$ [22]. Our obtained values for the temperatures of 1000 and 1100 °C with $n = 0.72$ and 0.56 are similar to those of 0.63 - 0.83 found by Tsai et al. [10] and Hng et al., [21] for samples with lower V₂O₅ content, indicating that $1/n$ depends on the V₂O₅ concentration; the higher the V₂O₅ content, the higher the grain growth rate (the lower the value of n). However, at 900 °C, the grain growth is high only for short sintering time < 1 h, i.e., a rapid grain growth is observed from the nanoscale size of the milled powders to the microscale size of the grains of the ceramic shown in Fig. 2(a).

Figure 4. (a) Grain size vs. sintering time. The solid curves in (a) are the fits using Eq. (2). (b) Arrhenius plot of the data on (a). The linear fits are obtained using Eq. (3).

After this initial stage, for $t > 1$ h the thermal energy transferred to the sample due to the heating energy at 900 °C is scarcely larger than the activation energy, hence, a very low grain growth rate is observed as depicted in Fig. 4(a). It is well known that particles with large surface area/volume ratio have also a large surface free energy, which competes

with the formation energy; thus, a reduction of the surface area leads to a reduction of the total energy of the system. This issue explains the rapid grain growth at the very first stages.

To calculate K_0 and Q Eq. (1) is now manipulated in order to plot the $\ln(G^n/t)$ dependence of the inverse of the absolute temperature. For this purpose, we use the average value of n from the sintering temperatures of 1000 and 1100 °C. Thus Eq. (1) became:

$$\ln\left(\frac{G^{0.64}}{t}\right) = \ln K_0 - \frac{Q}{RT} \quad (4)$$

Calculating the values of G^n/t for all the data, we obtain the plot shown in Fig. 5. The plot shows some dispersion, in particular for the data corresponding to the sintering at 900 °C. To accurately calculate the mentioned parameters, the average value of $\ln(G^n/t)$ for each temperature is plotted and is shown in the inset in Fig. 5. In the case of the data for the temperature of 900 °C, the value for n of 5.6 was used. Surprisingly, the data coincide well with the linear fit from the data of 1000 and 1100 °C.

Figure 5. $\ln(G^n/t)$ vs. $1/T$ plot to calculate activation energy and pre-exponent factor. Each point in the graph of the inset represents the average value of the data points for each temperature.

This feature indicates that the activation energy is equal for all temperatures. With these data points, the equation of the straight-line fit was evaluated. The value of the slope corresponds to Q/R from where the activation energy Q is calculated to be 317.7 kJ/mol,

and the intersection with the vertical axis is $\ln K_0$ where $K_0 = 2.52 \times 10^{16} \mu\text{m}^{0.64}$.

3.2. Magnetic properties

The magnetic field dependence of the magnetization M - H curves are presented in Fig. 6(a) as two sets of curves: the as-measured M - H curves (with negative slope) and the M - H curves after the subtraction of the diamagnetic component of bulk ZnO (with positive slope). The used diamagnetic susceptibility of ZnO is $\chi_m = -0.33 \times 10^{-6} \text{ emu/gr}$ [23]) The curves correspond to selected ceramics where one can find the major difference on the sintering conditions, namely, those sintered at 900 and 1100 °C for 1 and 14 h. These samples will be named as x-y, where x corresponds to the sintering temperature (900 or 1100 °C) and y to the sintering time (1 or 14 hours). Hence, 900-1 corresponds to the sample sintered at 900 °C for 1 hour. The as-measured curves are dominated by the diamagnetic component of ZnO undoped grains. As commented previously, V from V_2O_5 only diffuse along the grain boundaries, as non-lattice diffusion has been detected over the threshold of 1 at.% of the EDS technique [16]. After the subtraction of the diamagnetic magnetization of the samples, using the mass of the sample and the χ_m of ZnO, we obtain the M - H curves where a positive slope, likely due to the paramagnetic contribution of V_2O_5 susceptibility ($\chi_m = 0.70 \times 10^{-6} \text{ emu/gr}$), dominates the shape of the loops as shown in Fig. 6(a) and, more clearly, in the inset showing a magnification of the first quadrant of the magnetic curves at high magnetic fields. The difference between the slope values of the curves is due to the different contributions of the paramagnetic nature of the secondary phases $\text{Zn}_3(\text{VO}_4)_2$ and ZnV_2O_4 , which are clearly present in the samples 900-1, 900-14 and 1100-1. The curve with lower slope is that of the sample 1100-14 in which the maximum FM magnetization has been measured. This feature (i.e. the lower slope value) indicates that this latest sample possesses a lower amount of secondary phases as depicted in the XRD patterns, upon the resolution limit of the diffraction technique.

The pure FM component of the samples has been obtained by mathematically subtracting a linear curve with positive slope to the M - H curves in Fig. 6(a). The final FM curves are shown in Fig. 6(b). One can observe that saturation magnetization is reached in all

samples at 1 T, and that the magnetization increases as we increase the sintering time and/or the sintering temperature. The highest saturation magnetization, M_s , of 0.9 Am^{-1} is obtained on the sample sintered at 1100°C for 14 h. This low value of M_s is due to the existence of FM ordering only at the grain boundaries of the ceramic and at the proximity to the secondary phases (which can hinder the FM coupling). The maximum measured magnetization can be compared to other systems in the form of thin films (e.g., $M_s = 11.22 \text{ Am}^{-1}$ for a V concentration of 2 wt.% where V ions are homogeneously distributed [24]) or nanoparticles (with a magnetization of 1.68 Am^{-1} with a V concentration of 2 at.% [26]). It is important to note that in the ZnO:V system synthesized in form of thin films or nanoparticles, the magnetization depends on the concentration of the V magnetic ions. This help to explain the low value of M_s in our samples, as the concentration of V is fairly low (for example, only 0.5 at.% in sample 1100-14) and that V atoms are additionally only located at the grain boundaries, whose thickness in ZnO ceramics is $\sim 2.5 \text{ nm}$ [25].

Figure 6. SQUID M - H curves: a) as measured and after the subtraction of the diamagnetic component from bulk ZnO. The inset represents the magnification of this latest set of curves at high magnetic fields. b) The pure ferromagnetic component of the samples.

The zero-field-cooled (ZFC) and field-cooled (FC) measurements in the interval of 5 to 350 K for two samples with opposite sintering conditions in time and temperature (samples 900-1 and 1100-14) are shown in Fig. 7(a) and 7(b), respectively. For the sample 900-1, the two ZFC and FC curves overlap perfectly, showing a typical paramagnetic behavior (with a marked increase of the magnetization at low temperatures), whereas the ZFC and FC curves of sample 1100-14 also present a FM contribution, indicated by the existence of a plateau followed by a decrease to zero at the Curie temperature (T_C).

Additionally, there is a thermal hysteresis, shown by the intersection of the curves in the interval of 245 and 310 K, as can be seen in the inset of Fig. 7(b). The onset of the reduction of magnetization with increasing temperature at 270 K in the FC curve and at 240 K in the ZFC curve may be associated to the T_C of some FM regions of the sample, probably due to different V concentrations as suggested by theoretical calculations of Mamouni et al. [26] where the T_C varies from 98 to 445 K for different V concentrations < 15 at.%. This issue will be analyzed later in this paper. It is noteworthy the absence of a blocking temperature in the ZFC curve in the considered range of temperatures, which could point out the presence of a superparamagnetic phase, at least upon the lowest measured temperature of 5 K indicates that FM clusters are too small indicating that V atoms forming the DMO are highly diluted [15].

The inverse of the susceptibility, $1/\chi$, of the FC curves in the interval 5 to 20 K is shown in Fig. 7(c). The behavior at higher temperatures does not show a linear trend, indicating that the sample is not purely paramagnetic, also FM ordering is present in both samples but with different values of magnetization (higher on the sample 1100-14). The intersection of the fitted lines of the $1/\chi$ curves with the temperature axis, the known paramagnetic Curie temperature (θ_p), is located -2 K and ~-0.5 K for the samples 900-1 and 1100-14, respectively, indicating a weak anti-FM coupling of the paramagnetic ions. The intersection of the fit line with the temperature axis considering a larger temperature interval produces lower θ_p , hence stronger anti-FM coupling. To evaluate the magnetic

moment of these V atoms from the slope of the fitted line, we used the following expression where the Curie constant, C , depends on the concentration of the magnetic ions:

$$C(x) = xC_0 = xN(g\mu_B)^2S(S+1)/3k_B \quad (5)$$

Figure 7. The ZFC and FC curves of the samples 900-1 and 1100-14 are shown in a) and b), respectively. The inset in b) is a magnification of the thermal hysteresis on the ZFC-FC curves of the sample 1100-14. In c) is shown the inverse of the susceptibility obtained from the FC curves for both samples. d) M - H loops before and after the thermal hysteresis; the inset shows the detail of the M - H loops at low magnetic fields.

Where g is the Landé g -factor, x is the atomic vanadium concentration, N is the number of magnetic ions per unit volume, μ_B the Bohr magneton, and k_B is the Boltzmann constant. For the two samples, 900-1 and 1100-14 with V concentrations of 2 and 0.5 at.% the magnetic moment per paramagnetic ions are $0.72\mu_B$ and $1.27\mu_B$, respectively, which can be compared to $3\mu_B$ for an isolated V^{2+} atom according to the Hund's rules or

with $3.46\mu_B$ for a spin only magnetic moment calculated from the expression $\sqrt{s(s+1)}$. The magnetic moment per magnetic ion of the ferromagnetically coupled atoms cannot be estimated from the M - H loops, as we cannot infer about the amount of the ferromagnetic and paramagnetic phases. Thus, the magnetic moment of the FM coupled atoms should be higher.

Finally, in Fig. 7(d) are shown the M - H loops of the sample 1100-14 at 240 and 320 K. The only difference between the two curves is the M_s value. In the inset is shown the shape of the loops at low magnetic fields, demonstrating the hysteresis for both curves, and therefore FM ordering still exists on the sample at 240 and 320 K. Additionally, no change is observed on the coercivity.

4. Conclusions

In this work, $Zn_{0.95}V_{0.05}O$ ceramics were systematically elaborated by sintering compressed ZnO and V_2O_5 nanopowders at different temperatures. The grain growth exponents for the sintering processes at 900, 1000 and 1100 °C are 5.6, 0.72 and 0.56, respectively. It is worth to note the extremely fast grain growth for the sintering at 1100 °C. The low activation energy leads to a faster grain growth at higher temperatures. The enhancement is attributed to the liquid-phase sintering process induced by liquid V_2O_5 with a melting point of 690 °C. The growth at 900 °C follows a rapid rate just at the first growth stages for $t < 1$ h. Afterwards, the growth is very slow as the thermal energy is scarcely larger than the activation energy. The magnetic properties of the ceramics revealed that the contribution of the paramagnetic nature of the secondary phases is strong. However, pure ferromagnetism associated to a DMO is obtained in all samples. The highest ferromagnetic signal is obtained on the sample sintered at 1100 °C for 14 h, which in turn is that with the lowest content of secondary phases.

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