Doping of ZnO with Mn or Co: Two different behaviours for the same synthesis approach

M. PEITEADO
Department of Electroceramics, Instituto de Cerámica y Vidrio, CSIC, 28049 Madrid, Spain.
*Corresponding author: Dr. MARCO PEITEADO Department of Electroceramics, Instituto de Cerámica y Vidrio (CSIC)
Kelsen 5, 28049 Madrid, SPAIN. Tel: +34-917355840 Fax: +34-917355843. E-mail address: mpeiteado@icv.csic.es

In the last years the research in ZnO has seen a period of intensive work which can be attributed to the new available synthesis methods and characterization techniques. New potential applications have thus emerged for ZnO-based ceramics, provided that a stable and reproducible doping would be achieved. However this still represents a major challenge. In this new trend, Mn and Co represent a couple of interesting candidates for the obtaining of new ZnO-doped structures. But although a lot of work has been done in the past with both systems, a detailed analysis of the specialized literature yet reveals a worrisome lack of knowledge about these materials. In the present contribution the diffusion behavior and the solid state reactivity of both Zn-Mn-O and Zn-Co-O systems is analyzed in order to determine the possibility of obtaining a homogeneous doping of ZnO. The obtained results indicate that, whereas a stable Co:ZnO solid solution is easily attainable, the achievement of a homogeneous Mn:ZnO solid solution would be restricted to severe experimental conditions that limit its application for practical purposes.

Keywords: ZnO, transition metal doping, diffusion, spinels, spintronics.

Dopado de ZnO con Mn o Co: dos comportamientos diferentes para un mismo planteamiento de síntesis

En los últimos años, la investigación en ZnO ha experimentado un periodo de intensa labor que bien puede atribuirse a los nuevos métodos de síntesis y a las nuevas técnicas de caracterización disponibles. En consecuencia han surgido nuevas aplicaciones potenciales para los materiales basados en ZnO, siempre y cuando se alcance un dopado estable y reproducible del cerámico. Sin embargo, esto es algo que todavía supone un serio reto. Dentro de esta nueva tendencia, el Mn y el Co representan un par de candidatos interesantes para la obtención de nuevas estructuras de ZnO dopado. Sin embargo, aunque se ha trabajado con ambos sistemas desde hace bastante tiempo, lo cierto es que un análisis detallado de la literatura especializada de los últimos años todavía revela un serio desconocimiento entorno a dichos materiales. En este trabajo se ha analizado la difusión y la reactividad en estado sólido de ambos sistemas, Zn-Mn-O y Zn-Co-O, con objeto de determinar si es posible obtener un dopado homogéneo del ZnO. Los resultados obtenidos indican que sí es posible conseguir una disolución sólida estable cuando se emplea cobalto como dopante, la obtención de una disolución sólida con manganeso sólo es posible bajo ciertas condiciones experimentales muy estrictas que limitan su aplicación práctica.

Palabras clave: ZnO, dopado con metales de transición, difusión, espinelas, espintrónica.

1. INTRODUCTION

The potential properties of semiconductor zinc oxide have been known for a long time and actually the past century have seen different periods of intensive ZnO research covering topics like growth, doping, transport, band-structure, on essentially bulk samples (1,2). Since the mid nineties a renaissance of this research on ZnO-based ceramics has been observed which essentially finds its basis on the new available synthesis methods and characterization techniques (3,4). As a result possibilities are now opened to obtain for example a material for blue/UV lasers, a diluted ferromagnetic material for spintronics and/or a transparent, highly conducting oxide as a cheaper alternative to ITO, among others (2). But although many of these applications are related to structures of reduced dimensionality like nanostructured assemblages, thin films, or epitaxially grown layers, in most of the cases a stable and reproducible doping is compulsory, and this still represents a major challenge. That is the case for example of spintronics, which represent a new generation of electronic devices that combine the complementary properties of ferromagnetic materials and semiconductor structures (5): in a so called diluted magnetic semiconductor (DMS) a stoichiometric fraction of the host semiconductor atoms is randomly replaced by magnetic atoms and the resulting alloy is semiconducting, but can possess well-defined magnetic properties that conventional semiconductors do not have. This was actually the initial prediction of Dietl and co-workers (6) but, obviously, the accomplishing of these materials would strongly depend on the thermal equilibrium solubility of the dopant in the host semiconductor. Pursuing this situation several systems have been investigated, among which those based in ZnO doped with 3d transition metal ions have shown the most promising results so far. More specifically
it has been reported that the wide band gap semiconductor ZnO could exhibit ferromagnetism with a Curie temperature (Tc) above room temperature when the oxide is doped with a few atomic percent of Mn or Co (7-12). It happens however that the specialized literature of the past decade comprises a nearly fifty-fifty split in the papers evidencing room-temperature ferromagnetic behaviour for these DMS materials and the papers in which such a possibility is completely rejected. Behind this lack of reproducibility some authors claim that much of the discourse could have been precipitated by inadequate materials characterization but in addition it suggest a worrisome lack of knowledge about these two systems, Zn-Mn-O and Zn-Co-O, with the issues of structure, composition, and secondary-phase formation not being carefully enough addressed (13).

In the particular case of the Zn-Mn-O system, the ionic radius of Mn²⁺ in tetrahedral coordination (0.66 Å) is relatively close to that for Zn²⁺ in the fourfold coordination of the wurtzite structure (0.60 Å) (14). This would suggest moderate solid solubility without phase segregation; however, in air atmosphere Mn²⁺ is stable only above 1000ºC (15), so the formation of secondary phase formation has to be as well considered, that will limit, if not prevent, the possibility of solid solution. Actually the first reports on the reactivity between ZnO and manganese oxides date back to the early 1960s and in distinct contributions Tuisant (16), Bates (17) and Driessens (18) started to suggest the existence of different unidentified spinel-like compounds: mixed oxides of the formula ZnₓMn₃₋ₓO₄+ᵧ where manganese would be present in different oxidation states and distributed in different proportions in the tetrahedral and octahedral sites of the spinel structure. Since these early works however few efforts have been made and it was not until 2006 when the topic was taken up again by Blasco and Garcia (19). These authors analyzed the low-temperature part of the Zn-Mn-O diagram in the Zn-rich region and as a result, new single phases with a spinel-like structure were found and isolated, again ascribed to the formula Mnₓₜ–ₓZnₓO₄. Although no specific data were provided for the high temperature range, the obtained results somehow indicated that the thermal evolution of this system should be determined by the formation and evolution itself of different secondary spinel-type phases and in turn by the different redox processes experimented by Mn ions in air. Accordingly the attainment of a homogenous Mn:ZnO solid solution is constrained to strict and sophisticated experimental conditions in which the 2⁺ oxidation state of manganese could be retained at low temperatures (20-24).

The situation for the Zn-Co-O system is not less controversial. For the predicted ferromagnetism some authors have for example suggested a carrier-mediated exchange mechanism in the ZnO matrix of a homogenous Co²⁺:ZnO solid solution (25-27); this implies atomic-scale dissolution of Co ions in wurtzite ZnO. However the substitution of Co²⁺ for Zn²⁺ in ZnO is not so obvious since under thermodynamic equilibrium the solubility of Co in the zincite oxide is only around 6.5 atoms % at 800 ºC, and then decreases with temperature (28). Some papers claim that the equilibrium solubility of Co into ZnO might be exceeded by using non-equilibrium film growth processes (28-30). However, the lack of reproducibility of the prepared ZnCoO films, even by the same deposition technique, shows how difficult it is to insert cobalt in the ZnO matrix in a controlled way. Hence the formation of secondary phases is again a possibility. The red-ox processes experimented by the Co²⁺/Co³⁺ couple under air atmosphere can lead to the formation of different compounds with different crystal structures, so again affecting the diffusion trends of the system.

So within this framework, the main goal of our work was to determine the possibility of obtaining a homogeneous doping of ZnO with these two species, manganese and cobalt. By systematically analyzing the diffusion behavior and the solid state reactivity of different prepared bulk samples, the aim was to fill the gaps in our knowledge with regards to these systems with potential applications in future technologies but whose phase diagrams, for example, are still in the research stage.

![Figure 1. Penetration profile of Zn into the MnₓOᵧ pellet after firing the couple at 700ºC for 12h. Dashed line on the left of the SEM image, highlights the thickness of the layer of new phase developed at the contact surface of the pellet.](image-url)
2. EXPERIMENTAL PROCEDURE

The solid state interaction of both the ZnO-MnO$_2$ and the ZnO-CoO$_2$ systems was first investigated by using the well-known technique of the diffusion couples. This technique has been proved quite successful for studying the interaction between different binary, ternary and multiphase ceramic systems (31). ZnO, MnO$_2$ and CoO analytical grade chemicals (Sigma-Aldrich) were used as raw materials to prepare the pellets of the couples. The preparation of the couple is described elsewhere (32): a 20 mm diameter base of ZnO powder was first pressed at 50 MPa; subsequently a 6 mm diameter pellet of MnO$_2$ or CoO powder, previously pressed at 200 MPa, was placed over this base, and the die was filled with more ZnO powder till the cobalt pellet was plenty covered. The whole ensemble was pressed at 250 MPa. The diffusion couple thus obtained was fired in air atmosphere at temperatures ranging from 600 to 1000 ºC with 12 hours dwell time. Up to five samples were fired at each temperature.

Following the results of the diffusion analyses, the thermal evolution of both systems was investigated on powders obtained by a highly reactive co-precipitation method. Polycrystalline samples with nominal composition Zn$_{1-x}$TM$_x$O (with TM = Mn or Co and x = 0, 0.01, 0.02, 0.05, 0.1 and 0.2) were prepared via a single-source oxalate precursor which ensures random atomic-scale mixing of the involved ions (25). The precursor Zn$_{1-x}$TM$_x$(C$_2$O$_4$)$_2$·2H$_2$O was obtained by room temperature co-precipitation with oxalic acid of aqueous solutions of the respective acetates: Zn(CH$_3$COO)$_2$·2H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O and Co(CH$_3$COO)$_2$·4H$_2$O. Reagent-grade raw materials (Sigma-Aldrich) were used in all cases. The precipitated oxalate was calcined at 400ºC to cleanly decompose it into the corresponding oxide. More details about the synthesis method are described elsewhere (33). In order to understand the nature of the involved phases the calcined powders were fired at temperatures ranging from 400 to 1300ºC using different dwell times. For a more detailed structural analysis pellets were also prepared that were cautiously introduced into the furnace once the heating temperature was reached; at that temperature they were subjected to a 100 hours of dwell time and finally they were rapidly quenched in liquid nitrogen to freeze them in a high-temperature state.

Characterization of the couples (contact surface and interior of the respective pellets) was carried out by means of Energy Dispersive Spectroscopy microanalysis (EDS) by using a Cold Field Emission-Scanning Electron Microscope (Model S-4700 Hitachi) and by X-Ray diffraction (XRD) on a Bruker AXS Endaevor 4 Diffractometer. Since the low firing temperatures impede to achieve dense enough pellets, samples were not polished to avoid any contamination of the couples during this process. Instead, samples were fractured and pellets were carefully separated, and problems arising with topology were overcome by the use of a double-tilt sample holder in the microscope.

The composition of the samples after the precipitation process was verified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Thermo Jarrell Ash Atomscan 25 Spectrometer. The sintered powders and pellets were ground and characterized by XRD and transmission electron microscopy (TEM). For the XRD profile analyses, step-scanned patterns were collected between 15 and 65º on a Bruker AXS Endaevor 4 Diffractometer in steps of 0.02º and a counting time of 12s per step. The lattice parameters were estimated by fitting the powder XRD profiles, using the

Figure 2. Microstructure of Zn$_{0.8}$Mn$_{0.2}$O sample calcined for 12 hours at 700ºC. Left: Bright field TEM image showing big ZnO particles together with the agglomerates of small particles of secondary phase. Right: Magnified part of the small particles and the corresponding SAED pattern taken from these agglomerates, indexed according to a spinel related structure (cubic, a = 0.835 nm).
nonlinear least-squares method. For the TEM investigations the samples were examined by a field-emission electron-source High-Resolution Transmission Electron Microscope HR-TEM Jeol 2010 F equipped with an EDS microanalysis (LINK ISIS EDS 300). In the particular case of the Zn-Mn-O system, the variations of the Mn oxidation states inside the investigated phases were analyzed employing Electron Energy-Loss Spectroscopy (EELS) on an EELS system (Gatan DigiPEELS 766). For detailed EELS (ELNES) analysis of the Mn-L\(_2,3\) ionization edges the microscope was operated at 200 kV in a diffraction mode (image coupling). More details of the working conditions for the EELS characterization are described elsewhere (34,35).

3. RESULTS AND DISCUSSION

3.1 Zn-Mn-O system

The analysis of the diffusion behaviour of the ZnO-MnO\(_2\) couple revealed several interesting features. First, just short range surface diffusion of both manganese and zinc species into the respective ZnO and MnO\(_2\) pellets was observed below 700ºC; this obeys to an energetic requirement but is as well related to the differences between the wurtzite and the rutile-type crystal structures of, respectively, ZnO and MnO\(_2\) (32). Above this temperature the reduction of Mn (IV) to Mn (III) and the subsequent formation of Mn\(_2\)O\(_3\) (36), opens the possibility for further diffusion. However, as a result of an avalanche diffusion of zinc into the Mn\(_2\)O\(_3\) structure, a new phase layer develops at the contact surface of the manganese oxide pellet and this phase closes the paths for further diffusion in both directions: Figure 1 depicts the penetration profile of Zn into the Mn\(_2\)O\(_3\) pellet after firing the couple at 700ºC for 12h; the new phase formed at the contact surface of the pellet is highlighted on the left side of the SEM image and, as observed, beyond this layer no more zinc was detected inside the Mn\(_2\)O\(_3\) pellet. The characterization of this new layer by a combination of XRD and SEM-EDS revealed a spinel-like structure with a variable content of zinc and manganese as the temperature was increased. Furthermore, initially the layer is composed by a mixture of cubic and tetragonal spinels, but above 900 ºC, just a tetragonal spinel is present at the interface forming that physical barrier for further diffusion of both zinc and manganese species. In the interval between 700 and 900ºC, some Mn(III) also diffuses into ZnO pellet, although no homogeneous solid solution was ever formed.

The investigation of the Zn\(_{1-x}\)Mn\(_x\)O nominal system was then followed on the samples prepared by the highly-reactive co-precipitation method. Initially the analyses of the powder samples by means of XRD showed that already from the decomposition of the oxalate precursor (around 400ºC), a binary system is obtained comprising ZnO and a secondary phase with a spinel-like structure. Characterization of the samples in the Transmission Microscope confirmed this finding. In the Bright Field Image of Figure 2, corresponding to the Zn\(_{0.8}\)Mn\(_{0.2}\)O sample calcined for 12 hours at 700ºC, two types of particles can be observed: particles in shape of hexagonal prisms and smaller particles arranged together in the form of large platelet-like agglomerates. The general appearance of the two-phase system did not change substantially with temperature, apart from the increase in particle size. Selected area electron diffraction (SAED) pattern taken from the larger particles matched with the ZnO wurtzite structure (37). Meanwhile the SAED pattern taken from the agglomerates of the smaller particles showed diffraction rings characteristic of a polycrystalline sample that were indexed according to a spinel structure, see Figure 2. EDS of individual particles of these agglomerates indicate both the presence of zinc and manganese, again with a concentration changing with the starting composition and the heating temperature. To definitely clarify this point, the microstructural characterization was extended to the pellets treated and quenched as indicated in the experimental section. The result is illustrated in the tentative scheme of Figure 3 in which different fields of stability are obtained for different Mn\(_{3-x}\)Zn\(_x\)O\(_4\) spinel phases, with manganese

\[\text{Figure 3. Stability regions in the Zn-Mn-O system in air as a function of temperature and composition. T1: tetragonal ZnMnO\(_2\) spinel, C: cubic spinel, T2: tetragonal spinel, and Z: hexagonal ZnO. White dots represent the composition of C, T1 and T2 phases as measured by EDS microanalysis on some selected samples.}\]

\[\text{Figure 4. Degree of the tetragonal distortion of the T2 phase as a function of temperature for the tested Mn\(_{3-x}\)Zn\(_x\)O\(_4\) compositions (the data at 1300ºC already correspond to the T1 phase).}\]
in different oxidation states and distributed in different proportions in the tetrahedral and octahedral sites of the spinel structure. More specifically it was observed that for \( x > 1 \), the system evolves from a cubic spinel at low temperatures to different tetragonal spinels as the temperature is increased. The tentatively suggested boundaries between the different stability regions were verified by ICP-AES analyses and EDS measurements on some selected samples (35).

The logical question was then: what is going on behind such thermal evolution and the observed transformations? We found out that all these results should be interpreted in terms of the amount of Mn\(^{3+}\) present in the Mn\(_x\)Zn\(_{3-x}\)O\(_4\) structure. Mn\(^{3+}\) is an active Jahn-Teller ion (d\(^5\)) which in octahedral coordination leads to a strong geometrical distortion of the cell. In the spinel structure Mn\(^{3+}\) ions preferentially locate at the octahedral sites (18), so the more the Mn\(^{3+}\) in the spinel composition the higher the distortion of the molecule. In our case as the temperature goes higher more Mn\(^{4+}\) is reduced to Mn\(^{3+}\) and, as a consequence, the distortion increases passing from the cubic phase to the different tetragonal structures as observed in Figure 3. The process is accompanied by the precipitation of ZnO, and culminates around 1300°C when all manganese is eventually reduced to Mn\(^{3+}\) and we have then the higher tetragonal distortion (T1 phase in Figure 3).

To corroborate this scenario we estimated the cell parameters of the involved phases: for all compositions with \( x > 1 \) the increase in the temperature leads to a decrease in the value of the parameter \( a \) as well as to a marked increase in the value of parameter \( c \) (35). Furthermore, Figure 4 depicts the evolution of the degree of distortion of the tetragonal cell for these compositions, and again a gradual increase is obtained with temperature which concurs with the observed transformations in Figure 3. Composition with \( x = 1 \) represents a particular case since in this phase all manganese is in the \( 3^+ \) state for the whole temperature range, so it always shows the higher distortion (T1 phase).

Finally in order to experimentally verify the changes in the Mn\(^{4+}\)/Mn\(^{3+}\) ratio of the spinel phases quenched from different temperatures, a detailed fine-structure analysis was conducted by means of EELS. Due to its high spatial resolution capability, EELS can be used to investigate the valence states of transition metal dopants at the nanometer scale, especially in heterophase materials (38). In particular we used Energy-loss near-edge structures (ELNES) since there is one characteristic feature, the intensity ratio \( L_3 \) to \( L_2 \) of the \( L_{2,3} \) ionization edge of the transition metal, which strongly depends on the oxidation state of the excited atoms (39). In our samples, the Mn-\( L_{2,3} \) ionization edge is due to the excitations of the 2p\(^{1/2}\) and 2p\(^{3/2}\) electrons into the narrow band of unoccupied 3d energy states, and it has been shown that its intensity increases as the oxidation state of Mn decreases (40). With this mind, different experimental EEL spectra were collected from the spinel phases of the Mn\(_{1.33}\)Zn\(_{1.67}\)O\(_4\) representative composition; as it can be observed in Figure 5 the intensity of the \( L_3 \) to \( L_2 \) manganese ratio gradually increased with the temperature, so indicating...
that increasing proportion of Mn (IV) is reduced to Mn (III) with increasing temperatures. Therefore it can be concluded that a decrease in the manganese oxidation state is certainly taking place, which governs the thermal evolution of the Zn-Mn-O system.

3.2 Zn-Co-O system

The situation was completely different for the second system under analysis, the Zn-Co-O system. As before, we first investigate the solid state diffusion and the reactivity of the couples, but this time no secondary phase was developed at the contact surface of the diffusion pellets for the whole range of tested temperatures. The data depicted in Figure 6 represent the maximum diffusion distance as a function of temperature for the Zn and Co species into the corresponding pellets of the couple. By maximum diffusion distance we assume the distance beyond which no more diffusion is detected by EDS (41). As observed, two different patterns are obtained for Zn and Co species. Whereas the diffusion of Zn into the Co xOy pellet continuously increases from 700ºC, the diffusion of Co reaches a maximum at 800ºC and then continuously decreases with temperature until 1000ºC, when it is completely inhibited. The dashed lines in the plot of Figure 6 represent the temperature values at which the transformations between the CoO and Co3O4 compounds take place (42) and as observed they accurately concur with the temperatures at which the diffusion of Co takes place. Accordingly, it seems that the diffusion behavior in this system, particularly in the case of cobalt ions going into the ZnO structure, is determined by these transformations between the two cobalt oxides. Looking thoroughly into the crystal structures of both compounds (14, 15) it was found that temperatures higher than those tested in this study are required for the Co3 ions to release the rock-salt arrangement of cobalt monoxide. On the contrary, cobalt ions can easily leave the spinel arrangement of the Co3O4 compound, so they diffuse into the ZnO wurtzite structure (they do diffuse as Co2 since there is no evidence of Co3 ions being stable in the tetrahedral coordination of the wurtzite lattice (14)). Such diffusion has however a limited temperature range since as observed at high temperature Co2 reduces back to Co0 and this leads again to the formation of the rock-salt structure.

In other words, whereas just energetic requirements are behind the diffusion of zinc ions into the cobalt oxide, the diffusion of cobalt into ZnO strongly depends on the crystal structure of the starting cobalt oxide. In this sense, an increase in the reactivity of the system might be critical to obtain reliable Co2:ZnO solid solution materials. Working again with samples prepared by the highly-reactive oxalate synthesis method it was found that now, opposite to the previous Zn-Mn-O system, it is certainly feasible to obtain a homogenous Co2:ZnO solid solution. Figure 7 resumes the SEM-TEM-EDS characterization of the Zn0.99Co0.01O representative composition. As observed, already after calcining at 400ºC for 4 min (decomposition of the precursor) a homogenous soft green colored powder is obtained which as revealed by TEM consisted of larger particles embedded into agglomerates of smaller particles (Figure 7b). EDS of both, smaller and larger particles shows presence of Co dissolved in the ZnO matrix. Furthermore,

Figure 7. a) FE-SEM micrograph of the Zn0.99Co0.01O co-precipitated powder after calcination at 400ºC for 4 min. b) Bright field TEM image of this same powder. c) FE-SEM micrograph of the Zn0.99Co0.01O sample treated at 1100ºC/2h and d) EDS analysis of this sample. The black dot in image c) shows a representative area with the EDS analyses were performed.
the calcined powder was pressed and sintered at 1100°C/2h and the FE-SEM characterization showed again the absence of secondary phases (Figure 7c). The EDS analyses on polished surface yielded 1 atom % of Co inside the ZnO grains, so evidencing the existence of a stable Coii:ZnO solid solution (Figure 7d). Therefore, from these results it can be inferred that in the co-precipitated samples the formation of the CoO rock-salt structure from the Coii precursor is inhibited. Instead, the Coii ions diffuse into the ZnO wurtzite structure at lower temperatures; once inside they do not segregate as Coii ions to the grain boundaries, no spinel phase (whatever Co3O4 or ZnCo2O4) is thus formed and the subsequent transformation to the rock-salt structure is therefore avoided. Hence a stable Coii:ZnO solid solution can be obtained up to high temperature.

4. CONCLUSIONS

The different analyses performed on the present contribution have shown that a different behaviour should be expected when bulk ZnO is doped with Mn or with Co. In the Zn-Mn-O system several stability regions have been described as function of temperature and composition, but no trace of homogeneous Mn:ZnO solid solution is ever detected. The obtained results indicate that the continuing Mn (IV) to Mn (III) reduction triggers the observed evolution through the formation of different MnxZnyO phases. The possibility of a homogeneous Mn:ZnO solid solution is restricted to severe experimental conditions in which the oxidation state II of manganese could be retained at low temperature. On the contrary the analysis of the solid state interaction in the Zn-Co-O system reveals that the formation of a stable Co:ZnO solid solution is feasible, although it is determined by the crystal structure from which Coii ions diffuse into the wurtzite lattice; no diffusion can be expected from the rock-salt structure of cobalt monoxide, so the formation of this compound must be avoided to achieve reliable Coii:ZnO solid solution materials.

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