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Diffusion and reactivity of ZnO–MnO$_x$ system

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Abstract

The solid state interaction between ZnO and MnO$_x$ in air was investigated at different temperatures by means of the diffusion couple technique. No diffusion is observed at temperatures below 973 K. Above this temperature, Mn(IV) is already reduced to Mn(III) and the subsequent formation of Mn_2O_3 impels the diffusion of manganese into the ZnO pellet. However, it never enters the wurtzite lattice, so no homogeneous Mn:ZnO solid solution is formed. Simultaneously, Zn greatly diffuses in the manganese pellet, and as a consequence, a new phase layer develops at MnO$_x$/reaction zone interface. A mixture of cubic and tetragonal spinel-type phases initially comprises this layer. However at higher temperatures, the tetragonal $ZnMn_2O_4$ spinel is the unique phase present in the interface, and it forms a physical barrier for further diffusion of both zinc and manganese species in the respective pellets of the couple. Differences arising between ZnO, MnO_2 and Mn_2O_3 crystal structures are behind these diffusion behaviors.

Keywords: ZnO; Diffusion couples; Spinel; Solid state chemistry; Magnetic semiconductors

1. Introduction

Materials for spintronic devices combine the complementary properties of ferromagnetic material systems and semiconductor structures. Dietl et al. [1] were the first to predict ferromagnetic order above room temperature in III–V and II–VI-based *diluted magnetic semiconductors* (DMS), in which a stoichiometric fraction of the host semiconductor atoms is randomly replaced by magnetic ions. This prediction triggered a worldwide search for new DMS materials and so far one of the most promising results has been found for the system Mn:ZnO [2–4]. However, looking thoroughly into the literature, most of the results and the provided explanations are contradictory, with some reports evidencing room temperature ferromagnetic behavior and some others presuming its absence [5–8]. Behind these discrepancies, it is found that the mechanism leading to ferromagnetic ordering is still far from being understood. But also, disagreements arise because the success of theoretical predictions falls on the formation of a homogenous Mn:ZnO solid solution, and up to now, there is no clear evidence that this could be easily achieved in the proposed ceramic diluted systems. For example, leaning on the similarity between Zn^{2+} ionic radius and the radius of the metal impurities, some authors support the formation of Mn:ZnO solid solution in ZnO/MnO_2 mixtures prepared by a conventional solid state route [2]. In analogous experimental conditions other authors however found no manganese entering in the ZnO wurtzite structure; it was rather zinc which diffused into the grains of dopant MnO_2, giving place to segregation of secondary phases that will limit, if not prevent, the possibility of solid solution [9]. Besides the system is even more complex since in air atmosphere MnO_2 self-reduces with temperature to give Mn_2O_3 first and Mn_3O_4 later [10]. More recently, room temperature ferromagnetism has been also found in MnO_2-doped polycrystalline ZnO samples treated at very low temperatures [11] as well as in ZnO/MnO$_x$ multilayers obtained by pulsed laser deposition [12]; however, a different mechanism is proposed in these studies which is more related to an interface phenomenon and to the possibility of Mn for diffusing and coexist in different oxidation states. Furthermore, according to these results,

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no Mn-doped ZnO is in fact obtained, but rather a Zn-doped MnO_x diffusion zone with a not well-defined stoichiometry. In other words, it seems like not even the diffusion behavior of the system is known and a clear picture of the ZnO/MnO_x diffusion guidelines remains to be described. In the present contribution, we face this goal 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 [13–15]. While using it, we are taking into account that when reactants are not in direct contact, the reaction is entirely dependent on the diffusion of reactants [16]. The information here provided, although not directly related to the preparation of DMS systems, will help in the current discussion on the existence of ferromagnetic ordering in ZnO doped with transition metal oxides. Besides it offers some interesting data for the solid state chemistry community taking into account that the phase diagram of ZnO/MnO_x pseudo-binary system is still the source of research.

2. Experimental procedure

ZnO and MnO_2 analytical grade chemicals (Sigma-Aldrich) were used as starting powders to prepare the pellets of the diffusion couple. However, due to the mentioned reduction processes of MnO_2 compound, the initial MnO_2 pellet will be referred from now on as the MnO_x pellet. Fig. 1 illustrates a scheme of the prepared couple. A 20 mm diameter base of ZnO powder was first pressed at 50 MPa; subsequently, a 6 mm diameter pellet of MnO_2 powder, previously pressed at 200 MPa, was placed over this base, and the die was filled with more ZnO powder till the manganese pellet was fully covered. The whole ensemble was pressed at 250 MPa. The diffusion couple thus obtained was fired in air atmosphere at temperatures ranging from 773 to 1273 K with 12 h dwell time. These time–temperature conditions were chosen on the basis of the experimental schedules applied to obtain DMS materials according to the literature [17]. Up to five samples were fired at each temperature.

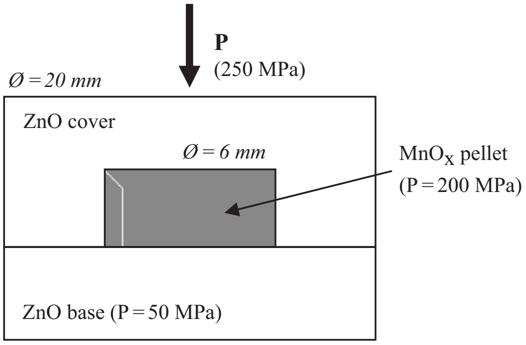

Fig. 1. Preparation of the ZnO/MnO_x diffusion couple (see explanation in the text).

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 Endeavor 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. Besides there was a risk that new phases formed at the interface of the two-phase ceramic could be removed with polishing. Instead of that, 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.

3. Results

EDS analyses of samples fired at 773 K for 12 h show no evidence of manganese going inside zinc oxide pellet. In the same way, it seems like this thermal treatment is not enough to provoke the diffusion of zinc into MnO_x pellet, at least in such a couple-type assembly (see Fig. 2). In addition, XRD analyses bring about the same spectra for the interior and the contact surface of the respective pellets, i.e., the same peaks of hexagonal wurtzite are detected inside and in the surface of ZnO, and the same peaks of cubic Mn_2O_3 and tetragonal MnO_2 are obtained in both regions of manganese oxide pellet (Fig. 3); the presence of Mn_2O_3 at this temperature is in agreement with the expected reduction of the starting Mn(IV) to Mn(III) [10]. Firing at 873 K does not produce a much more different situation. Still no diffusion is detected in any direction, and XRD analyses show again the same crystalline phases for both the interior and the contact surfaces of the respective pellets. The only remarkable difference is that only peaks of single Mn_2O_3 phase are now detected in the spectra of manganese oxide pellet, indicating that complete reduction of Mn(IV) could be achieved after heating 12 h at this temperature.

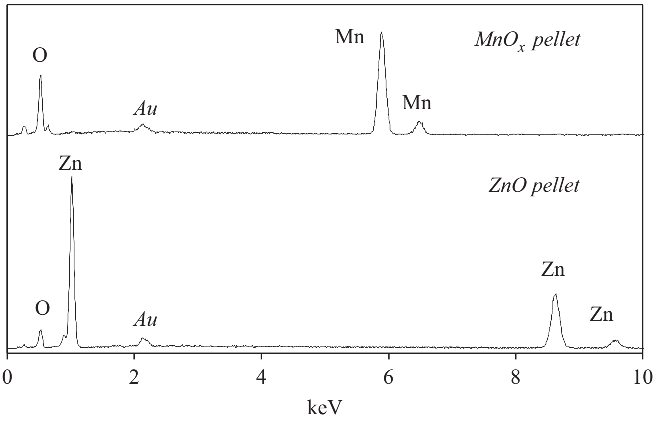

Fig. 2. EDS spectra of the contact surface of MnO_x and ZnO pellets after firing the couple at 773 K for 12 h.

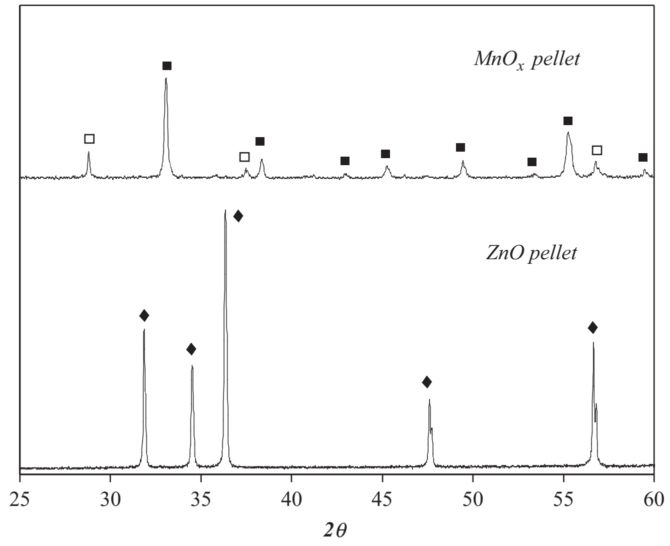

Fig. 3. XRD analysis of ZnO and MnO_x pellets after firing the couple at 773 K for 12 h. In both cases, the same spectra were obtained at the interior and the surface of the respective pellets: (◆) ZnO, (■) Mn_2O_3 and (□) MnO_2.

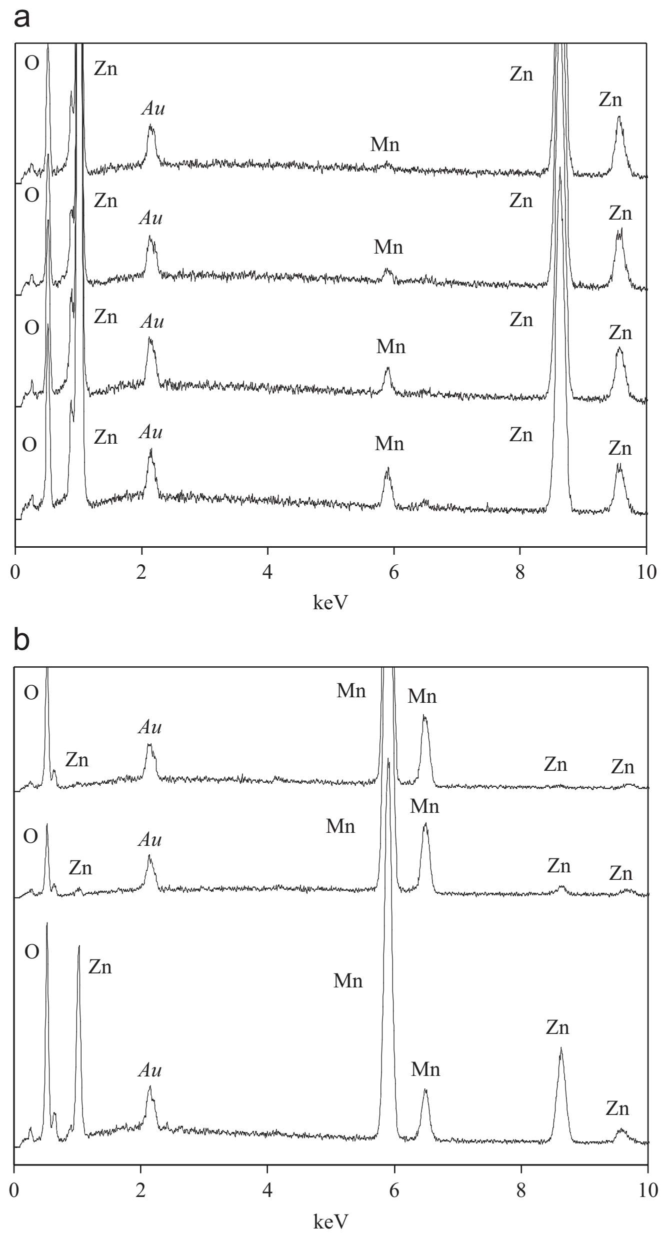

Fig. 4. EDS analyses of the couple fired at 973 K for 12 h performed at different distances from the contact surface. (a) ZnO pellet. From below: spectra of the contact surface, 20 μm inside, 50 μm inside and 100 μm inside. (b) MnO_x pellet. From below: spectra of the contact surface, 15 μm inside and 30 μm inside.

The situation noticeably changes when increasing the temperature to 973 K, since now both manganese and zinc are, respectively, detected in ZnO and MnO_x pellets. In the case of ZnO pellet, quantification of EDS signals yields around 2 at% of Mn in the vicinity of the contact surface, although a significant degree of data scattering was observed in these measurements. This percentage decreases with distance to the surface, and around 100 μm inside, the presence of Mn is roughly symbolic (Fig. 4a). On the other hand, the diffusion of Zn yields a massive percentage in the surface of MnO_x pellet, up to 17 at%; then it drastically reduces with distance, to completely disappear after 30 μm inside the pellet (Fig. 4b). This is more clearly seen in the Zn profile of penetration showed in Fig. 5, which evidences a very large amount of zinc in the first 15 μm of MnO_x pellet. In addition, FE-SEM image in this figure also reveals the formation of a layer of different coloration on the surface of the pellet (10–15 μm thickness). It follows then that the reaction of new phase formation is taking place at the MnO_x/reaction zone interface. These results were corroborated by XRD analyses. Once again spectra of ZnO pellet show the same peaks of hexagonal ZnO for both the interior and the contact surface of this pellet. From the analysis of these spectra, no substantial changes were observed on the lattice parameters of wurtzite structure, so indicating that the Mn detected by EDS is rather located at grain boundaries and not going into solid solution. With regards to the spectra of MnO_x pellet, again cubic Mn_2O_3 is the only phase observed in the interior of the pellet, but peaks of new phases are now detected in its surface (Fig. 6). Most of the peaks correspond mainly to tetragonal $ZnMn_2O_4$ phase, which is known to have a *normal* spinel structure with Zn^{2+} and Mn^{3+} ions, respectively, located in tetrahedral sites and octahedral sites [18]. But also some peaks can be ascribed to $ZnMnO_3$ compound [19–21], which crystallizes on a cubic symmetry with lattice parameter $a \sim 8.35$ Å (JCPDF file no. 19-1461); the use of highly reactive precursors has recently shown that this cubic phase has a spinel structure since the allowed reflections clearly agree with the *Fd*-3*m* group [22,23]. New experiments are in progress to more precisely define the exact formula of this cubic phase, but the fact is that these two Zn–Mn–O phases ($ZnMn_2O_4$ and "$ZnMnO_3$") can be described under the nominal composition $Mn_{3-x}Zn_xO_4$ ($1 \leqslant x \leqslant 2$), with manganese in different oxidation states and distributed in different proportions in

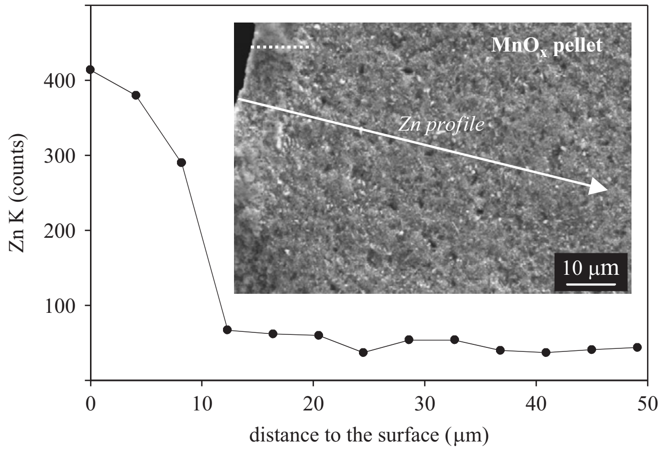

Fig. 5. Penetration profile of Zn into MnO$_x$ pellet (couple fired at 973 K for 12 h). Dashed line on the left of SEM image highlights the thickness of the layer of new phases formed at the contact surface of the pellet.

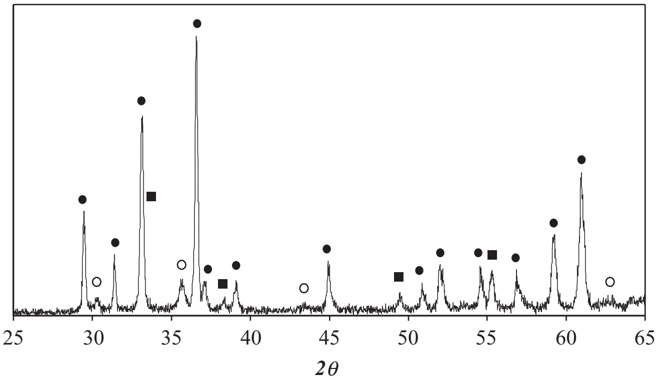

Fig. 6. XRD spectra of the contact surface of MnO$_x$ pellet after firing the couple at 973 K for 12 h: (●) $ZnMn_2O_4$, (○) $ZnMnO_3$ and (■) Mn_2O_3.

the tetrahedral and octahedral sites of the spinel structure [22]. The role of these secondary phases on the ferromagnetic response of nominal $Zn_{1-x}Mn_xO$ systems is still the source of discussion, but up to now none of these pure phases has been reported to be magnetic at room temperature [24].

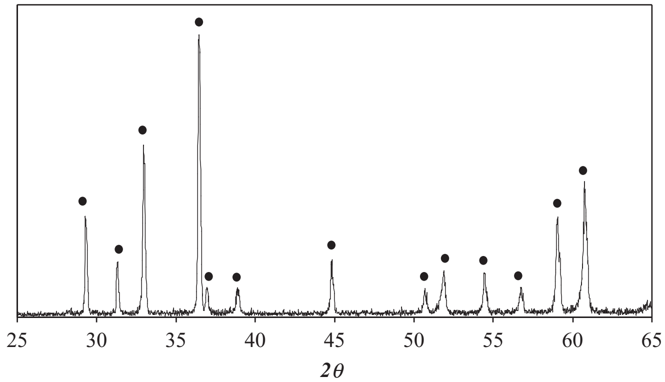

Fig. 7. XRD spectra of the contact surface of MnO$_x$ pellet after firing the couple at 1173 K for 12 h. All peaks now belonging to $ZnMn_2O_4$ phase.

Increasing the temperature to 1073 K does not promote substantial changes in the obtained analyses, but a new interesting behavior is observed when going to 1173 K. As in the previous temperatures, ZnO is highly detected in the surface of MnO$_x$ pellet, being drastically reduced after 10–15 μm inside (similar profile as in 973 K). EDS analyses yields a Mn to Zn ratio slightly above 2, close to the ratio in $ZnMn_2O_4$ composition, and XRD of the contact area now shows peaks corresponding only to this tetragonal spinel phase (Fig. 7). Back-scattered electrons image in Fig. 8 again shows the presence of a layer of different composition at the contact surface of MnO$_x$ pellet. But the most interesting finding is that now no trace of Mn is detected by EDS in the pellet of zinc oxide, neither inside nor in the contact surface. Therefore, it seems that once the formation of the tetragonal spinel phase is completed, this phase forms a physical barrier in the surface of the MnO$_x$ pellet which impedes the diffusion of manganese into ZnO.

Finally, the same behavior was observed for the samples treated at 1273 K, with the formation of the spinel layer at the surface of MnO$_x$ pellet and no diffusion of Mn into ZnO. In fact, although we did not make further tests, it is expected that such situation will prolong to higher temperatures since the stability of the $ZnMn_2O_4$ spinel-like phase is known to extend to temperatures above 1673 [19]. Moreover, recent studies also show the possibility of a partial reduction of Mn(III) to Mn(II) occurring in $ZnMn_2O_4$, leading to the formation of a solid solution of Mn(II) ions inside the spinel structure [25]. The formation of this solid solution, in which the amount of Mn(II) ions should increase on increasing more and more the temperature, will extend the stability of the spinel phase at very high temperatures and will also contribute to block the paths for further diffusion along the ZnO–MnO$_x$ interface [25].

4. Discussion

According to these results, it is then possible to outline a scheme of the diffusion trends in the ZnO–MnO$_x$ couple. Temperatures around 973 K are required to provoke the diffusion of both manganese and zinc into the respective structures. Obviously, this obeys to an energetic requirement, but it is also related to the structure of the crystalline phases present in the system. ZnO has a wurtzite structure in which Zn(II) cations are four-fold coordinated with ionic radius of 0.60 Å, whereas MnO_2 possesses a rutile-type structure with Mn(IV) in six-fold coordination and ionic radius of 0.53 Å [26]. When going to tetrahedral coordination, the ionic radius of Mn(IV) decreases to 0.39 Å [26]. This fact, in addition to the considerable charge mismatch, makes rather unfeasible the substitution of Mn^{4+} for Zn^{2+} in the ZnO the lattice. On the other hand, diffusion of Zn into MnO_2 is even more hindered since the rutile structure is quite compact, with a small amount of interstitial positions. The ionic radius of Zn^{2+} increases up

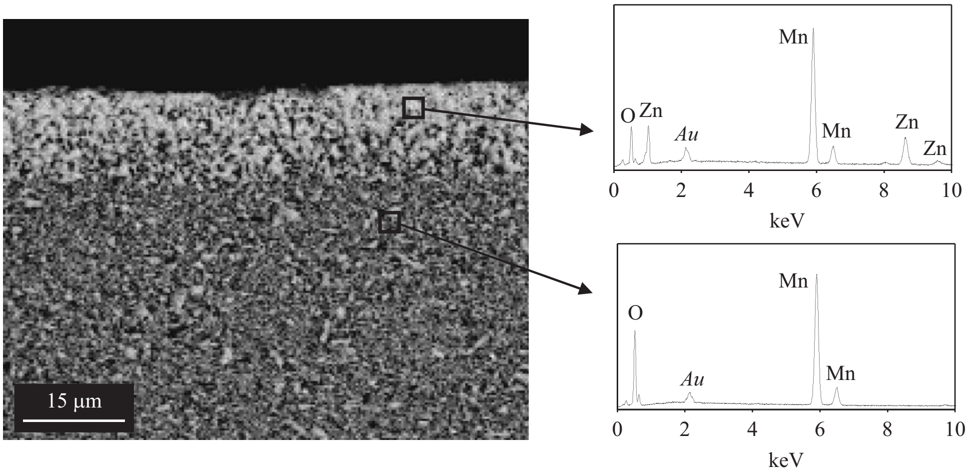

Fig. 8. BEI-SEM image and EDS spectra of MnO_x pellet after firing the couple at 1173 K for 12 h.

to 0.74 Å in octahedral coordination [26] so again substitution on Mn sites can be entirely discarded. Hence, whenever ZnO and MnO_2 are the phases present in the system, just short range surface diffusion should be expected.

But the situation is different when Mn_2O_3 is formed above 873 K. This compound has a bixbyite structure in which Mn(III) ions are six-fold coordinated. The ionic radius is 0.58 Å in low spin configuration and 0.64 Å in high spin configuration [26]. Both the charge mismatch and the ions size are now more similar so, theoretically, diffusion of Mn(III) into ZnO structure could be more favorable. However, there is no evidence of Mn(III) being stable in tetrahedral coordination [27]; therefore, once again substitution into ZnO lattice is impeded and manganese could only settle in the interstices of wurtzite structure. In other words, although Mn(III) diffuses better than Mn(IV) through the surface and grain boundaries of ZnO grains (it is detected far inside the ZnO pellet), again no solid solution is obtained. Thus, when we make an EDS spot analysis on a single ZnO grain no Mn is detected, but it does when the analysis is extended to a wider area. This comes to explain the scattering of data found on the sample fired at 973 K. With regards to the diffusion of Zn^{2+} into manganese pellet, it seems like this cation diffuses more easily through the surface and lattice of Mn_2O_3. In fact, it happens that the transformation of tetragonal MnO_2 to cubic Mn_2O_3 entails a dimensional change which promotes the formation of micro-cracks and even the fracture of grains in smaller units. Subsequently, new highly reactive interfaces are formed and then an *avalanche* effect is observed: at 973 K, Zn diffusion is activated in a system with a lot of new paths to diffuse, and as a result of this interaction, a new phase layer develops at the contact surface of manganese pellet. Two spinel-type phases initially form this layer, but as long as the reduction of manganese proceeds and the diffusion of Zn progresses, the tetragonal $ZnMn_2O_4$ spinel becomes the only phase at higher temperatures; furthermore, once the formation of $ZnMn_2O_4$ is completed, the paths for further diffusion are closed and no zinc and no manganese are ever detected inside Mn_2O_3 and ZnO, respectively.

Therefore, no trace of Mn:ZnO solid solution is found to be formed in this binary system for the whole temperature range. This in addition to the fact that the formed Zn–Mn–O phases are not expected to allow long range ordering of magnetic ions [24], suggest that the observed ferromagnetism in $Zn_{1-x}Mn_xO$ bulk systems is more related to an interface phenomenon than to the formation of a dilute magnetic semiconductor.

5. Conclusions

The diffusion behavior of ZnO/MnO_x couple in air has been studied at different temperatures employing a combination of X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy. No diffusion is detected in the system at temperatures below 973 K and this is closely related to the differences between ZnO and MnO_2 structures. Reduction of Mn(IV) to Mn(III) and the subsequent formation of Mn_2O_3 open the possibility for diffusion and Zn becomes the dominant diffusing species in the couple. As a consequence, a new phase layer develops at MnO_x/reaction zone interface. Initially, this layer is composed by a mixture of cubic and tetragonal spinel-like phases, but above 1173 K, the tetragonal $ZnMn_2O_4$ spinel is the only phase present in the interface and forms a physical barrier for further diffusion of both zinc and manganese species. In the interval between 973 and 1173 K, some Mn(III) also diffuses into ZnO pellet, although no homogeneous solid solution is ever formed.

Acknowledgments

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