

Local fields in Co and Mn Co-doped ZnO

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Abstract The magnetic properties of ZnO co-doped with 5 at. % Co and 5 at. % Mn ($\text{Zn}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}$) synthesized by a solid-state reaction were investigated by means of ^{57}Co emission Mössbauer spectroscopy. The majority of the probe ions (80 %) residing in defect-free substitutional Zn sites take the oxidation state of $^{57}\text{Fe}^{2+}$, and the others presumably form local defects taking the state of $^{57}\text{Fe}^{3+}$ at room temperature. Both components show doublets, and RT ferromagnetism was thus absent in the sample. For the measurement at 10 K, spectral broadening was observed, implying a possible presence of a weak magnetic component.

Keywords ZnO · co-doping · Mössbauer spectroscopy · Dilute magnetic semiconductor

1 Introduction

Physical properties of zinc oxide (ZnO) doped with impurity ions of transition metal elements have been one of the most intriguing research topics in current materials science. Especially, magnetic elements such as Mn, Fe, and Co are expected to play an important role

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in the application of ZnO to future electronic and spintronic devices [1, 2]. Since the first theoretical prediction of the emergence of ferromagnetism in dilute magnetic semiconductors (DMS) [3], many papers have reported magnetic properties of ZnO; however, there is still a controversy as to whether their ferromagnetism is indeed induced by solute impurities [4]. This is because possible precipitation of secondary phases of the magnetic impurities cannot be ruled out. It is therefore necessary to investigate how the impurity ions reside in the matrix. In such a case, microscopic techniques with nuclear probes can demonstrate their power in revealing local structures and fields at impurity sites because of their high sensitivity. Especially for the analysis of magnetic impurities, such as Fe and Co, Mössbauer spectroscopy of the $^{57}\text{Fe}(\leftarrow^{57}\text{Co})$ probe is very much suited for obtaining local information at the impurity sites. Many researchers have worked on this intriguing subject by means of Mössbauer spectroscopy so far, and discussed local fields at the sites of the ^{57}Fe probe [2, 5–7]. Because the presence of local magnetism depends on the type of dopant elements and on the doping method, the observed magnetic sextets have been attributed to various origins: not only to ferromagnetic ordering but also to the interaction between paramagnetic Fe^{3+} and implantation defects resulting in long relaxation times [5]. As one of the doping methods, the effects of simultaneous doping of two different transition elements have also been examined [2, 8], and it is reported that the co-doping can eliminate the formation of a secondary phase by a strong synergetic effect [2]. For the exploration of DMS, it is thus of great importance to investigate ZnO co-doped with various combinations of transition metal elements.

Among a variety of combined impurities, Co and Mn co-doped ZnO is a promising candidate for DMS [9–11]. The objective of the present study is to investigate the presence of magnetism in ZnO co-doped with Co and Mn ions through measurements of local fields by means of emission Mössbauer spectroscopy of $^{57}\text{Fe}(\leftarrow^{57}\text{Co})$. In the present paper, we discuss the possibility of low-temperature magnetism in the co-doped ZnO based on an obvious temperature dependence of the spectra.

2 Experiments

For the synthesis of $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}$, impurity metal ions (Co and Mn) were introduced in powder ZnO by a conventional solid-state reaction with the assistance of 10-wt.% citric acid. Stoichiometric amounts of Co and Mn metal powders with purities of 99 % and ZnO powder (99.999 %) were homogeneously mixed in a mortar. The uniform mixture was then pressed into a disk, and it was sintered on a platinum plate in air at 1373 K for 7 d. After examination of the possible formation of secondary phases of the impurities by a powder XRD pattern, commercially available ^{57}Co HCl solution was added in droplets onto the sample disk, which was repressed after the XRD measurement, and it again underwent heat treatment in air at 1373 K for 24 h for the diffusion of the radioisotope. Emission Mössbauer spectrometry was performed on the ^{57}Co -doped $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}$, which is denominated $\text{ZnCoMn}(^{57}\text{Co})\text{O}$ hereafter, at room temperature (RT) and at 10 K. A stainless steel foil was employed as the absorber. The isomer shift and velocity were calibrated by those of $\alpha\text{-Fe}$ measured at RT. It should be noted that impurity-free pure ZnO was also doped with ^{57}Co , called $\text{Zn}(^{57}\text{Co})\text{O}$ hereafter, in the same procedure taken for the $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}$ sample for comparison of the spectra.

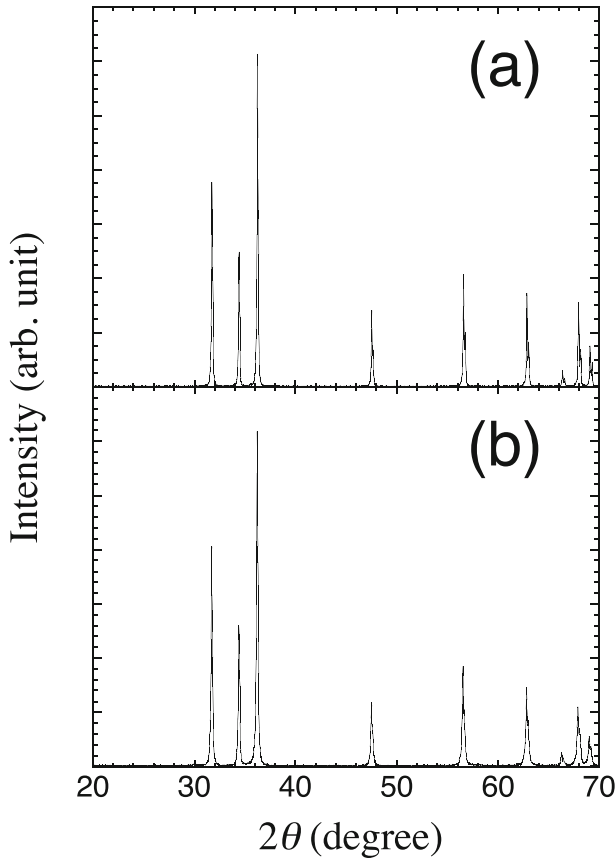


Fig. 1 Powder X-ray diffraction patterns (a) of undoped pure ZnO and (b) of $Zn_{0.90}Co_{0.05}Mn_{0.05}O$

3 Results and discussion

The powder XRD pattern of $Zn_{0.90}Co_{0.05}Mn_{0.05}O$ is shown in Fig. 1 together with that of undoped pure ZnO for comparison. According to earlier studies, impurity metal ions in ZnO are likely to aggregate to form binary spinel structures with Zn such as $ZnCo_2O_4$, $ZnMn_2O_4$, $ZnFe_2O_4$, and even $ZnIn_2O_4$ when doped at concentrations above their solubility limits [12–14]. In spite of the quite heavy doping, however, only diffraction peaks for ZnO can be seen within the present detection precision as shown in Fig. 1(b), demonstrating that the Co and Mn impurities mostly occupy tetrahedral Zn sites without forming detectable secondary phases.

Figure 2 shows the emission Mössbauer spectra for $Zn(^{57}Co)O$ and $ZnCoMn(^{57}Co)O$, and the hyperfine interaction parameters obtained from the spectra using a fitting program, MossA [15], are listed in Table 1. As shown in Fig. 2(a), the RT spectrum of $Zn(^{57}Co)O$ can be reproduced by a single doublet (D1) component. This component is assigned to $^{57}Fe^{2+}$

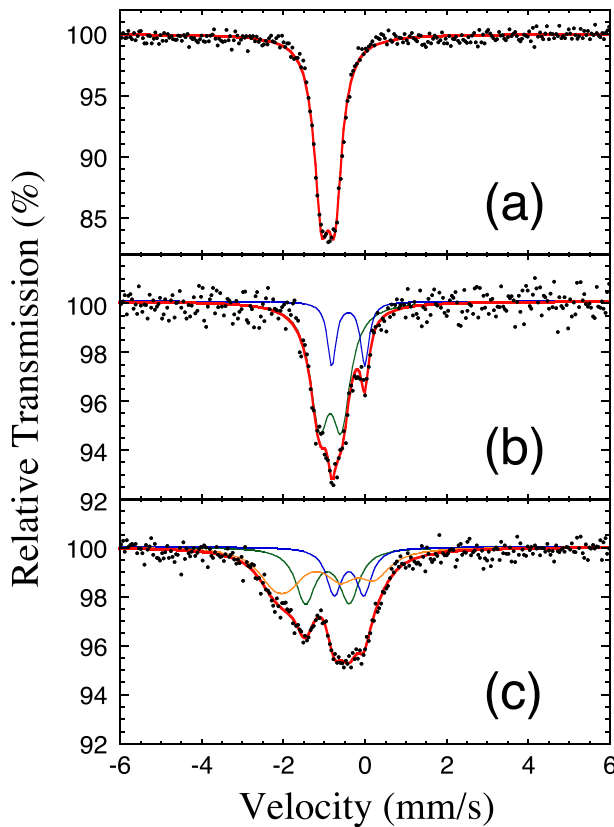


Fig. 2 Emission Mössbauer spectra (a) of Zn(^{57}Co)O at RT, (b) of ZnCoMn(^{57}Co)O at RT, and (c) of ZnCoMn(^{57}Co)O at 10 K. The D2 and M1 components are shown with blue and orange lines, respectively. The sign of the velocity is employed as it was obtained in the emission experiment

at defect-free substitutional Zn sites from the parameters [5, 16]. Because substitutional Co in ZnO is reported to be in Co^{2+} state [9], it is found that the divalence is preserved after the electron capture decay of $^{57}\text{Fe}^{2+}$ ($\leftarrow ^{57}\text{Co}^{2+}$).

For ZnCoMn(^{57}Co)O, a spectral change from Zn(^{57}Co)O is obvious as shown in Fig. 2(b), and we thus added another doublet component (D2) for the fit. This spectrum clearly shows that part of the impurity ions can no longer be accommodated in the substitutional lattice sites due to 10 at. % doping in total, resulting in the formation of local defects. The hyperfine interaction parameters in Table 1 suggest that D2 corresponds to $^{57}\text{Fe}^{3+}$. There would be two conceivable sites for this component. One is a precipitate such as that discussed by Gunnlaugsson *et al.* [6]; in this case, its concentration should be below the present detection limit of the XRD measurement (Fig. 1(b)). As described above, the most likely precipitate in ZnO which ^{57}Co can be incorporated in by thermal diffusion would be Co oxides with spinel structure such as Co_3O_4 , CoMn_2O_4 , and ZnCo_2O_4 . However, the present secondary phase, if any, is different from any of these spinels because reported Mössbauer parameters for $^{57}\text{Fe}^{3+}$ in the oxides are at variance with the present values [17–19]. This assignment is therefore considered to be less plausible. The other candidate for the site of D2 component is $^{57}\text{Fe}^{3+}$ substituting for lattice Zn adjacent to a Zn vacancy. This

Table 1 Hyperfine interaction parameter values for the ^{57}Co emission Mössbauer spectra in Fig. 2

| Sample | Temperature | Component | δ (mm/s) | ΔE_Q (mm/s) | Γ (mm/s) | B_{hf} (T) | Fraction (%) |
|-----------------------------|-------------|-----------|-----------------|---------------------|-----------------|---------------------|--------------|
| Zn(^{57}Co)O | RT | D1 | 0.90(1) | 0.33(1) | 0.43(1) | – | 100 |
| ZnCoMn(^{57}Co)O | RT | D1 | 0.85(1) | 0.53(1) | 0.55(2) | – | 79(2) |
| | | D2 | 0.41(1) | 0.81(1) | 0.25(2) | – | 21(2) |
| | 10 K | D1 | 0.92(1) | 1.07(2) | 0.59(6) | – | 32(4) |
| | | D2 | 0.39(1) | 0.73(3) | 0.45(3) | – | 21(2) |
| | | M1 | 1.12(2) | 1.88(8) | 0.93(6) | 2.6(2) | 48(4) |

idea arises from the notion of charge balance: a cation vacancy (V_{Zn}) is likely to adjoin a cation of higher valence $^{57}\text{Co}^{3+}$; which is, in the present case, considered to disintegrate to $^{57}\text{Fe}^{3+}$ by the electron capture decay [$^{57}\text{Fe}^{3+}(\leftarrow^{57}\text{Co}^{3+})$].

The detection of the doublets above shows that RT magnetism is absent for the present sample. To check for low-temperature magnetism, we subsequently obtained the Mössbauer spectrum of ZnCoMn(^{57}Co)O at 10 K as shown in Fig. 2(c). At this low temperature, spectral broadening is evident in the spectrum when compared with the RT spectrum in Fig. 2(b). This broadening can be interpreted in two ways: 1) a large FWHM of the quadrupole splitting of the D1 component or 2) an addition of another component of Fe^{2+} with magnetic ordering. For the former interpretation, the large FWHM would originate from a wide distribution of the electric field gradient at the ^{57}Fe nucleus at this low temperature. It is difficult to elucidate this large distribution at the low temperature, however. For the latter interpretation, the emergence of a weak magnetic component (M1) is suggested, which is taken into account for the fit of the spectrum in Fig. 2(c) and the result of the fit is listed in Table 1. What should be noted here is that the sum of the fractions of D1 and M1 observed in the 10-K spectrum in Fig. 2(c) is the same as the single fraction of D1 in the RT spectrum in Fig. 2(b) within their uncertainties. This observation plausibly demonstrates that the substitutional D1 component at RT underwent a partial transition to the magnetic phase of M1 at 10 K. If this interpretation is correct, it can be said that the $^{57}\text{Fe}(\leftarrow^{57}\text{Co})$ probe ions forming D1 at RT are in two different surroundings. At the present stage, it is uncertain whether the origin of the magnetic M1 is the so-called dilute magnetism. There may also be the possibility, for instance, that the probe nuclei at the surfaces of fine particles feel surface magnetism, which is inferred from the fact that some nonmagnetic materials in the bulk exhibit ferromagnetic properties when they are transformed to low dimensional materials such as nanoparticles. For a more detailed discussion for the magnetic properties of the present sample, complementary investigation of bulk magnetism by means of a magnetization measurement would be a great help.

4 Summary

In the present work, structural and magnetic properties of ZnO co-doped with 5 at. % Co and 5 at. % Mn ($\text{Zn}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}$) synthesized by a solid-state reaction were investigated by means of a powder XRD measurement and ^{57}Co emission Mössbauer spectroscopy. It was found that the majority of the probe ions (80%) substituting for Zn take the charge state $^{57}\text{Fe}^{2+}$ and the others presumably form local defects taking the charge state of $^{57}\text{Fe}^{3+}$ at RT.

The Mössbauer spectrum measured at 10 K shows a spectral broadening, leaving two possible interpretations: 1) distribution of the electric field gradient at the ^{57}Fe probe nucleus and 2) emergence of a magnetic component. The finding of the temperature dependence of the spectra is very interesting if the latter is the case; at this stage, however, the origin of the weak magnetism is uncertain. For more information, Mössbauer measurements at various temperatures and a bulk magnetization measurement are now under way.

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