Vibration DOS of ^{57}Fe and Zn doped rutile Sn(Sb) oxides

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Abstract Sn oxides co-doped with Zn, Sb and ^{57}Fe were prepared by sol-gel method, and especially the doping effect of non-magnetic Zn ions was studied. The bulk saturation magnetization is in accordance with the intensity of the magnetic component in Mössbauer spectra. The nuclear inelastic scattering (NIS) spectra of these compounds were measured in SPring 8. The vibration density of states (VDOS) of ^{57}Fe doped Sn(Sb) oxides showed that the softening peaks around 15–20 meV appeared by doping less than 10% Zn ions. The clusters of non-magnetic $ZnFe_2O_4$ may be most probably formed under the limit of XRD detections. The results suggest that the strengthening of ferromagnetism, which appears in the dilute Zn doping, may occur due to the spin arrangement of dilute Fe^{3+} through magnetic defects rather than the formation of magnetic iron oxides.

Keywords Vibration density of states (VDOS) · Mössbauer spectroscopy ·
Nuclear inelastic scattering · Diluted magnetic oxide semiconductors ·
Zn doping effect of Fe and Sb doped SnO_2

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1 Introduction

Transparent diluted magnetic oxide semiconductors (DMS), which show ferromagnetism at room temperature, are expected to be one of the most intriguing spintronics materials [1, 2]. Ferromagnetic behavior can occur as an impact of low concentration of doped magnetic atoms on wide gap semiconductors. The ferromagnetism is presumed to be induced either due to the spin arrangement of magnetic atoms through localized spins trapped in oxygen vacancies or due to formation of precipitated magnetic clusters. It is necessary to reveal how the dilute or clustered ferromagnetic atoms are involved into metal oxide semiconductor.

Recently, we have measured nuclear resonant inelastic scattering (NIS) spectra of metal oxides using synchrotron radiation, and revealed that NIS measurement is useful for determination of dilution or cluster formation of doped ions [3]. We also have conducted ^{119}Sn Mössbauer study of Fe doped SnO_2 under magnetic fields. ^{119}Sn Mössbauer spectra were influenced a little by magnetic fields [4]. The co-doping of SnO_2 with Sb and Fe ions were found to improve electrical conductivity and magnetism. Sb ions enhance the solubility of Fe ions in SnO_2, widening the possibilities of enhancing the physical properties of cassiterite based materials [5]. Zn doping effect of 20% Fe and 10% Sb doped SnO_2 were studied, as well [6]. In the present study, we determine local vibration density of state (VDOS) distribution of ^{57}Fe in various Fe and Sb doped Sn oxides.
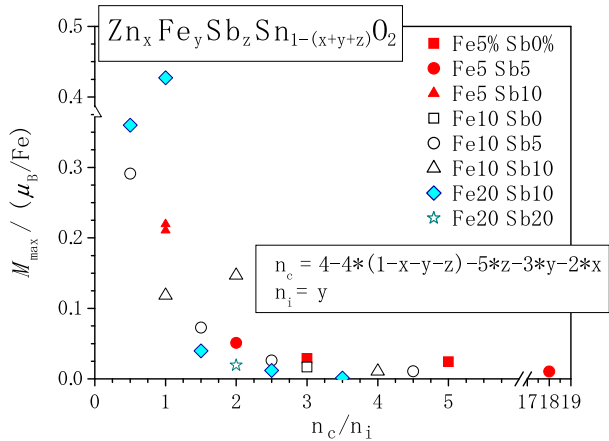
2 Experimental

^{57}Fe and Sb doped $SnO_{2-\delta}$ co-doped with Zn (less than 30%) were obtained by sol-gel method. $SnCl_2 \cdot 2H_2O$, $SbCl_3$, ZnO, metallic ^{57}Fe and natural Fe were dissolved by using HCl or HNO_3 and citric acid. Each solution was mixed according to the nominal amounts of compounds, and completed with ethylene glycol. The proper amount of enriched ^{57}Fe was mixed into natural abundant Fe solution to adjust into about 2% ^{57}Fe content. These solutions were condensed at 80–90°C and decomposed at 250°C during 2 h. The xerogel was oxidized in air at 550°C for 1 h, and, after milling, the powders were finally annealed at 550°C for 1 h. Mössbauer spectra were measured by using ^{57}Co(Cr) and calibrated using α-Fe foil. ^{57}Fe NIS spectra were measured in SPring8, using BL09, of which the energy resolution was 2.5 meV. Phonon DOS distributions were calculated from NIS spectra.

3 Results and discussion

Figure 1 shows the experimental saturation magnetization of $Zn_xFe_ySb_zSn_{1-(x+y+z)}O_{2-\delta}$ plotted against n_c/n_i, where $n_c = 4 - 4*(1 - x - y - z) - 5*z - 3*y - 2*x$ is the number of charge carriers, and $n_i = y$ is the number of doped magnetic ions. In this case, it is assumed that there are no precipitated products and no defects of SnO_2 such as oxygen vacancy, that is $\delta = 0$. The deviation among saturation magnetizations may be produced due to defects. Around $n_c/n_i = 1$, large saturation magnetizations were obtained, and the saturation magnetizations decreased when n_c/n_i increased. This is in good accordance with the results of Behan

Fig. 1 Relationship between saturation magnetization and n_c/n_i of $Zn_xFe_ySb_zSn_{1-(x+y+z)}O_2$

$Zn_xFe_ySb_zSn_{1-(x+y+z)}O_2$

■ Fe5% Sb0%
● Fe5 Sb5
▲ Fe5 Sb10
□ Fe10 Sb0
○ Fe10 Sb5
△ Fe10 Sb10
◆ Fe20 Sb10
☆ Fe20 Sb20

$n_c = 4-4*(1-x-y-z)-5*z-3*y-2*x$
$n_i = y$

Fig. 2 Typical Mössbauer spectrum of $Zn_{0.05}Fe_{0.20}Sb_{0.10}Sn_{0.65}O_{2-\delta}$

$Zn_{0.05}Fe_{0.2}Sb_{0.1}Sn_{0.65}O_{2-\delta}$
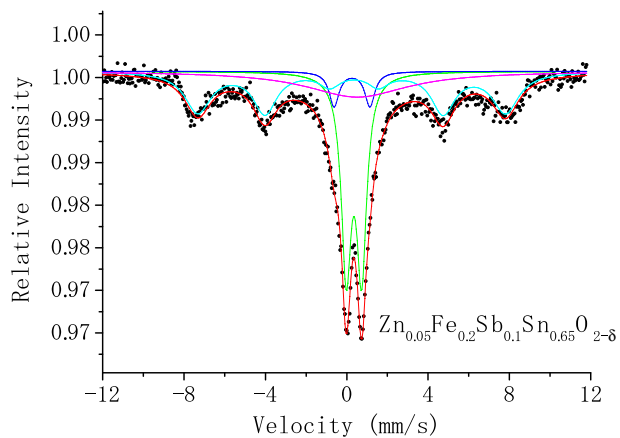
et al., who has found the same tendency in Al and Mn/Co doped ZnO [7]. This behavior was explained by a standard DMS model, where the localized spins of the doping magnetic ions are interacting with band electrons. The bulk magnetization depends then strongly on the carrier density. In our samples, the relatively high dilute magnetism is expected to occur due to the increased solubility of charge carriers. It is confirmed from XRD patterns that the main rutile structure of 10% Sb and 20% Fe-doped tin oxide has been kept up to additionally 10% doping of non-magnetic Zn ions. Sb^{5+} plays a role of stabilization of rutile structure of SnO_2 and induction of carrier density. Zn oxides seem to be dissolved in SnO_2, and not well crystallized at Zn concentrations less than 10%. At more than 10% Zn concentration, the impurity of Zn compounds such as Zn_2SnO_4 and $Zn_{2.33}Sb_{0.67}O_4$ was clearly detected by XRD. At lower Zn concentrations, the impurity may be nano particles of paramagnetic $ZnFe_2O_4$. However, the magnetization increased with doping Zn from 1% to 7% [6].

Typical Mössbauer spectrum of $Zn_xFe_ySb_zSn_{1-(x+y+z)}O_{2-\delta}$ is shown in Fig. 2. The magnetic split components in Mössbauer spectra are related with the intensity of

Fig. 3 ^{57}Fe VDOS of SnO$_2$
doped with **a** 5% Zn + 10%
Fe + 10% Sb, **b** 20% Fe +
10% Sb and **c** 5% Zn + 20%
Fe + 10% Sb. *Solid plots*:
calculated from phonon
creation peaks of NIS spectra.
Gray plots: calculated from
phonon annihilation peaks
of NIS spectra
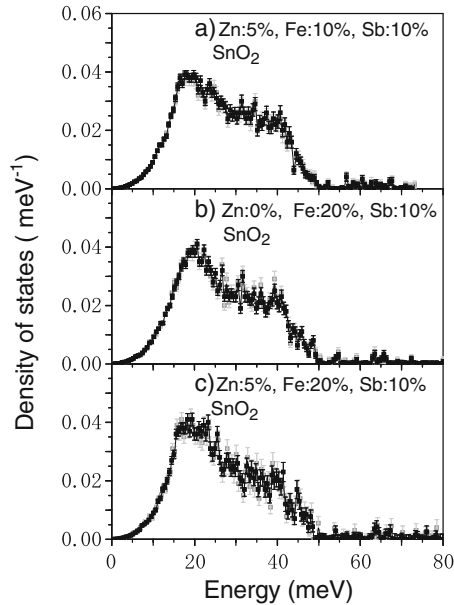
bulk magnetization in the range of less than 10% Zn doping rates. It is an interesting
phenomenon that the magnetic exchange interaction increases with dilution of Fe
ions by non-magnetic Zn ions. The results suggest that there are many defects
produced at the interface between tin oxides and zinc oxides.

From the analysis of NIS spectra it is found that even ^{57}Fe VDOS of 20% Fe
doped in SnO$_2$ (10% Sb) resembles ^{119}Sn VDOS of tin oxide itself and ^{57}Fe VDOS
of light Fe doped SnO$_2$ although the distribution was a little expanded as shown
in Fig. 3. When doping Zn into the Sn oxides, the VDOS distributions increased
a little around 15–20 meV. The softening of VDOS is generally observed for nano
iron oxide particles [8]. Supposing the formation of Fe products with Zn and Sb,
ZnFe$_2$O$_4$ emerged as most possible candidate, which should be a non-magnetic nano
particle. It is considered that the large saturation magnetization observed in the case
of doping less than 10% Zn ions is supposed to be due to dilution of Fe^{3+} into
rutile structure rather than formation of precipitated magnetic iron oxides, however,
the cluster formation of magnetic iron oxides may not be excluded completely out.
Therefore, magnetic components in Mössbauer spectra are considered to be due to
spin arrangement of dispersed iron ions through the magnetic defects rather than to
high-purity magnetic oxide clusters such as maghemite.

4 Conclusions

We have measured ^{57}Fe nuclear inelastic scattering of the Zn, Fe, and Sb doped
SnO$_2$ compounds at BL09 of SPring8. We concluded the followings; high doping of
20% Fe in 10% Sb doped SnO$_2$ is possible. Zn doping may make many defects at
the interface between SnO$_2$ and Zn compounds. VDOS analyzed from NIS spectra
showed that the peaks appeared at low energy range in VDOS by doping Zn

ions, which suggests the formation of most possible $ZnFe_2O_4$ clusters, non-magnetic ferrite. The enhanced magnetism observed at the range of less than 10% Zn doping is considered to be due to spin arrangement of dispersed Fe^{3+} ions through magnetic defects rather than to precipitation of magnetic iron oxides.

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