



^{57}Fe CEMS study on dilute metal ions codoped SnO_2 thin films prepared by spray pyrolysis

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Abstract Dilute Mn-Fe, Co-Fe and V-Fe codoped tin oxide films prepared by spray pyrolysis were characterized by ^{57}Fe conversion electron Mössbauer spectrometry (CEMS) at room temperature (RT) and at 20 K. Two kinds of paramagnetic Fe^{3+} species were detected at RT; one doublet 1 (D1) with $IS = 0.36\text{--}0.37$ mm/s, $QS = 0.69\text{--}0.75$ mm/s and $LW = 0.32\text{--}0.40$ mm/s, and another doublet 2 (D2) with $IS = 0.31\text{--}0.35$ mm/s $QS = 1.16\text{--}1.25$ mm/s and $LW = 0.46\text{--}0.52$ mm/s. CEMS at 20 K provided more distinguished doublets than at RT. It is found that especially D2 with relatively small IS and large QS values are influenced by other metal ions codoped in SnO_2 matrix, whereas D1 with relatively large IS and small QS has the parameters close to the models of Fe-VO1 and Fe-2VO1-Fe models (Nomura et al. Phys. Rev. B **75**, 184411 [2007](#); Mudarra Navarro et al. J. Phys. Chem. C **119**, 5596–5603 [2015](#)).

Keywords ^{57}Fe CEMS · Low temperature CEMS · Spray pyrolysis · Mn-Fe doped tin oxide · Co-Fe doped tin oxide · V-Fe doped tin oxide

1 Introduction

Oxide semiconductors with a large bandgap such as SnO_2 , TiO_2 and ZnO have shown interesting magnetic behaviors at RT by doping dilute magnetic ions. We have studied on dilute magnetism of SnO_2 doped with a several % Fe ions prepared by a sol-gel and thermal

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decomposition method [1]. *Ab initio* calculations on supercell models of SnO₂ doped with Fe species have been studied [2]. For example, the calculations showed that ferromagnetic and/or antiferromagnetic spin arrangements depend on the configuration of oxygen vacancies and Fe species occupied at lattice sites of SnO₂ crystal. However, atomic configurations in supercell models of SnO₂ with two different metal ions and defects become so complex that *ab initio* calculations cannot be easily applied to such complex models.

By the way, SnO₂ powders codoped with dilute Co and Fe ions [3, 4], Mn and Fe ions [5], Ni and Fe ions [6], and V and Fe ions [7] have shown enhanced ferromagnetic behaviors as compared with single metal ion doped SnO₂ powder. In their Mössbauer spectra, broad doublets and sextets have been observed.

In order to confirm previous results, we have prepared tin oxide thin films codoped with Mn-Fe, Co-Fe, and V-Fe metal ions by spray pyrolysis since metal mixed solutions can be easily prepared. ⁵⁷Fe and other metal ions codoped tin oxide films were characterized by ⁵⁷Fe CEMS at room temperature (RT) and at low temperature of 20 K. These results are reported here.

2 Experimental

Metal mixed solutions were prepared using 0.01 M chloride solutions of Mn, Co, V, and ⁵⁷Fe and 0.1 M Sn chloride solution. Tin oxide films were formed on quartz glass heated at higher than 400 °C by spraying each solution including 20% ethanol. Two metal ions codoped tin oxide films were measured by ⁵⁷Fe CEMS at RT using a He + CH₄ gas flow counter and at 20 K using a H₂ gas filled counter in cryogenic freezer [7]. Zero isomer shift (*IS*) and Doppler velocity scale were calibrated using RT Mössbauer spectrum of an α -Fe foil. The observed spectra were analyzed by Mosswin program.

3 Results and discussion

3.1 Mn and Fe codoped tin oxide film on quartz

Tin oxide thin film codoped with 4% Mn and 4% Fe ions was prepared at higher temperatures than 400 °C. RT and 20 K CEMS provided statistically good spectra as shown in Fig. 1, and the Mössbauer parameters are listed in Table 1. The CEMS spectra were composed of at least two doublets due to two kinds of paramagnetic Fe³⁺ species because asymmetric peaks were clearly observed. *IS* values of two doublets changed from 0.37 mm/s at RT to 0.50 mm/s at 20 K for doublet 1 (D1), and from 0.33 mm/s at RT to 0.45 mm/s at 20 K for doublet 2 (D2), respectively. The *IS* values increased by 0.12 and 0.13 mm/s are due to secondary order Doppler shifts (SOD) with temperature dependency. The change of the intensity and *QS* values measured at different temperatures was not so much large. The *QS* values changed only by 0.01 mm/s. The linewidth (*LW*) of D2 is larger than that of D1. Therefore, the above results suggest that a stack and stable oxide coating is formed by spray pyrolysis at the temperatures higher than 400 °C and that Fe³⁺ species of D2 is strongly influenced by deformed SnO₂ crystals by codoping other metal ions. It is known from X-ray absorption spectroscopy (XAS) that Mn ions have mixed states with Mn³⁺ and Mn²⁺ ions although the Mn and Fe codoped SnO₂ powder were prepared by a sol-gel and thermal decomposition method [6]. Comparing the ionic radius of doped ions (Mn²⁺(6) [3d⁵]: 0.83 nm, Mn³⁺(6) [3d⁴]: 0.645 nm and Fe³⁺(6) [3d⁵]: 0.645 nm) with that of tin (Sn⁴⁺ (6)

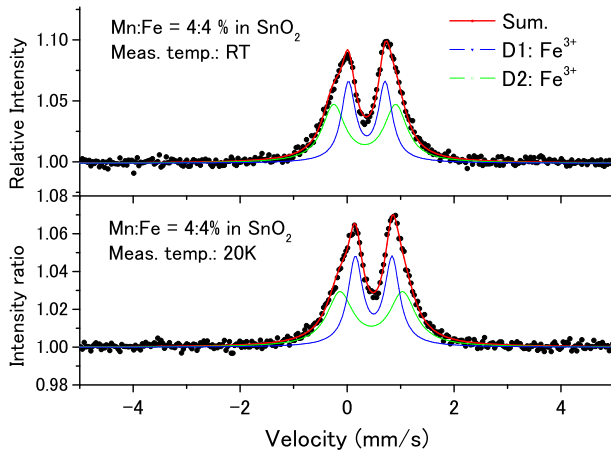


Fig. 1 RT and 20 K CEMS spectra of Mn and Fe codoped tin oxide film on quartz, prepared at 400 °C

Table 1 Mössbauer parameters of SnO₂ thin film codoped with Fe and metal ions

Contents	Mn:Fe = 4:4% at RT	Mn:Fe at 20K	Co:Fe = 2:2% at RT	Co:Fe at 20 K	V:Fe = 2:2% at RT	V:Fe at 20 K
Doublet (1):D1	[45.9%]	[48.4%]	[51.1%]	[66.0%]	[50.5%]	[41.8%]
(1) IS (mm/s)	0.368(2)	0.498(3)	0.362(1)	0.45(1)	0.365(4)	0.474(7)
(1) QS(mm/s)	0.687(8)	0.688(8)	0.69(2)	0.72(2)	0.75(2)	0.76(4)
(1) LW(mm/s)	0.32(1)	0.37(1)	0.34(3)	0.41(3)	0.40(2)	0.39(4)
Doublet (2):D2	[54.1%]	[51.6%]	[48.9%]	[34.0%]	[49.5%]	[58.2%]
(2) IS (mm/s)	0.330(4)	0.453(5)	0.31(1)	0.41(3)	0.345(5)	0.449(8)
(2) QS (mm/s)	1.16(3)	1.17(3)	1.16(7)	1.53(17)	1.26(3)	1.24(6)
(2) LW (mm/s)	0.52(2)	0.58(2)	0.54(5)	0.83(15)	0.46(3)	0.53(4)

[4d¹⁰]: 0.69 nm), the ionic radii of Mn³⁺ and Fe³⁺ are the same. Therefore, even if Mn³⁺ is located near Fe³⁺ substituted at Sn⁴⁺ sites, the lattice structure of tin rutile oxide is not so influenced, but if Fe³⁺ is located near Mn²⁺, the crystal lattice and charge of the rutile oxide may be influenced and the IS of Fe³⁺ may be much more minus shifted.

3.2 Co and Fe codoped tin oxide film on quartz

RT and 20 K CEMS spectra of tin oxide film codoped with 2% Co and 2% Fe, prepared at higher temperatures than 400 °C, are shown in Fig. 2. The parameters of two doublets observed at RT are as follows: one D1 with IS = 0.36 mms, QS = 0.69 mm/s, and LW = 0.34 mm/s and another D2 with IS = 0.31 mm/s, QS = 1.16 mm/s and LW = 0.54 mm/s. The relative intensity (51%) of a doublet D1 with small QS at RT increased to 66% at 20K, and the intensity (49%) of the doublet D2 with large QS at RT decreased to 34 % at 20 K. QS value of D2 increased from 1.16 mm/s at RT, to 1.53 mm/s at 20 K and the linewidth also increased from 0.54 mm/s to 0.83 mm/s. D2 is so strongly depending on the temperature that the charge of Fe³⁺ species can be affected by codoping with Co ions.

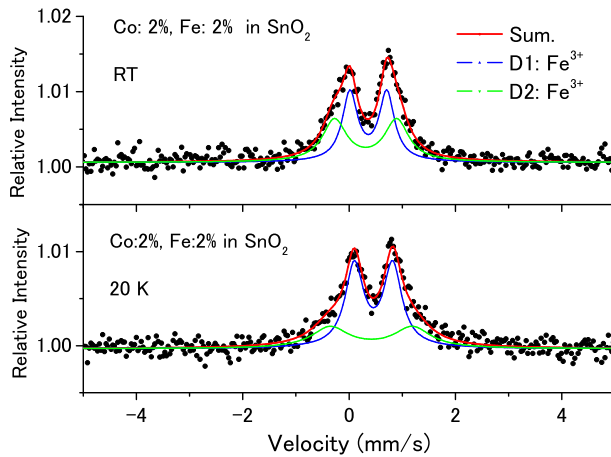


Fig. 2 RT and 20 K CEMS spectra of Co and Fe codoped tin oxide film on quartz, prepared at 400 °C

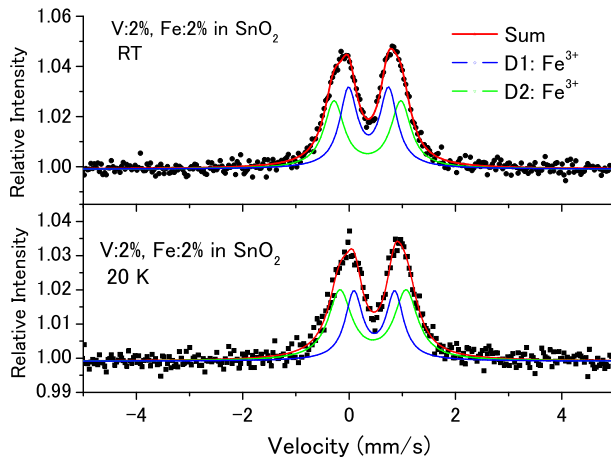


Fig. 3 RT and 20 K CEMS spectra of V and Fe codoped tin oxide film on quartz, prepared at 400 °C

These phenomena can be interpreted on the base of ionic radius and charge of codoped ions. It is known from XAS that Fe-Co mixed tin oxide powder prepared by a sol-gel and thermal method show $\text{Co}^{2+}/\text{Co}^{3+}$ mixed states [3]. Compared the ionic radii of Co^{2+} (6) ($[\text{3d}^7]$: 0.745 nm) and Co^{3+} (6) ($[\text{3d}^6]$: 0.545nm) with those of Fe^{3+} (0.64 nm) and Sn^{4+} (0.68 nm), codoped Co^{2+} and Co^{3+} ions are expected to influence the rutile structure as both expanded and compressed parts, respectively. It is interesting to note that the broaden linewidth of D2 as compared with D1 is well reflected as probing Fe^{3+} ions in deformed rutile structure. It is considered that the larger QS value of D2 was obtained at 20 K, based on the Co ion doping effect.

3.3 V and Fe codoped tin oxide film on quartz

RT and 20 K CEMS spectra of tin oxide film codoped with 2% V and 2% Fe on quartz prepared at higher temperatures than 400 °C are shown in Fig. 3. Mössbauer parameters

of D1 are almost all the same as those of other metal ions codoped tin oxide films, but the component D2 with $IS = 0.34$ mm/s and $QS = 1.26$ mm/s is a little different from D2 of the other films. It is found from IS values that both Fe species are incorporated as 3+ valence states into rutile structure of tin oxide. The QS value of D2 at RT is relatively large as compared with Mn-Fe codoped and Co-Fe codoped tin oxide films. The relative intensity of D2 increased at 20 K. Vanadium ions may influence the Fe states in tin oxide matrix. Double exchange interactions may be produced through oxygen atoms or oxygen vacancies. It is known from XAS that chemical states of vanadium ions are deduced as V^{5+} states [7] Fe^{3+} species of component D2 also may be much more influenced by V^{5+} included. The ionic radius of V^{5+} (6) [$3p^6$: 0.54 nm] is almost the same as that of Co^{3+} ions, but the valence of 5+ is large. When V^{5+} and Fe^{3+} ions with smaller ionic radius than Sn^{4+} ions are substituted at Sn^{4+} sites in rutile structure, only shrinking the lattice structure of SnO_2 is expected because of charge neutralization of codoping ions. As the results it is considered that the QS values of D2 at RT and 20 K were larger than those of the Mn-Fe and Co-Fe codoped SnO_2 and that the linewidths also were not so broaden as compared with the other codoped SnO_2 .

Thus, since the ionic radii and valence states of the other metal ions are different, the doped other metal ions have possibility to influence the lattice structure of SnO_2 matrix. If Fe^{3+} species occupied at vicinity of other metal ions, the Mössbauer parameters would be changeable. When the experimental parameters are compared with those calculated from configuration models of Fe^{3+} and oxygen vacancy, the configurations of Fe^{3+} species (D1) and oxygen vacancies are close to the models of Fe-VO1 and Fe-2VO1-Fe [1, 2], whereas the D2 parameters were not consistent with any configuration model of Fe species and oxygen vacancies, obtained until now.

On the other hand, the magnetic sextet was not observed in the spectra of codoped SnO_2 films, whereas the magnetic relaxation sextets appeared in the Mössbauer spectra of codoped SnO_2 powders as reported previously. It is probably due to the morphology of very thin films formed by different preparation methods.

4 Conclusion

It is found from RT and 20 K CEMS spectra that Fe species codoped with the other metal ions into tin oxide films have at least two kinds of Fe^{3+} states with different IS and QS values. Probably Fe^{3+} species with relatively large IS and small QS values (D1) are substituted with Sn^{4+} atoms with nearest oxygen vacancies in rutile structure of SnO_2 . Another Fe^{3+} species with relatively small IS and large QS (D2) may be located at vicinity of the other metal ion occupied sites, and/or interstitial sites of tin oxide matrix. Authors expect that *Ab initio* calculation can be applied in near future to complicated configuration models of two metal ions and vacancies included in tin oxides in order to clarify the magnetic properties.

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