

Dilute magnetic properties of Fe doped Al_2O_3 powders prepared by sol-gel method

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Abstract Aluminium oxides doped with 1% ^{57}Fe were prepared by sol-gel method, and annealed for 3 hours at various temperatures between 550°C and 1100°C. Amorphous phases were obtained below 1000°C, and crystalline $\alpha\text{-Al}_2\text{O}_3$ was formed at 1100°C. Although Al_2O_3 itself shows diamagnetism, the light doping of Fe ions into aluminium oxide induced a very weak ferromagnetism, but the ferromagnetism disappeared by longer annealing. Mössbauer spectra were composed of paramagnetic Fe^{2+} and Fe^{3+} species for samples heated below 750°C, and of paramagnetic Fe^{3+} above 850°C, in addition to a magnetic sextet and relaxation peaks of Fe^{3+} . The magnetic and quadrupole interactions of the sextet and the relaxation peaks and the density functional calculations suggest that the lightly doped Fe^{3+} ions are substituted at Al sites in the Al_2O_3 lattice.

Keywords Dilute magnetism · Fe doping · Amorphous and crystalline aluminium oxide · Mössbauer spectra · Nano-materials

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1 Introduction

Ferromagnetic phenomena have been observed at room temperature (RT) by doping diluted magnetic impurities into semiconductors and insulators with a large band gap [1–3]. We found that $Y_3Al_5O_{12}$ (YAG) doped with <1% Fe ions shows RT ferromagnetism, and we have analyzed the hyperfine structures by Mössbauer spectrometry [4]. Dilute ferromagnetic insulators (DMI) are also useful for spin transfer electronics as well as dilute magnetic semiconductors (DMS). Tunnel magnetic resistance is observed when Al_2O_3 is implanted with Fe ions, Co ions, and/or Au ions in vacuum [5, 6]. The single crystal Al_2O_3 plates, implanted with ^{57}Fe and Au ions, were characterized by conversion electron Mössbauer spectroscopy [6]. In this case, the implanted irons exist as metallic clusters and as Fe^{2+} ions. Al_2O_3 is a transparent insulator with a band gap of 6–8 eV, and the crystalline structure is the same corundum as $\alpha-Fe_2O_3$. In this paper, in order to investigate the magnetism of particles of 1% Fe doped Al_2O_3 , and to confirm the hyperfine structure produced by doping dilute Fe ions, we have studied sol-gel synthesized Fe doped alumina, heated at various temperatures.

2 Experimental

In order to prepare nominal compositions such as $Al_{1.98}Fe_{0.02}O_3$, citric acid solutions of Al ions and ^{57}Fe ions were mixed with ethylene glycol. The solutions were condensed at about 80°C to form a colloidal gel. After the gel was heated at 350°C for 2 hours to form xerogel, the xerogel was heated at various temperatures from 550°C to 1100°C for 3 hours, respectively. The colour of the powders prepared changed from dark brown to white with increasing heating temperature. These samples were analysed by X-ray diffractions (XRD: Cu target), vibrational sample magnetometry (VSM), and Mössbauer spectrometry. Mössbauer spectra were measured by using a ^{57}Co (Cr) source and the Doppler velocity was calibrated by using an $\alpha-Fe$ foil. Mosswin program was used for the analysis of the Mössbauer spectra.

3 Results and discussion

XRD patterns of prepared samples are shown in Fig. 1. Amorphous structures were obtained below 1000°C although crystalline $\alpha-Al_2O_3$ was partly included at 1000°C, and full crystalline $\alpha-Al_2O_3$ was obtained at 1100°C. The lattice parameter of $\alpha-Al_2O_3$ doped with 1% Fe increased by $a = 0.006$ nm from $\alpha-Al_2O_3$ because the ionic radius of Fe^{3+} (0.064 nm) is larger than that of Al^{3+} (0.051 nm). The crystallite size was about 45 nm at 1100°C. The light doping of Fe ions into alumina induced ferromagnetism although the alumina itself without magnetic ions showed diamagnetism. With increasing heating temperature, the saturation magnetization decreased up to 750°C and increased again above 950°C as shown in Fig. 2. The sample heated at 1100°C showed saturation magnetization of 0.0031 μ_B/Fe a.u. and coercivity of 285 Oe. The weak ferromagnetism was observed for all 1% Fe doped alumina heated for 3 hours.

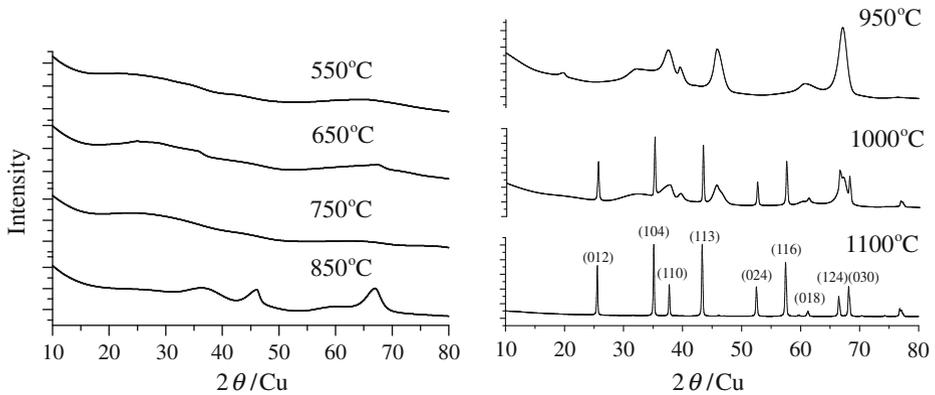


Fig. 1 XRD patterns of alumina doped with 1% ⁵⁷Fe, prepared by sol-gel method and annealed for 3 hours at various temperatures

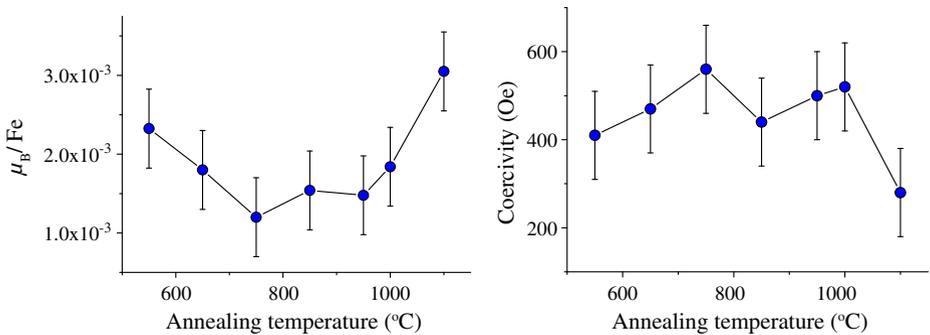


Fig. 2 Saturation magnetization and coercivity of alumina doped with 1% ⁵⁷Fe, prepared by sol-gel method and annealed for 3 hours at various temperatures

The Mössbauer spectra, as shown in Fig. 3, are decomposed into doublets, sextet, and broad magnetic peaks. For the sample heated below 750°C, the spectra are composed of two doublets, D1 (isomer shift (IS) = 0.51–0.86 mm/s, quadrupole splitting (QS) = 1.01–1.44 mm/s), and D2 (IS = 0.91–1.07 mm/s, QS = 1.93–2.2 mm/s). The former shows the mixed valence states of Fe²⁺ and Fe³⁺ and the latter is clearly assigned to Fe²⁺ ions. Above the heating temperature of 850°C, one doublet with IS = 0.32–0.38 mm/s and QS = 0.76–1.3 mm/s is clearly observed, which comes from the Fe³⁺ species. The isomer shifts of the broad magnetic peaks are visually observed to be close to nearly zero Doppler velocity. Metallic iron states should not exist in these samples, and the peaks were analysed by using the Blume-Tjon magnetic relaxation method. As a result, Mössbauer parameters of the magnetic relaxation peaks (IS = 0.028–0.45 mm/s, $\tau = 10^{-8.4}$ – 10^{-9} s, $V_{zz} = (0.17$ – $3.02) \times 10^{21}$ V/m²) were obtained, assuming an inner magnetic field, $B_{hf} = 50.4$ T, and asymmetry parameter, $\eta = 0.5$. The iron states in the relaxation peaks are clearly due to Fe³⁺ from the isomer shifts. The parameters of the contained magnetic sextet were IS = 0.23–0.36 mm/s, $B_{hf} = 48.8$ – 50.6 T, and QS (or 2ϵ) = 0.04–0.28 mm/s. With

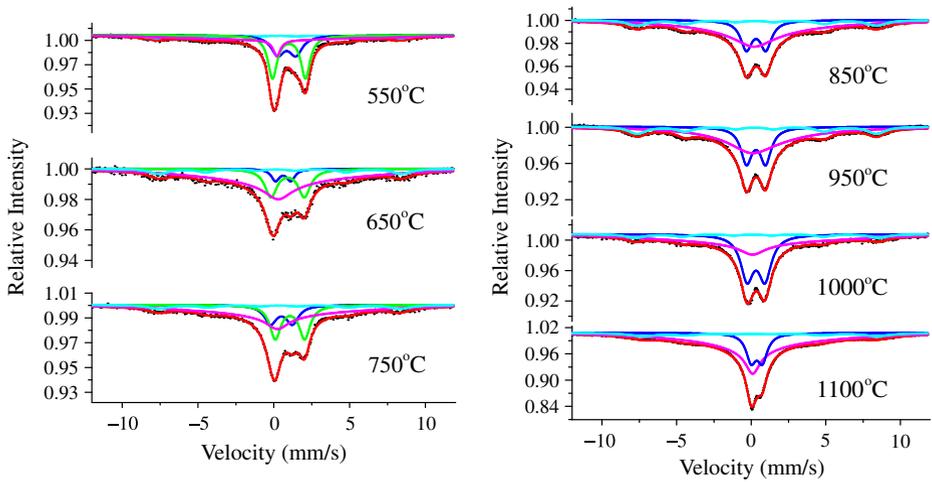
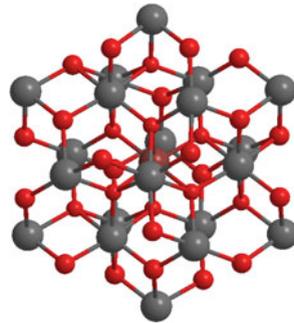


Fig. 3 Annealing temperature dependence on Mössbauer spectra of alumina doped with 1% ^{57}Fe

Fig. 4 The cluster of $\text{Fe@Al}_{20}\text{O}_{30}$ used for density functional calculation. *Brown*, *black*, and *red* balls indicate Fe, Al, and O atoms, respectively



increasing temperature, the doublet of paramagnetic Fe^{2+} decreased, and the doublet of Fe^{3+} increased. Above 850°C all Fe species were more oxidized into Fe^{3+} species, and the QS values of the doublets became small. The QS values of all magnetic sextets and the V_{zz} of relaxation peaks were positive.

Density functional calculations were performed using ORCA program package [7, 8] in order to estimate Mössbauer parameters of the Fe atom in substitutional position of Al in Al_2O_3 lattice. It was assumed that a Fe atom was located in the centre of a $\text{Al}_{20}\text{O}_{30}$ cluster (Fig. 4). Calculated Mulliken atomic charge and spin density of the Fe atom were 3.15 electrons and 4.25 electrons /a.u.³, respectively. The calculated Mössbauer parameters of Fe in $\text{Al}_{20}\text{O}_{30}$ cluster were $\eta = 0.513$, $\text{QS} = +0.102$ mm/s, and $\rho(0) = 11816.5475$ /a.u.³, which are in good agreement with the observed parameters. It was found that Fe atoms in Al_2O_3 have positive QS value.

The magnetic sextet with positive QS value and the relaxation peaks with positive V_{zz} suggest that Fe ions are incorporated into Al atom sites of alumina. Magnetic relaxation peaks varied with annealing temperatures. However, Mössbauer spectra of 5% Fe doped alumina showed a sextet (51T) with negative QS value (-0.2 mm/s)

in addition to a doublet, not including broadened peaks. It is found clearly from the negative QS value that a cluster of hematite (α -Fe₂O₃) is precipitated from Al₂O₃. There is no solid solution of Al and Fe oxides in the case of higher doping of Fe ions into Al₂O₃. The magnetic hysteresis of 1% Fe doped alumina disappeared also by further annealing for 6 hours, and the Mössbauer spectrum after longer annealing became similar to that before the treatment although the intensity ratios of the components were a little different. It is not clear what the origin of magnetically broadened patterns is; it might be due to antiferromagnetic order or might not be. It is considered that defects or a deformed surface of nano grains might induce very weak ferromagnetic order even if the materials were antiferromagnetic. It has been reported that lattice defects and deformations might be the most likely sources of weak ferromagnetism in Hf oxides [9] and YAG doped with dilute Fe ions [4].

4 Conclusion

Aluminium oxides doped with 1 % ⁵⁷Fe were prepared by the sol-gel method, and annealed for 3 hours at various temperatures. The Fe species were oxidized more at the higher annealing temperatures. The light doping of Fe ions into aluminium oxides induced a weak ferromagnetism at room temperature although the longer annealing lost the ferromagnetic hysteresis. Both the magnetic and quadrupole interactions of the sextet and relaxation peaks and the density functional calculations suggest that the Fe species are substitutional at Al atom sites in aluminium oxides in the case of light doping. However, higher doping of Fe ions at high temperatures induces precipitation of hematite clusters in the Al₂O₃ lattice.

References

1. Matsumoto, Y., Murakami, M., Shono, T., Hasegawa, T., Fukumura, T., Kawasaki, M., Ahmet, P., Chikyow, T., Koshihara, S., Koinuma, H.: *Science* **291**, 854 (2001)
2. Yun, F., Morkoc, H.: *Mater. Sci. Mater. Electron.* **16**, 555 (2005)
3. Nomura, K., Barrero, C.A., Sakuma, J., Takeda, M.: *Phys. Rev. B* **75**, 184411 (2007)
4. Nemeth, Z., Nomura, K., Ito, Y.: *Phys. Chem. C* **113**, 20044 (2009)
5. Hayashi, N., Sakamoto, I., Wakabayashi, H., Toriyama, T., Honda, S.: *J. Appl. Phys.* **94**, 2597 (2003)
6. Kinoshita, R., Sakamoto, I., Hayashi, N., Nomura, K., Honda, S., Ishida, T., Iio, S., Tashiro, H., Toriyama, T.: *Jpn. J. Appl. Phys.* **50**, 01BE01 (2011)
7. Romelt, M., Ye, S., Neese, F.: *Inorg. Chem.* **48**, 784 (2009)
8. Petrenko T., Sturhahn, W., Neese, F.: *Hyperfine Interact.* **175**, 165 (2008)
9. Coey, J.M.D., Venkatesan, M., Stamenov, P., Fitzgerald, C.B., Dorneles, L.S.: *Phys. Rev. B* **72**, 024450 (2005)