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Chemical Effects of Thermal Neutron Irradiation on α-$LiFeO_2$

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Chemical effects caused by the $^6Li(n, \alpha)^3H$ nuclear reaction in α-$LiFeO_2$ were studied with Mössbauer spectroscopy. Magnetite was observed on the irradiation. The amount of magnetite increased with irradiation fluence until about 10^{22} m^{-2} was reached. It then became a constant value of about 50% of the α-$LiFeO_2$ in the iron atom ratio. The G value for the formation of magnetite was initially 10^{-2} and decreased to about 10^{-3} at a fluence of 3×10^{22} m^{-2}.

Chemical energy conversion using the thermochemical Fe_3O_4 - FeO redox cycle has been proposed by some workers.[1, 2] The chemical reactions leading to H_2 formation are as follows.

$$Fe_3O_4 \longrightarrow 3FeO + 1/2O_2 \quad (1)$$

$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2 \quad (2)$$

Thus the overall reaction is $H_2O \longrightarrow H_2 + 1/2O_2$, that is, the decomposition of water into H_2 and O_2. Hydrogen can be used as a chemical energy source. Though the above cycle is probably the most practical cycle among the redox cycles proposed, the reaction (1) requires a very high temperature. This temperature imposes many problems and work has been done.

The authors have studied inorganic and organic chemical reactions induced by high energy particles produced by a nuclear recoil process or by an accelerator.[3] They have suggested the important role of hot zone created when high energy particles slow down. The characteristics of a hot zone are microscopic heating and radiolysis of the host materials; that is, the combination of the thermochemical and radiation-chemical reactions in it. Therefore, if the reduction of Fe^{III} is invoked by the high temperature and radiolysis introduced by a high energy particle in a hot zone, the reaction (1) will proceed at a temperature lower than the predicted thermodynamic temperature, about 2500 K.

For the preliminary study of the reduction of Fe^{III} by high energy particles, α-$LiFeO_2$ enriched with ^6Li was chosen. The ^6Li serves as the source of high energy particles due to the $^6Li(n, \alpha)^3H$ nuclear reaction.

A sample was prepared by heating a mixture of Fe_2O_3 and $^6Li_2CO_3$ at 1073 K for 17 hours in air. The $^6Li/(^6Li+^7Li)$ ratio was 0.95. The X-ray diffraction

pattern of the product agreed well with a reported one.[4] The Mössbauer spectrum of the product showed one doublet with I.S. and Q.S. values of 0.35±0.01 mm s^{-1} and 0.55±0.01 mm s^{-1}, respectively. These values are in good agreement with the reported values for cubic $LiFeO_2$ when the reported I.S. value was corrected using α-Fe as standard material for the velocity calibration.[5]

Samples for irradiation were prepared by pressing about 40 mg of the powder into a very thin disk (1.5 cm in diameter) on an Al foil. The pressed samples were wrapped and sealed in the Al foil, placed in capsules and irradiated in the S-pipe of the JRR-4 reactor with a nominal thermal neutron flux of 5 x 10^{17} m^{-2} s^{-1} for 3 to 12 hours. The nominal fast neutron flux was 5 x 10^{16} m^{-2} s^{-1}. The gamma ray dose rate at the irradiation port was about 14 C/(kg s). The samples were immersed in the cooling water(about 320 K) during the irradiation. Aluminum-gold(Au : 0.032% in weight) wires were used for exact estimation of thermal neutron flux. The Mössbauer spectra were measured at room temperature using a standard absorption method by a constant acceleration with a $^{57}Co/Rh$ source. Iron foil enriched with ^{57}Fe was used for calibration of velocity. The spectra were fitted by the least squares method into Lorentzians. The recoil-free fraction was assumed the same for all iron nuclei. Thus, the relative concentration of the iron compound was calculated using the relative areal intensity.

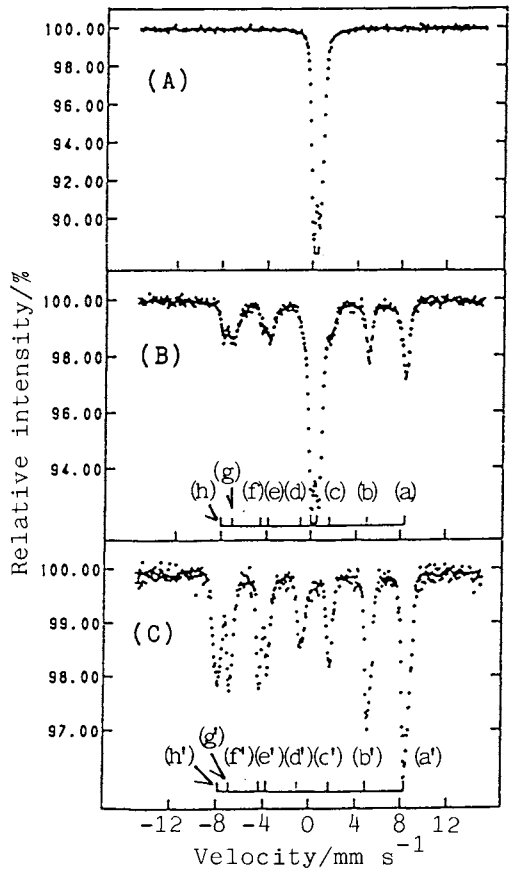

Fig. 1. Mössbauer spectra of the samples.
(A):Before irradiation
(B):After irradiation
(C):Magnetite

The Mössbaur spectra taken before (A) and after (B) thermal neutron irradiation are shown in Figure 1 together with the spectrum of magnetite (C). A comparison of (A) and (B) shows that new peaks are present after irradiation. The velocities and relative intensities of the peaks denoted to (a), (b), (e), (f), (g), and (h) in (B) and (a'), (b'), (e'), (f'), (g'), and (h') in (C) are compared in Table 1. The Mössbauer spectra obtained from various irradiation fluence were almost same as (B) in peak velocity, but the relative intensity of the product against the parent material depended on the irradiation fluence, showing formation of magnetite in the entire range of the thermal neutron fluence studied. The relative intensity of magnetite is plotted against irradiation fluence in Figure 2.

Four reasons will be considered for the formatin of magnetite due to the reactor

Table 1. Comparison of velocity and relative intensity between new peaks in the irradiated sample and magnetite

Velocity/mm s^{-1}		Relative intensity[a]	
Spectrum(B)	Spectrum(C)	Spectrum(B)	Spectrum(C)
(a)+8.18	(a')+8.22	(a) 1	(a') 1
(b)+4.89	(b')+4.99	(b) 0.65	(b') 0.67
(e)-3.66	(e')-3.58	(e), (f) 0.65[b]	(e'), (f') 0.66[b]
(f)-4.30	(f')-4.26		
(g)-6.82	(g')-6.71	(g), (h) 1.00[b]	(g'), (h') 0.99[b]
(h)-7.67	(h')-7.81		

a) Intensity normalized to the peak areas of (a) and (a').
b) The values are summation of (e) and (f), (e') and (f'), (g) and (h), and (g') and (h'), respectively.

irradiation. The first is the chemical effect caused by ^{3}H and ^{4}He formed with very high kinetic energy from the $^{6}Li(n, \alpha)^{3}H$ reaction, the second is the chemical effect of the FeO_2^- ion remaining after nuclear transformation of ^{6}Li, the third is the influence of the reactor radiation such as gamma rays and fast neutrons, and the fourth is a thermochemical reaction of the sample with the Al foil induced by heat evolved by the nuclear reaction. The number of ^{6}Li atoms transformed by the nuclear reaction of $^{6}Li(n, \alpha)^{3}H$ is about 10^{17} which corresponds to the 10^{-3} fraction of ^{6}Li in the sample. However, the number of iron atoms changed to magnetite is about 10^{20}. Therefore, the effect of the FeO_2^- ion is considered negligible. Considering the reactor radiation, the sample with the natural ^{6}Li isotopic ratio was irradiated to 3×10^{22} m^{-2} under the same condition as the ^{6}Li enriched sample, but no differences were observed. As the rate of heat evolution by a nuclear reaction is 10 J s^{-1} and the sample was in direct contact with the cooling water, the thermochemical reaction of aluminum with the sample is considered negligible. To examine the possibility of a thermochemical reaction, the Mössbauer spectra of the samples heated by electric furnace at 573, 673, and 773 K for 5 hours were taken, but no change was observed for spectra taken before and after heating. Therefore, the reaction induced by $^{6}Li(n, \alpha)^{3}H$ reaction is responsible for the formation of magnetite in the irradiated α-$LiFeO_2$. The $G(Fe_3O_4)$ value for the formation of magnetite, which was defined as the number of magnetite formed per 100 eV of incident energy by the $^{6}Li(n, \alpha)^{3}H$ reaction (4.7 MeV), was initially

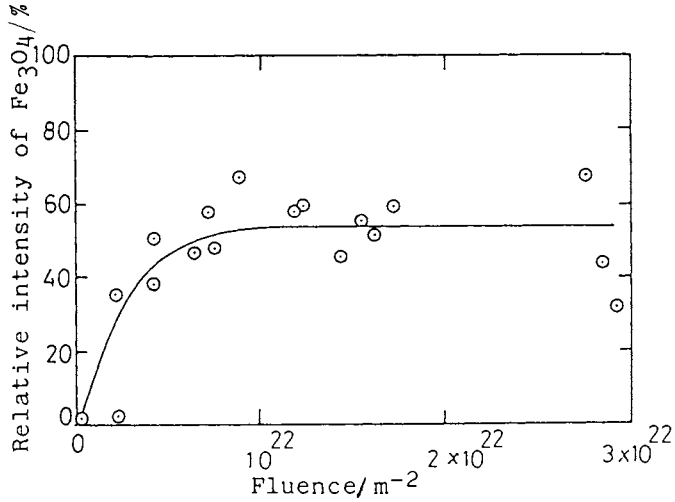

Fig. 2. The relative intensity of magnetite against thermal neutron fluence.

10^{-2}. This number decreased to 10^{-3} at a fluence of 3×10^{22} m^{-2}.

A mathematical expression of temperature, size and duration time of a hot zone was proposed by Mozumder.[6] However, the model does not predict chemical reactions occurring in the hot zone. The most interesting point from the present study is the specific formation of magnetite. Though the reaction path leading to the formation of magnetite is not clear at present, the present result may suggest that the reaction of the radiolysis products in the hot zone occurs specifically, not in a random manner, in spite of the random configuration of the radiolysis products within the hot zone immediately after formation by the high energy particles.

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