Fe2SiO4-Fe3O4固溶体の12GPaまでの相関係と物理的性質

Phase relations and physical properties of Fe2SiO4-Fe3O4 solid solution under pressures up to 12 GPa

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Phase study of the Fe2SiO4-Fe3O4 solid solution system has been carried out under high pressures up to 12 GPa at 1200℃ by multianvil apparatus. A complete spinel solid solution between Fe3O4 and g-Fe2SiO4 has been found at pressures over 10 GPa. g-Fe2SiO4 having a normal spinel structure is stable at pressures above 7 GPa. A spinelloid structure similar to aluminosilicate V (Pmma) in the NiAl2O4-Ni2SiO4 system is found in a wide intermediate compositional range x=0.37 to 0.73 in Fe3-xSixO4 at pressures between 3 GPa and 9 GPa. X-ray single-crystal structure analyses of several samples of Fe3-xSixO4 spinel indicate the site occupancy of (Fe3+1-x+ySi4+x-y)[Fe2+1+xFe3+1-x+ySi4+y]O4. This cation distribution gives an effect on the electrical conductivity mainly due to the electron hopping between Fe3+ and Fe2+ in the octahedral site. Measurement of the electrical conductivity of the spinel solid solution had been made at low temperatures in the range 80K-to-300K. The transition temperature of the Verwey order between Fe3+ and Fe2+ decreases with Si content in Fe3-xSixO4 and their energy gap becomes smaller with Si.

Table 1. Structure parameters of Fe3-xSixO4

Sample(x)	0.0*	0.09	0.28	0.75	0.92	1.0
a(Å)	8.3940	8.392(2)	8.374(2)	8.286(1)	8.256(1)	8.2374(9)
u	0.3797	0.3792(3)	0.3769(1)	0.3700(2)	0.3666(1)	0.3658(2)
R		0.019	0.021	0.030	0.025	0.021
wR		0.020	0.020	0.030	0.024	0.021
site occupancy						
Oct (x 2)						
Ai(Fe)	1.0	0.998	0.975	0.963	0.999	1.0
Ai(Si)	0.0	0.002	0.025	0.037	0.001	0.0
Tetr (x 1)						
Ai(Fe)	1.0	0.914(7)	0.769(4)	0.324(7)	0.082(5)	0.0
Ai(Si)	0.0	0.086	0.231	0.676	0.918	1.0
VISi/Sitotal	0.0	0.044	0.179	0.099	0.021	0.0
Temp. factor						
b11(A) x10-5		188(4)	163(4)	185(8)	131(7)	119(8)
b11(B)		250(3)	235(3)	274(5)	193(3)	121(8)
b12(B)		21(4)	26(3)	25(5)	0(3)	-5(4)
b11(Oxy)		285(7)	302(7)	327(13)	204(7)	137(9)
b12(Oxy)		21(13)	67(25)	79(22)	3(9)	-5(12)
Bond distance						
A-O(Å)	1.886	1.878(2)	1.840(1)	1.722(2)	1.667(1)	1.653(1)
B-O(Å)	2.059	2.063(2)	2.078(1)	2.114(2)	2.136(1)	2.138(1)
(B-O)/(A-O)	1.092	1.099	1.129	1.228	1.281	1.293
VA(Å3)	3.441	3.399(2)	3.200(1)	2.621(2)	2.379(1)	2.314(2)
VB(Å3)	11.627	11.692(2)	11.955(1)	12.563(2)	12.904(1)	12.92(2)
VB(Å3)/VA(Å3)	3.379	3.440	3.736	4.793	5.424	5.58

*　Shull Wollan and Kochler (1951)
** Yamanaka (1986)

Table 2. Temperature dependence of electrical conductivity (s) W -1m-1

Fe3-xSixO4	288K	93K
x=0	2.643 x 102	9.872 x 101
x=0.018	2.315 x 100	8.915 x 10-3
x=0.28	2.790 x 10-2	1.327 x 10-5

Fe3-xSixO4	Verwey transition	electrical conductivity

	temperature (K)	gap (Dlogs)
x=0.0	124.0	0.853
x=0.018	120.9	0.425
x=0.28	102.2	0.299