Title	Dielectric Properties of α-Fe_2O_3 (Commemoration Issue Dedicated to Professor Tetsuya HANAI On the Occasion of His Retirement)
Author(s)	Iwauchi, Kozo; Kiyama, Masao
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1991), 69(4): 375-382
Issue Date	1991-12-30
URL	http://hdl.handle.net/2433/77406
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 69, No. 4, 1991.

Dielectric Properties of α-Fe_2O_3

Kozo IWAUCHI* and Masao KIYAMA*

Received August 22, 1991

Plate like and cubic type α-Fe_2O_3 powders were prepared by the precipitation from aqueous solution. The change of physical properties with the plate shape and thickness is investigated. Dielectric constant shows a peak near 70 K. Lattice deforms to produce ionic displacement at this temperature. The smaple of α-Fe_2O_3 shows several dielectric relaxations below room temperature.

KEY WORDS: α-Fe_2O_3

INTRODUCTION

The change of the Morin temperature T_M with the size of particle of α-Fe_2O_3 has been studied[1]. The change of property with particle shape is interesting. The plate like sample with hexagonal symmetry can be prepared. This sample has clear anisotropy concerning the crystal symmetry. Dielectric property of the powder has been studied[2,3]. Stable character of the oxide has been confirmed. The dielectric constant of powder α-Fe_2O_3 is about 6 at room temperature and increases from 6 in the lower temperature because of the increase of density. The change of dielectric constant and conductivity in the wide temperature range from 4.2 K to room temperature were examined. The behavior of dielectric constant for plate like α-Fe_2O_3 and cubic type α-Fe_2O_3 was examined. The origin of dielectric peak or increase near 70 K will be studied. The dielectric relaxation below room temperature will be also investigated.

EXPERIMENTAL

The sample α-Fe_2O_3 with cubic particle shape has been prepared by the oxidation of Fe_3O_4 with cubic particle shape which was prepared by the precipitation of $Fe(OH)_2$ from $FeSO_4$ solution by adding NaOH solution at 70°C in air[2]. Plate like α-Fe_2O_3 was prepared as follows. In the solution of $Fe(NO_3)_3$ and Na_2SiO_3, excess NaOH was added with the concentration of 1.0 mol/l NaOH obtained. These alkaline solution was heated at 200 ℃ for 4 hrs with autoclave.[4] The product sample was analysed by x-ray diffraction. The mean thickness of the plate like sample along c direction has been measured by x-ray line broadening and BET method with N_2 adsorption. By the existence of Si ions single crystal with plate of c plane grows and the thickness of plate along c axis can be controlled by the concentration of Si ions. The magnetic measurement was made by magnetic balance and dielectric measurement was made by YHP 4274 A LCR meter. Fig. 1 shows the morphology of the plate like α-Fe_2O_3 by electron

---

* 岩内 幸蔵, 木山 雅雄: Laboratory of Dielectrics, Institute for chemical Research, Kyoto University, Uji, 611 Japan

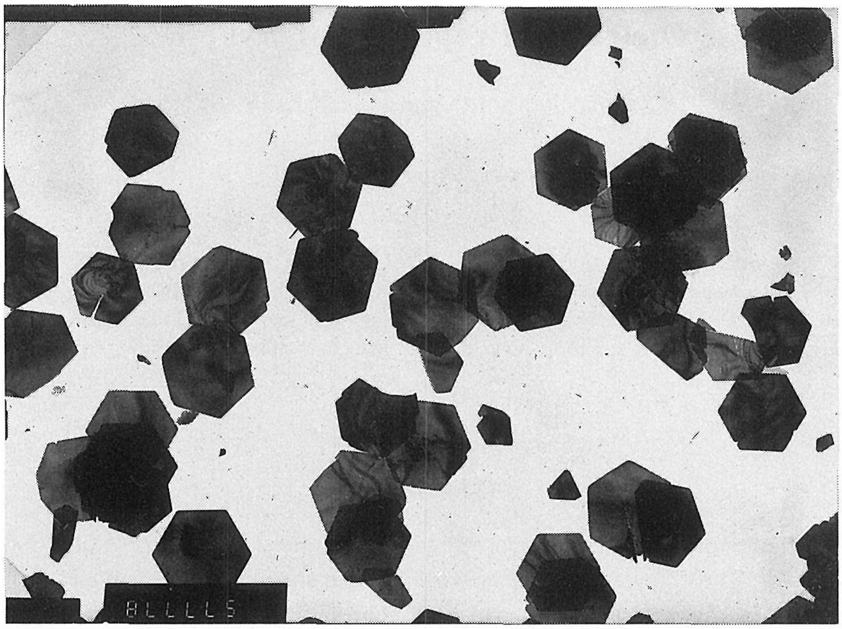

Fig. 1. Electron microscope photograph of the plate like α-Fe_2O_3 powder sample. Multiplication is 5000. Hexagonal plate crystals are seen.

Table 1. Characteristic of the plate like α-Fe_2O_3

Bet	(m^2/g)	8.7
apparent density	(g/cc)	0.05
Tap density	(g/cc)	0.08
Oil absorption	(cc/100g)	26.0
Noisture	(wt %)	0.6
ph value	(−)	9.55
diameter	(m)	2.1
Thicknessw	(A)	326
Aspect ratio	(−)	64

microscope. The characteristic of powder are shown in Table 1. Dielectric measurement of powder smaples was carried out by pressing the powder into the cell in which powders can be pressed into the pellet of 17 mm diameter and 0.1 mm thickness.

RESULTS AND DISCUSSINOS

T_M decreases rapidly with the decrease of thickness. Dielectric properties of α-Fe_2O_3 with plate like crystal are shown in Fig. 2. Dielectric constant at 4.2 K is close to 6 and increase slowly near room temperature. The value of $\varepsilon = 6$ is the appropriate value in concern with the dielectric constant for many other samples of α-Fe_2O_3 powder which has been measured[2,3]. Dielectric constant has a small peak near 70 K independent of frequency. Above 180 K there are increase of ε depending on frequency.

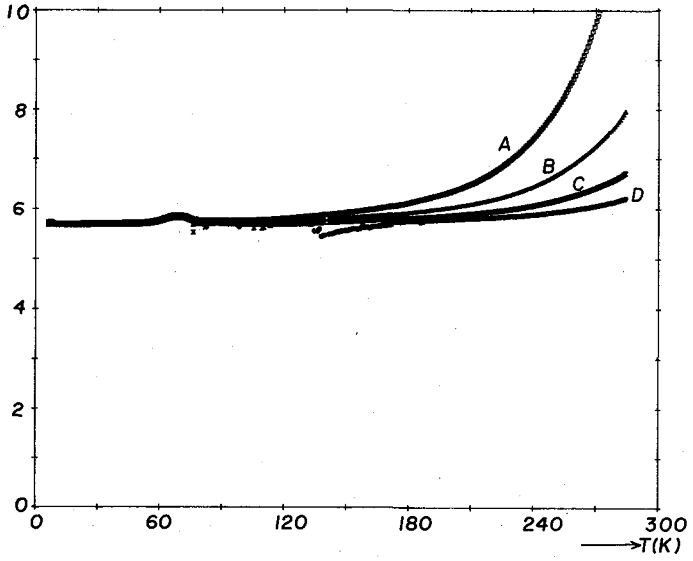

Fig. 2. Temperature dependence of dielctric constant ε' of plate like α-Fe_2O_3 powder. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

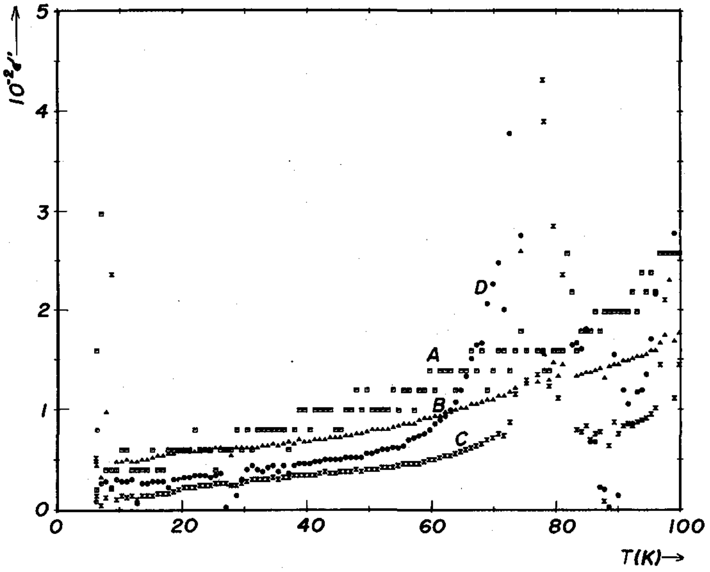

Fig. 3. Temperature dependence of dielctric loss ε'' of the plate like α-Fe_2O_3 powder. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

This kind of frequency dependent increase of ε is caused by the space charge polarization of contamination. The increase of ε at 70 K in Fig. 2 is first found for the sample with plate like particle. Figure 3 shows the temperature dependence of dielectric loss ε'' of this sample. The peak of ε'' are also seen. We must investigate the mechanism of increase of ε'' at 70 K for this sample. The sample of α-Fe_2O_3 with cubic particle

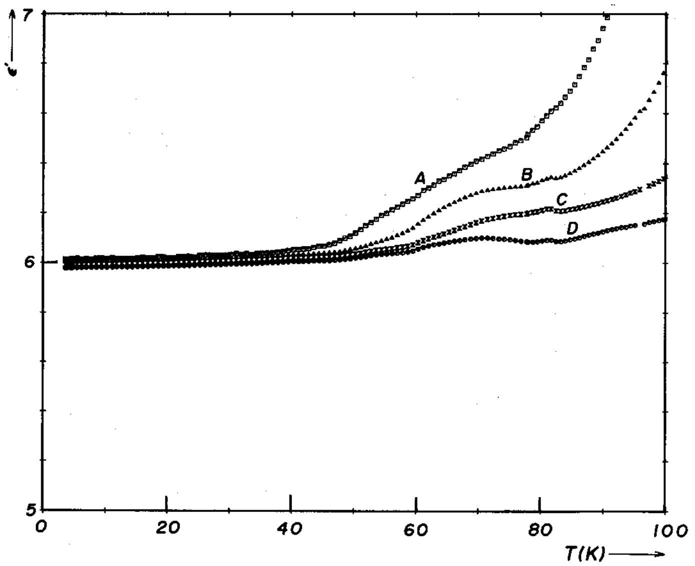

Fig. 4. (a)Temperature dependence of dielctric constant ε' of cubic type α-Fe_2O_3 powder below 100 K. A,B,C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

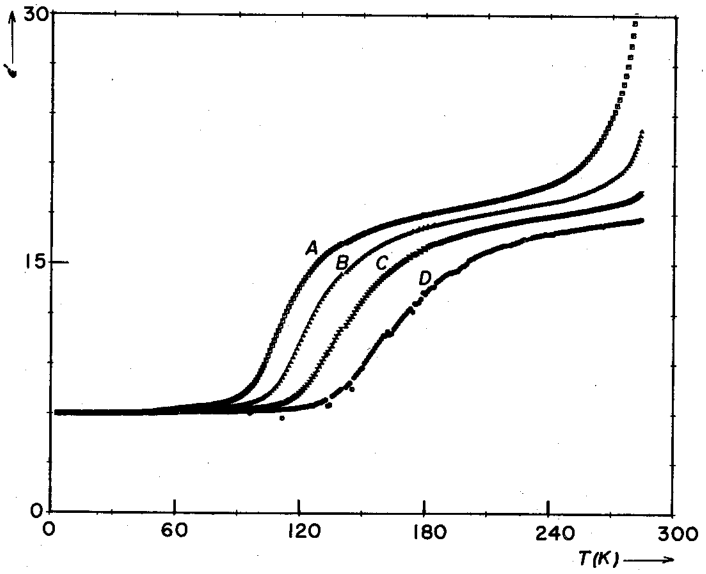

Fig. 4. (b)The temperature dependence of dielectric constant ε' of the same sample as (a) in the wide temperature range from 4.2 to 300 K. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

shows the temperature dependence of ε' as shown in Fig. 4(a). The increase of ε' with relaxation style is seen around 70 K. In this case ε' does not decreases above 70 K but levels off followed by the dielectric relaxation in the temperature range from 90 to 210 K. This type of relaxation seems to be the Debye dielectric relaxation. Ions begin to move near 70 K. The dielectric constant of 6 is the low temperature value of α-Fe_2O_3. Only for 100 kHz dielectric constant decreases a little after the increase at 70 K. This

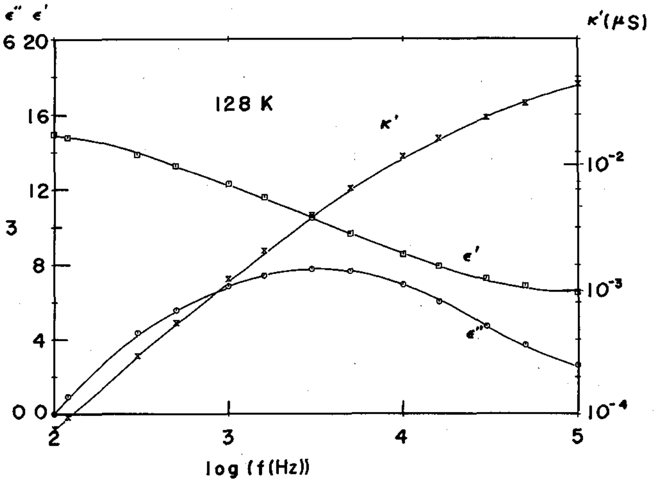

Fig. 5. Frequency dependence of dielctric constant ε', loss ε'' and conductivity $\kappa'(\mu S/cm)$ of cubic type α-Fe_2O_3 sample at 128 K.

sample of α-Fe_2O_3 has different ions and hence dielectric constant increases from the level of 6 to higher level of 20 in the temperature rnage from 90 to 210 K(Fig. 4(b)). Fig. 5 shows the deelctric dispersion of cubic type α-Fe_2O_3 measured at 128 K. From the experimental value obtained; $\varepsilon_l=14.9$, $\varepsilon_h=6.83$, $\kappa_l=7.57\times10^{-5}\mu S/cm$ and $\kappa_h=0.438\mu S/cm$, we obtained the the number of different ions $n_0=.58\times10^{21}$ and $n_0/N=0.0589$ assuming ferrous ions exist in α-Fe_2O_3 and electron hops between the nearestneighbor Fe^{++}-Fe^{+++} ions. This result seems to be rather larger for the concentration of ferrous ions in α-Fe_2O_3. There may be other mechanism of electron hopping in the oxides. On the other hand the dielectric constant of plate like α-Fe_2O_3 keeps the value of 6 until

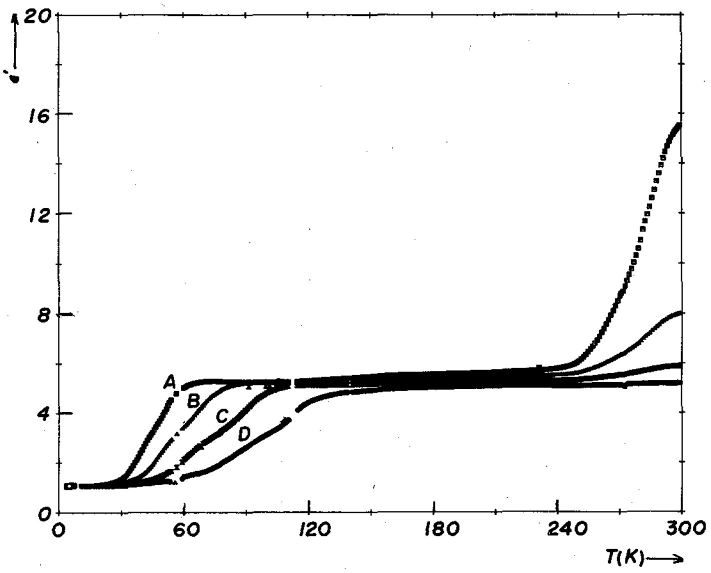

Fig. 6. Temprature dependence of dielctric constant ε' of Jhonson Massay Co. 99.999% α-Fe_2O_3 powder. A,B,C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

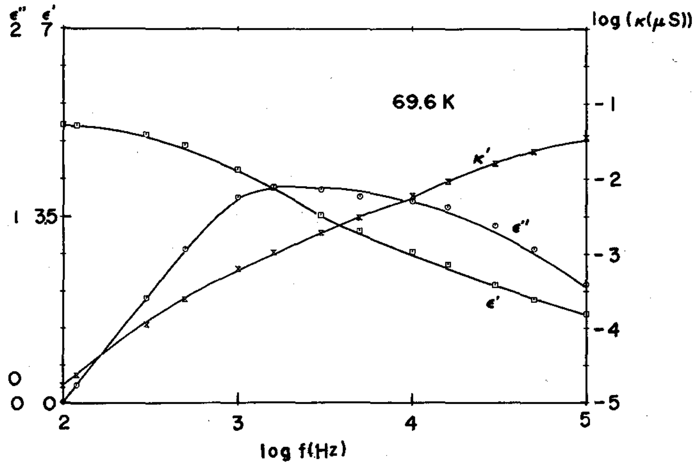

Fig. 7. Frequency dependence of dielctric constant ε', loss ε'' and conductivity κ'(μS/cm) of the sample of Fig. 6 at 69.6 K.

about 200 K and then begins increasing for higher temperature. The dielctric constant ε of 6 is arising from the electronic polarization of this material. The small increase of ε at 70 K is seen for both samples. Deformation of lattice to produce ionic displacement happens at this temperature. The plate like sample has more stoichiometric composition than cubic type α-Fe_2O_3. Arrangement of crystal plane (c-plane) perpenadicular to the electric field make the latiice anomaly clearer.

The temperature dependence of dielctric constant ε of the Jhonson Massay Co. α-Fe_2O_3 is shown in Fig. 6. This sample has the highest purity of 99.999% α-Fe_2O_3. This sample has large particle size and has not uniform shape. In the temperature range from 4.2 to 110 K this sample shows large dielectric relaxation. Fig. 7 is the dielectric dispersion of this sample at 69.6 K. Dielectric constant increases from 1.5 to 5.3 in the temperature range from 4.2 to 120 K. This type of dielectric relaxation with large $\Delta\varepsilon$ in the powder cell has been once found for γ-Fe_2O_3[2]. From these experments we suppose that this dielectric relaxation is caused by the structural effect between powder and cell. From the Maxwell theory of two phase mixture (Fig. 8) we obtain the following results by using observed limiting values[5,2]:

$$\varepsilon_l = 5.2056, \quad \kappa_l = 1.686 \times 10^{-5} \mu S/cm$$

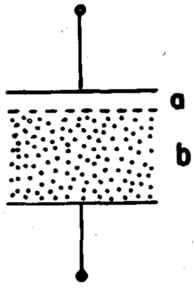

Fig. 8. Shematic two phase model in the cell.

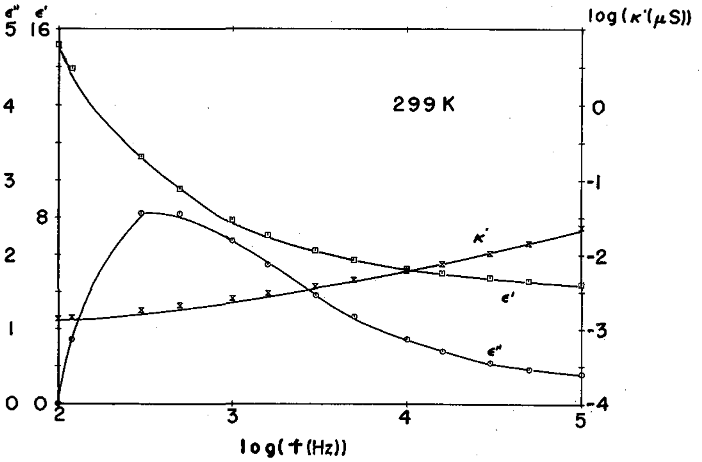

Fig. 9. Frequency dependence of dielctric constant ε', loss ε" and conductivity κ'(μS/cm) of the sample of Fig. 6 at 299 K.

$\varepsilon_h=1.6685, \quad \kappa_h=0.03538\mu S/cm$

by assuming $\varepsilon_a=1$ (phase a is considered as air gap), and $\kappa_b>>\kappa_a$.

$\Phi=0.8$(Φ is the fraction of b phase)

$\varepsilon_b=1.988$

The phase b is considered as α-Fe_2O_3 powder sample. The result of $\varepsilon_b=1.988$ is too small compared with $\varepsilon=6$ of α-Fe_2O_3 as mentioned above. The precise situation of this polarization is not well known yet. This large dielctric relaxation masks the peak of dielectric constant at 70 K which is observed for plate like and cubic type samples. After this dielectric relaxation this sample has the dielectric constant of about 6 which is the value of dielectric constant usually found for other smaples.

Dielectric constant of Fig. 6 increases again at 300 K. Another dielectric relaxation appears near 300 K. Dielectric dipersion of this relaxation is shown in Fig. 9. This dielectric relaxation is considered to be caused by the interfacial polarization arising from the heterogeneous structure of the sample becase activation energy required for the relaxation at about room temperature is higher than that of electron hopping process which is seen in these oxides[6,7]. By using the equations of interfacial polarization[2] we calculate the dielectric constant and conductivity of heterogeneous structure. The limiting values of observed dielectric constant and conductivity are as follows. $\varepsilon_l=15.33$, $\varepsilon_h=5.13$, $\kappa_l=1.37\times10^{-3}\mu S/cm$, $\kappa_h=0.0235\mu S/cm$. Here we assume $\varepsilon_b=6$ and $\kappa_b>>\kappa_a$ and obtain $\varepsilon_h=6\varepsilon_a/(6+\Phi(\varepsilon_a-6))$, $\varepsilon_l=\varepsilon_a/(1-\Phi)$ and therefore $\varepsilon_a=3.4$, $\Phi=0.778$, $\kappa_a=\frac{\kappa_l}{1-\Phi}=0.304\times10^{-3}\mu S/cm$ and $\kappa_b=22.16\mu S/cm$. This result represents that the conductivity of phase b (main component) is $22.16\mu S/cm$ and dielectric constant $\varepsilon_b=6$ and fraction of this phase is 0.778. Dielectric constant of phase a is 3.4 and conductivity, $0.304\times10^{-3}\mu S/cm$. The conductivity of main phase ($22.16\mu S/cm$) is rather higher considering the conductivity of α-Fe_2O_3 which has been ever studied in our work. The conductivity of phase a of this sample ($10^{-10}S/cm$) is appropriate. If the phase a which has lower conductivity and dielectric constant, is assumed to be the grain boundary of this oxide, the volume fraction of this phase (0.222) is too large. Anyway it is concluded that the Jhonson Massay Co. 99.999% high purity α-Fe_2O_3 is not composed of uniform phase of stoichiometric α-Fe_2O_3 but composed of electrically different component. The sample of α-Fe_2O_3 prepared by this experiment-plate like crystal has uniform structure except having some amount of impurity ions. Arrangement of the plate like particle with c plane makes the dielectric property distinguished.

REFERENCES

(1) T. Takada, N. Yamamoto, T. Shinjo, M. Kiyama and Y. Bando, *Bull. Inst. Chem. Res. Kyoto. Univ.* **43,** 406 (1965).

(2) K. Iwauchi, *Japan. J. Appl. Phys.,* **10,** 1520 (1971).

(3) K. Iwauchi, S. Yamamoto, Y. Bando and N. Koizumi, *Bull. Inst. Chem. Res., Kyoto Univ.,* **48,** 159 (1970).

(4) T. Nakamura, T. Takada, M. Kiyama and T. Kurata, *Bull. Inst. Chem. Res., Kyoto Univ.* **68** (1991) 275

(5) J.C. Maxwell, Electricity and Magnetism (Oxford University Press, London, 1873), Vol. 1, Sec. 328.

(6) K. Iwauchi, M. Kiyama, N. Koizumi and Y. Bando, *Bull. Inst. Chem. Res., Kyoto Univ.,* **52,** 596 (1970).

(7) K. Iwauchi and N. Koizumi, Ferrites; Proceedings Int. conf. Jap. 106 (1980).