Pergamon

Cement and Concrete Research, Vol. 26, No. 12, pp. 1801-1808, 1996
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0008-8846/96 $15.00 + .00

PII S0008-8846(96)00177-9

# ANISOTROPIC LIGHT ABSORPTION OF THE FERRITE SOLID SOLUTIONS $Ca_2(Fe_{1-x}Al_x)O_5$

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(Refereed)
(Received April 11, 1996; in final form October 10, 1996)

## ABSTRACT

In the ferrite phase of the system $Ca_2(Fe_{1-x}Al_x)O_5$ ($x = 0 \sim 0.67$) Mg replaces Fe and Al up to 0.044 atom/formula irrespective of the composition x. In the presence of sufficient oxygen in the atmosphere tetravalent Fe ions are formed with resultant increase of both anisotropic light absorption and electric conductivity, due to a mechanism involving transfer of a positive electron hole from $Fe^{4+}$ ions to $Fe^{3+}$ ions in the vicinity. Coexistence of trivalent Y ions reduces this effect. Under low oxygen pressures the positive charge deficiency due to the replacement is compensated by creating oxygen defects; and the ferrite phase lightens with increase in yellowness. *Copyright © 1996 Elsevier Science Ltd*

## Introduction

The dark gray color of portland cement comes from the ferrite phase. The ferrite phase of the system $Ca_2(Fe_{1-x}Al_x)O_5$ is reddish yellow to brown in color in itself with weak anisotropic light absorption. With incorporation of Mg ions, however, the light vibrating perpendicular to the *b*-axis is absorbed strongly with the lightness decreasing to a considerable degree.

It was proved in our previous study on $C_4AF$ ($x = 0.5$) that divalent Mg ions replace trivalent Fe and Al ions in the ferrite structure, creating tetravalent Fe ions in the oxydizing atmosphere to compensate the positive charge deficiency (1). These extrinsic $Fe^{4+}$ ions cause the strong anisotropic absorption of visible light. With scarce oxygen in the atmosphere, oxygen vacancies are formed instead with the anisotropic light absorption remaining weak.

Independently of our results, Scrivener and Taylor (2,3) came to the conclusion, referring to the semiconducting properties of the ferrite phase, that the color of portland cement is dark when the ferrite phase contains sufficient $Mg^{2+}$ replacing $Fe^{3+}$ with the formation of a little $Fe^{4+}$. Light color in a clinker is caused by insufficient oxidation of the ferrite phase during cooling and does not necessarily denote that the kiln atmosphere during burning is reducing.

In the present investigation, the incorporation of Mg was studied for other members of the solid solution series than $C_4AF$; *i.e.*, $C_2F$ (x = 0), $C_6AF_2$ (x = 0.33) and $C_6A_2F$ (x = 0.67). The replacement of Fe by Zn in $C_2F$ was investigated as well. Furthermore, $Y_2O_3$ was made to coexist with MgO in $C_2F$, intending to depress the formation of extrinsic $Fe^{4+}$ ions by the coupled ion exchange of $Ca^{2+} + Fe^{3+} \rightarrow Y^{3+} + Mg^{2+}$.

The electric conductivity and color change with partial oxygen pressures was measured for $C_4AF$ with MgO in solid solution. The Seebeck thermoelectric effect was measured to decide the kind of charge carriers. The results, in association with those in the previous reports, led to the comprehensive understanding of the color change of the ferrite phase with incorporation of Mg ions.

## Experimental

A series of $C_2F$ solid solution samples with varying Mg concentration were prepared by adding MgO to $C_2F$. With $C_6AF_2$ and $C_6A_2F$, only excess amount of MgO was added to determine the solubility limit. The mixtures, after firing at 1250°C with intermediate grinding, were kept at 1350°C for 1 to 7 days to grow homogeneous ferrite crystals large enough for electron probe microanalysis and spectral transmission measurement under the microscope. Further, solo replacement of Fe by Zn and coupled exchange of Ca and Fe by Y and Mg in $C_2F$ were undertaken. Table 1 summarizes the compositions of the samples prepared.

The chemical composition of each ferrite phase was given by the average of more than 15 quantitative spot analyses by an electron probe microanalyzer (JCMA–733, JEOL, accelerating voltage:15kV, specimen current: 0.012μA, electron probe diameter:1μm). The correction for intensities were made by the standard ZAF routines.

Spectral transmittance was measured in the visible spectrum region between 400 and 800nm using an optical microscope equipped with a photometer and a grating monochrometer (Nikon P102 and G70). The transmission was measured in the minimum and maximum absorption directions (parallel and perpendicular to the *b*-crystallographic axis, respectively). For comparison, the maximum transmittance around 780nm in the direction parallel to X(= *b*) was made equal for each specimen.

TABLE 1

Sample Compositions (wt%)

| Sample | CaO | $Fe_2O_3$ | $Al_2O_3$ | MgO | ZnO | $Y_2O_3$ |
|---|---|---|---|---|---|---|
| M1 | 41.26 | 58.74 | | | | |
| M2 | 41.15 | 58.60 | | 0.25 | | |
| M3 | 41.05 | 58.45 | | 0.50 | | |
| M4 | 40.84 | 58.16 | | 1.00 | | |
| M5 | 40.25 | 57.31 | | 2.44 | | |
| M6 | 43.51 | 41.30 | 13.19 | 2.00 | | |
| M7 | 47.10 | 22.35 | 28.55 | 2.00 | | |
| Z1 | 40.84 | 58.16 | | | 1.00 | |
| Z2 | 40.02 | 56.98 | | | 3.00 | |
| MY1 | 40.47 | 57.62 | | 0.50 | | 1.41 |
| MY2 | 39.68 | 56.50 | | 1.00 | | 2.81 |
| MY3 | 38.11 | 54.27 | | 2.00 | | 5.62 |

### TABLE 2

### Number of Atoms in One Chemical Formula Unit*

| Sample | Ca | Fe | Al | Mg | Zn | Y | Chemical formula** |
|---|---|---|---|---|---|---|---|
| M1 | 2.036(14) | 1.976(9) | | | | | $Ca_2Fe_{1.990}O_5$ |
| M2 | 2.041(16) | 1.963(11) | | 0.014(1) | | | $Ca_2(Fe_{1.979}Mg_{0.014})_{\Sigma 1.993}O_5$ |
| M3 | 2.047(21) | 1.947(14) | | 0.032(2) | | | $Ca_2(Fe_{1.965}Mg_{0.032})_{\Sigma 1.997}O_5$ |
| M4 | 2.043(13) | 1.944(9) | | 0.041(4) | | | $Ca_2(Fe_{1.961}Mg_{0.041})_{\Sigma 2.002}O_5$ |
| M5 | 2.040(26) | 1.944(18) | | 0.044(2) | | | $Ca_2(Fe_{1.960}Mg_{0.044})_{\Sigma 2.004}O_5$ |
| M6 | 2.031(42) | 1.285(37) | 0.665(18) | 0.044(1) | | | $Ca_2(Fe_{1.293}Al_{0.669}Mg_{0.044})_{\Sigma 2.006}O_5$ |
| M7 | 2.028(36) | 0.829(40) | 1.129(28) | 0.035(2) | | | $Ca_2(Fe_{0.834}Al_{1.135}Mg_{0.035})_{\Sigma 2.004}O_5$ |
| Z1 | 2.028(16) | 1.970(11) | | | 0.017(2) | | $Ca_2(Fe_{1.979}Zn_{0.017})_{\Sigma 1.998}O_5$ |
| Z2 | 2.110(25) | 1.903(18) | | | 0.035(17) | | $Ca_2(Fe_{1.946}Zn_{0.036})_{\Sigma 1.982}O_5$ |
| MY1 | 2.034(13) | 1.923(9) | | 0.033(2) | | 0.033(1) | $(Ca_{1.967}Y_{0.033})(Fe_{1.956}Mg_{0.034})_{\Sigma 1.990}O_5$ |
| MY2 | 1.995(12) | 1.897(11) | | 0.061(4) | | 0.066(3) | $(Ca_{1.934}Y_{0.066})(Fe_{1.933}Mg_{0.062})_{\Sigma 1.995}O_5$ |
| MY3 | 1.916(14) | 1.878(10) | | 0.074(2) | | 0.129(3) | $(Ca_{1.871}Y_{0.129})(Fe_{1.920}Mg_{0.076})_{\Sigma 1.996}O_5$ |

*Number of oxygen atoms 5. **Number of atoms in Ca sites 2.
Figures in parentheses: standard deviations.

The electric conductivity measurement was made at every 50°C between 50°C and 250°C, using specimens synthesized by solid state reaction. $C_4AF$ with 0.5 % of MgO in solid solution was prepared for the measurement of electric conductivity and color change with partial oxygen pressures. The pelletized raw mixtures were heated at 50°C/min up to 1000°C, kept for 30 min, further heated at 30°C/min up to 1400°C, kept for 10 min and then cooled spontaneously down to 300°C in the furnace without power supply. During firing the inside of the furnace was kept at given partial oxygen pressures by flowing mix gases of oxygen and nitrogen ($O_2 < 10^{-4}$atm).

## Results

Incorporation of Foreign Elements. Table 2 gives the chemical compositions of the ferrite solid solutions as represented by the chemical formulas with five oxygen atoms. With $C_2F$ and $C_6AF_2$, the maximum number of Mg atoms in one chemical formula unit is 0.044, in fair agreement with that in $C_4AF$ (0.045). The number of Ca atoms was always a little larger than 2. According to the phase equilibrium diagram, such excess Ca atoms probably came from submicroscopic CaO crystallites dispersed in the crystals. In the last column of Table 2 are given the chemical formulas with two Ca atoms in one formula unit. The sum of the atoms in the Fe and Al sites is very close to 2.

Mg vs. Fe in $C_2F$ Solid Solutions. As shown in Fig.1, the relation between Mg and Fe in the $C_2F$ solid solutions gave a straight line of slope −1 with the sum very close to 2, indicating that Mg replaces Fe in the structure. With $C_6AF_2$ the ratio Al/(Fe + Mg) was exactly 1/2 in support of the replacement of Fe by Mg as well. With $C_6A_2F$, however, the A/F ratio was much less than 2 even if Mg was added to Al. In view of the crystals having grown in the presence of a small amount of the liquid phase, the decrease in A/F suggests, as in $C_4AF$ in

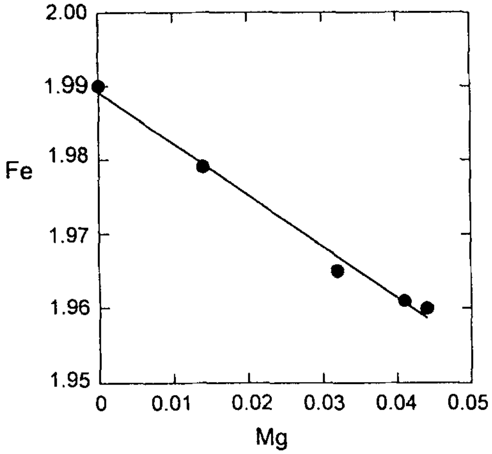

FIG. 1.
Mg vs. Fe in $C_2F$ solid solutions.

the previous study (1), that the liquid was rich in $Al_2O_3$ and increased in quantity with the increase of MgO added.

Zn also replaced Fe to a certain extent. It is conceivable that the occurrence of $Fe^{4+}$ by the replacement of $Fe^{3+}$ by $Mg^{2+}$ may be depressed if trivalent ions, *e.g.* $Y^{3+}$ ions, are introduced simultaneously to the Ca-sites. In fact, as shown in Fig. 2, the coupled ion exchange occurred to a certain degree with increased solubility limit of Mg, beyond which continued the solo replacement of Ca by Y.

Anisotropic Light Absorption. Fig. 3(a) shows the transmittance of visible light for $C_2F$ for the plane polarized light vibrating parallel and perpendicular to X(= b). The absorption

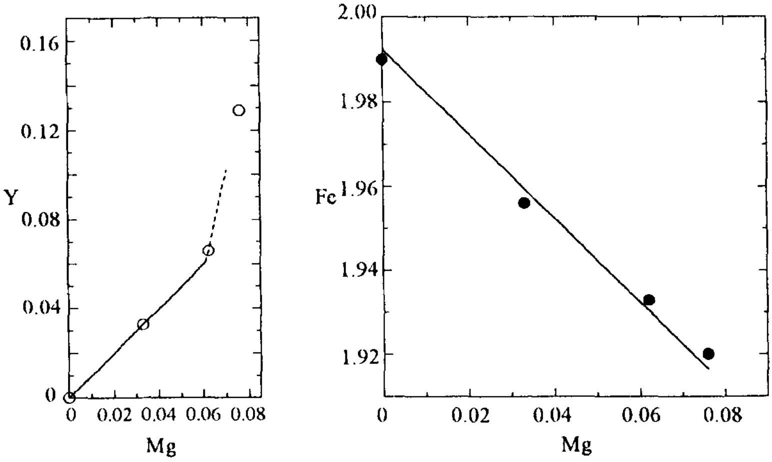

FIG. 2.
Mg vs. Y (left) and Mg vs. Fe (right) in $C_2F$ solid solutions with coupled ion exchange $Ca^{2+} + Fe^{3+} \rightarrow Y^{3+} + Mg^{2+}$.

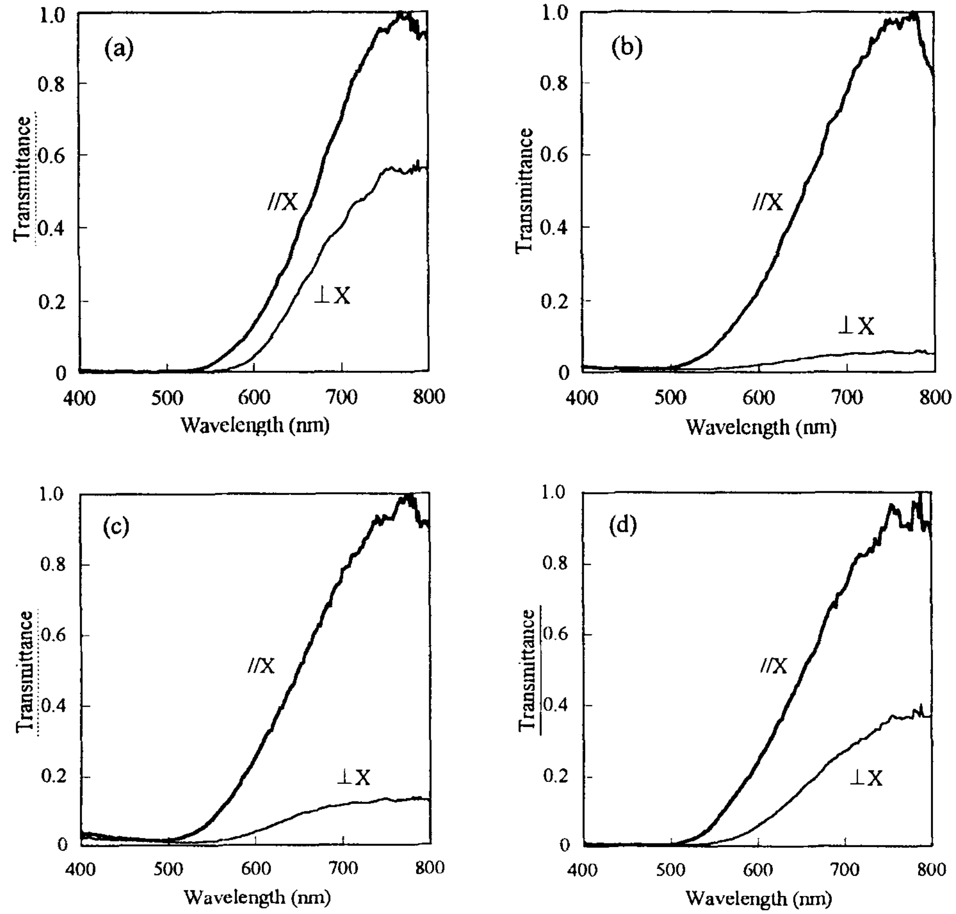

FIG. 3.

Transmission spectra of $C_2F$ and its solid solutions in the minimum and maximum absorption directions. (a) M1(= $C_2F$), (b) M4, (c) Z1, (d) MY2.

formula is X = weak (reddish orange) Y, Z = medium (dark reddish brown). The incorporation of Mg in $C_2F$ strongly increased the absorption in the YZ-plane, as in $C_4AF$, and led to the darkening in color (Fig. 3(b)). The decrease in transmittance or the increase in absorption occurred uniformly over the entire visible region with no appreciable change in the shape of the spectral distribution curve. The incorporation of Zn also decreased the transmittance to a significant degree (Fig. 3(c)). As compared with the solo replacement of Fe by Mg, the coupled exchange by $Y^{3+}$ and $Mg^{2+}$ apparently reduced the absorption of light in the YZ-plane (Fig. 3(d)).

Electric Conductivity and Color. Fig. 4 gives the specific electric conductivity as a function of 1/T for $C_2F$ and its solid solutions, showing the semiconducting properties of these materials. With incorporation of the maximum amount of MgO the specific conductivity was

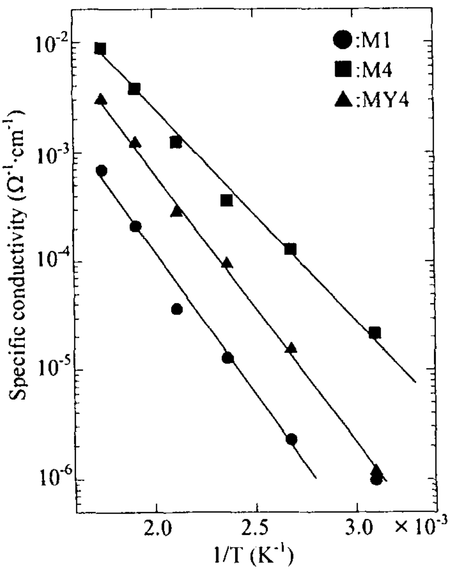

FIG. 4.
Specific electric conductivity of $C_2Fss$.

increased at least by an order of magnitude; whereas the coexistence of equivalent $Y_2O_3$ apparently reduced the increment.

The Seebeck thermoelectric effect was measured to determine the kind of charge carrier for the Mg-doped $C_4AF$. The coefficient Q as defined below is positive for holes and negative for electrons.

$$Q = dV/dT = -(V_h - V_c)/(T_h - T_c)$$

where $V_h - V_c$ is the difference in open e.m.f. and $T_h - T_c$ the difference in temperature between the hot and cold ends of the specimen. The charge carrier has thus been proved to be positive holes.

The electric conductivity and color change with partial oxygen pressures was measured for the Mg-doped $C_4AF$. As shown in Fig. 5, the specific electric conductivity decreased noticeably with the decrease of the partial oxygen pressures. The b- and L-values, which represent respectively yellowness and lightness of the specimen in the Lab color system in reflected light, increased with decreasing partial oxygen pressures (Fig. 6).

## Discussion

In the ferrite phase doped with Mg (or Zn) the strong absorption for the light vibrating perpendicular to X occurred uniformly in the entire visible spectrum region. This strong absorption of visible light can be explained as arising from a relaxation process involving transfer of a hole promoted by the photon from $Fe^{4+}$ to $Fe^{3+}$ in the vicinity, *i.e.*, interconversion between $Fe^{3+}$ and $Fe^{4+}$. This is in accordance with the *p*-type semiconductivity of the Mg-doped $C_4AF$ determined from the thermoelectric effect.

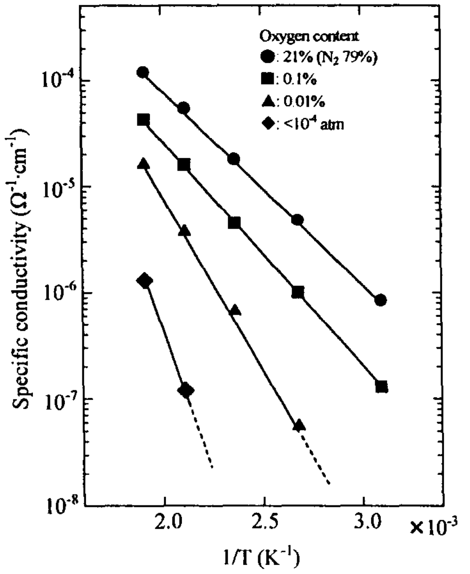

FIG. 5.
Specific electric conductivity change of $C_4AFFss$ with partial oxygen pressures.

In the presence of sufficient oxygen in the atmosphere positive electron holes are extrincically introduced with the replacement of $Fe^{3+}$ or $Al^{3+}$ by $Mg^{2+}$. This process is described as follows using the Kroger-Vink notations (4).

$$4CaO + 2MgO + (Fe_2O_3, Al_2O_3) + \frac{1}{2}O_2 \rightarrow 4Ca_{Ca}^{\times} + 2Mg_{(Fe,Al)}' + 2(Fe, Al)_{(Fe,Al)}^{\times} + 10O_O + 2h^{\cdot}$$

where $Mg_{(Fe,Al)}'$ and $h^{\cdot}$ indicate Mg atoms to be on Fe,Al-sites with one extra negative charge and positive electron holes, respectively. The formation of positive holes is depressed by the oxidation of $Fe^{2+}$ ions, the concentration of which, however, is usually low enough as given in Fig. 6. With poor oxygen in the atmosphere the deficiency of positive charge due to the replacement can be compensated by creating oxygen vacancies.

$$4CaO + 2MgO + (Fe_2O_3, Al_2O_3) \rightarrow 4Ca_{Ca}^{\times} + 2Mg_{(Fe,Al)}' + 2(Fe, Al)_{(Fe,Al)}^{\times} + 9O_O + V_O^{\cdot\cdot}$$

where $V_O^{\cdot\cdot}$ indicates oxygen vacancies with effective positive charges with respect to the host lattice. In fact, the concentration of $Fe^{4+}$ in the ferrite phase varies between the above two extremes depending on the atmospheric oxygen pressures, in agreement with the observations by Taylor and Scrivener (2,3) that light color occurred even if conditions in the kiln were normally oxidizing.

## Summary

(1) The solubility limit of Mg in the ferrite phase of the system $Ca_2(Fe_{1-x}Al_x)O_5$ ($x = 0 \sim 0.67$) has been proved to be constant (0.044 atom/formula at 1350°C) irrespective of

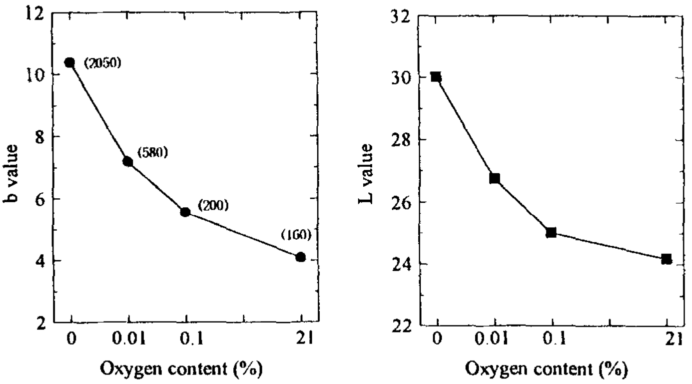

FIG. 6.

Color change of $C_4AFss$ with oxygen content in the atmosphere. b-value (left), L-value (right). Figures in parentheses indicate $Fe^{2+}$ concentration in ppm.

the composition x. $Mg^{2+}$ replacing $Fe^{3+}$ in the ferrite structure produces extrinsic $Fe^{4+}$ in the presence of sufficient oxygen in the atmosphere.

(2) Both anisotropic light absorption and electric conductivity of the ferrite phase increased with the concentration of $Mg^{2+}$ in solid solution. The results were explained by a mechanism involving transfer of a hole with interconversion between $Fe^{3+}$ and $Fe^{4+}$.

(3) The light absorption and electric conductivity decreased as the oxygen content in the atmosphere was lowered. The ferrite phase lightened with increasing degree of yellowness.

## Acknowledgment

I. M. thanks the Japan Cement Association for financial support.

## References

1. I. Maki, K. Fukuda, E. Oba, H. Yoshida, M. Mitsumatsu and S. Ito, *Cem. Concr. Res.*, 25 863(1995).
2. H.F.W. Taylor and K.L. Scrivener, *Proc. Conf. in Tribute to Micheline Moranville Regourd*, pp. 53-61, October, 1994, Sherbrooke, Quebec, Canada.
3. K.L. Scrivener and H.F.W. Taylor, *ZKG* 48, 34(1995).
4. F.A. Kröger and V.J. Vink, Solid State Physics, Vol. 3 (ed. by F. Seitz and D. Turnbull), p.307, Academic Press, Inc., NY.