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The role of dopants on the formation and defect structures of the M-type of calcium ferrite

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The formation mechanisms of M-type calcium ferrite were further assessed by doping Y_2O_3, $BaCO_3$ and $SrCO_3$. It was found that the ionic radius, rather than the valence is the predominant factor in the formation of the magnetoplumbite phase of calcium ferrite. The $CaO \cdot 2Fe_2O_3$ phase which played a precursor role in the formation of the M-type calcium ferrite was further verified. The defect structures based on the substitution of Ca^{2+} by La^{3+}, the charge compensation by Fe^{2+}, and release of oxygen were supported by DTA–TGA and conductivity data. The conductivity was assumed to occur through a hopping mechanism as it increased with increasing temperature. The estimated values of the activation energy based on the small-polaron conduction were 0.35 to 0.40 eV in the high temperature region and 0.027 to 0.054 eV in the low temperature region. Moreover, the preexponential factor in the conductivity equation is an exponential function of the fraction of the M phase in the specimen.

1. Introduction

Hexagonal ferrites with magnetoplumbite (M) structure are widely used in the electronics industry as permanent magnets. The chemical composition is usually characterized by $MFe_{12}O_{19}$, where M stands for barium, strontium or lead [1]. According to the accepted phase diagram of the $CaO–Fe_2O_3$ system [2] no M-type calcium ferrite exists in spite of the close chemical affinity of calcium, strontium and barium. This might be attributed to the smaller ionic radius of Ca^{2+} (0.106 nm) compared with those of Ba^{2+} (0.143 nm), Sr^{2+} (0.127 nm) and Pb^{2+} (0.132 nm). Ichinose *et al.* [3] discovered, however, that M-type calcium ferrite could be developed by adding a small amount of lanthanum oxide. Although Yamamoto *et al.* [4–6] and Lotgering *et al.* [7] have made extensive studies of the magnetic properties of this M-type calcium ferrite, they did not determine the formation mechanism of the M-type Ca–La ferrite. Recently, Fang *et al.* [8] have proposed a possible formation mechanism for the M-type calcium ferrite, in which $CaO \cdot 2Fe_2O_3$ (denoted by CF_2) plays a precursor role.

Although La_2O_3 could induce the M-type calcium ferrite, the other rare earth elements have been reported not to have the same effect [3]. It is known, however, that in the barium or strontium ferrite system, Ba^{2+} or Sr^{2+} could be partially or entirely replaced by lanthanide ions [9]. This involves a charge compensation mechanism such as lanthanide vacancies, trivalent iron reduction or its substitution by divalent ions such as Ni^{2+} or Zn^{2+}. Moreover, $BaO \cdot 6Fe_2O_3$ can be replaced completely by a combination of a trivalent and a monovalent ion, for instance, $Ag^{1+} + La^{3+}$ or $Na^{1+} + La^{3+}$ [10, 11]. Furthermore, it has been shown [12] that in magnetoplumbite hexaluminates, M^{2+} such as magnesium, manganese and cobalt, could stabilize the spinel blocks of these phases by reducing the number of vacancies in the unit cell and make the preparation of the magnetoplumbite phase easier.

The electrical properties would be changed owing to the change of the defect structures. Frantsevich *et al.* [13] reported that for La^{3+}-doped barium ferrite, the magnetic properties are only slightly affected by the addition, whereas the electrical conductivity changes by several orders of magnitude.

The objectives of this investigation are to pursue the role of dopants on the formation of the M-type calcium ferrite and to study the defect structures and electrical properties of M-type calcium ferrite.

2. Experimental procedure

Samples were prepared from Merck's reagent-grade powders (Merck Co., St. Louis, MO) of $BaCO_3$, $SrCO_3$, Y_2O_3, $CaCO_3$ and Fe_2O_3. These powders in appropriate ratios were well mixed for about 20 h and calcined in air at 1180° C for 4 h to form the desired compounds. In order to form CF_2 completely, the mixed powder in the desired ratio was calcined at 1200° C for 4 h. Some doped CF_2 compacts were inserted into a furnace at 1180° C for 4 h and then quenched in water. After calcination, the powders and pellets were X-rayed (using Fe Kα radiation) to identify the phases present. The phases detected are summarized in Table I. The La^{3+}-doped calcium ferrite specimens were employed in an electrical conduction study. The electrical conductivity was measured using a LCR meter (HP, 4276A).

Figure 1 An X-ray pattern of CF_2 doped with 1 wt % $BaCO_3$, fired at 950° C for 4 h, showing the occurrence of the M phase. (▲: F, ◆: CF, and ●: M)

3. Results and discussion

3.1. The effects of dopants on the CaO–Fe_2O_3 system

In previous work, [8] the authors have shown that the M-type structure in the CaO–Fe_2O_3 system could be completely synthesized at 1180° C for 4 h by adding more than 4 wt % La_2O_3 and CF_2 could be a precursor in forming the M-type calcium ferrite, however, in order to investigate possible factors for dopants to induce the M phase in calcium ferrite, dopants with different valences and nearly the same ionic radius (Ba^{2+} and Sr^{2+}) and dopants with smaller ionic radius and the same valence (Y^{3+}), compared with La^{3+}, were selected. Table I shows that CF_2 and CaO : $6Fe_2O_3$ (a mixture, denoted as CF_6) were doped with different amounts of Y_2O_3, $BaCO_3$ and $SrCO_3$, respectively, which were calcined at 1180° C for 4 h. For both systems when doped with Y_2O_3, independent of the amount of Y_2O_3, the major phases were Fe_2O_3 (denoted by F) and $4CaO \cdot 7Fe_2O_3$ (denoted by C_4F_7) but no M phase was detected. The C_4F_7 phase increased with increasing amount of Y_2O_3.

TABLE I Summary phases and designations in this experiment

Matrices	Dopants (wt %)	Phases					
		F	M	CF	C_4F_7	CF_2	unknown
	Y_2O_3						
	2.21	*			* ↓		* ↑
	2.79	*			*		*
	7.25	*			*		
CF_2	$BaCO_3$						
	3.95		*	*			
	4.97		*	*			
	13.55		*	*			*
	$SrCO_3$						
	2.13		*	*			
	3.77		*	*			
	10.50		*	*			*
	Y_2O_3						
	0.87	*			* ↓		
	1.10	*			*		
	2.90	*			*		
CF_6	$BaCO_3$						
	1.50	* ↑	* ↓			* ↑	
	1.90	*	*			*	
	5.48	*	*				*
	$SrCO_3$						
	0.80	* ↑	* ↓			* ↑	
	1.43	*	*			*	
	4.16	*	*				

The designations of the phases are: Fe_2O_3(F), $CaO \cdot 6Fe_2O_3$(M), $CaO \cdot Fe_2O_3$(CF), $4CaO \cdot 7Fe_2O_3$(C_4F_7), $CaO \cdot 2Fe_2O_3$(CF_2) and CaO : $6Fe_2O_3$(CF_6). The direction of the arrow indicates an increase of the amount of phases.

Although dopants of $BaCO_3$ and $SrCO_3$ induced the M phase in the CF_2 system, the amount of the M phase did not increase with increasing dopant. In the CF_6 system, the M phase also developed for the (barium, strontium) dopants but it increased with increasing dopant, which, however, was larger than the amount of the M phase induced by La_2O_3 at the same doping levels. Two points should be noted; firstly, why did both systems doped with Y_2O_3 have the same results? Secondly, in the CF_2 system, no CF_2 was retained but according to the proposed mechanism [8], CF_2 should exist at low doping levels for $BaCO_3$ and $SrCO_3$ dopants if they play the same role as that of La_2O_3.

In view of these results, one has to pursue the causes resulting in these differences comparing with La^{3+} doped CF_2 or CF_6 [8]. A further experiment has been carried out at lower temperature. Fig. 1 shows that when CF_2 doped with $BaCO_3$ was fired at 950° C for 4 h, a small amount of M phase occurred but CF_2 disappeared. It has been shown, however, in previous work [8] that the M-type La^{3+} doped calcium ferrite could only be formed at temperatures higher than 1150° C. In the light of the fact that the M-type barium ferrite can form at lower temperatures than the M-type calcium ferrite, the present M phase might arise from the reaction of $BaCO_3$ and F at 950° C. Apparently, CF_2 might decompose at such a low temperature, which however, is inconsistent with our previous result [8] and other reports [14, 15].

In order to evaluate the stability of CF_2, it was reheated to 1150° C without soaking in two ways: immediately and a few days after furnace cooling from 1180° C. For the former case, Fig. 2a shows that CF_2 slightly decomposed into $CaO \cdot Fe_2O_3$ (denoted as CF) and F. For the latter case, Fig. 2b, CF_2 has almost completely decomposed into CF and F. It should be noted that CF_2 did not decompose at room temperature and both cases could become CF_2 phase after being retreated at 1180° C. CF also existed after the decomposition of CF_2, thus a test was carried out to see if these dopants react with CF. It can be seen in Fig. 3 that $BaCO_3$ did not react with CF to become the M phase, and neither did $SrCO_3$ and Y_2O_3. These results further suggest that the appearance of the M phase at lower temperature is due to the existence of

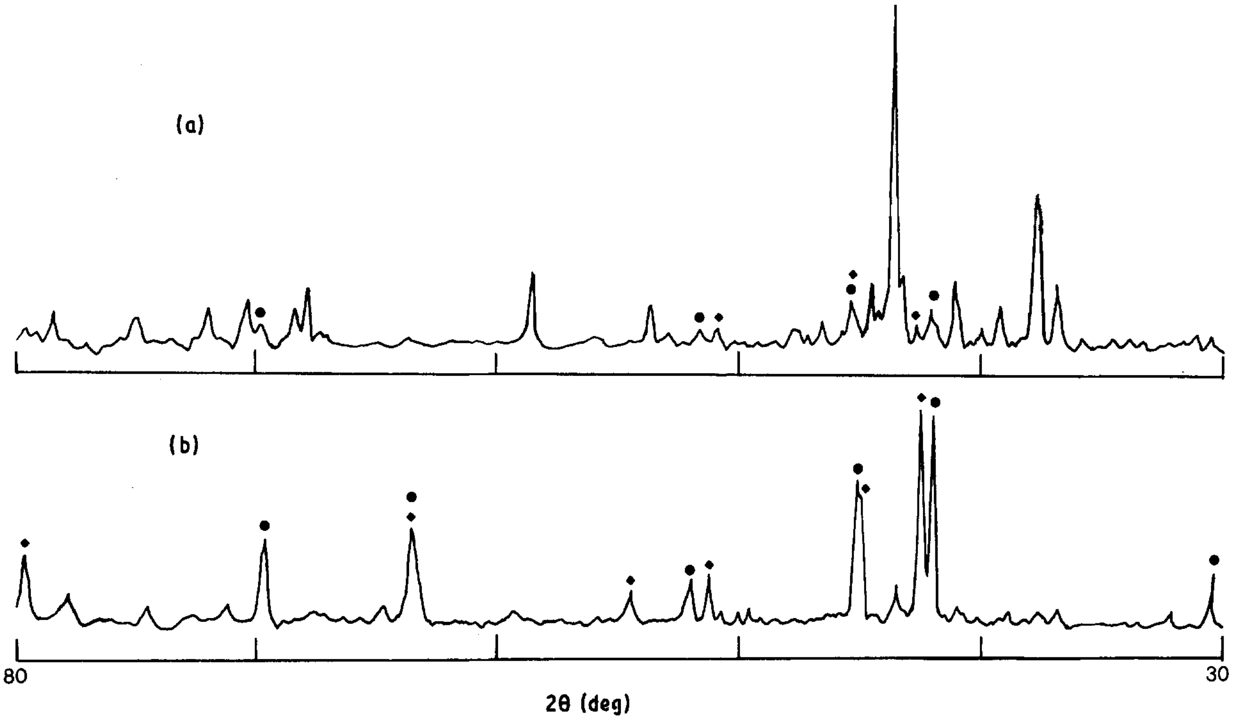

Figure 2 Two specimens of CF_2 were reheated to 1150° C without soaking in two ways: (a) immediately and (b) a few days after furnace cooling. (●: F, ◆: CF and the rest peaks are CF_2)

F, which reacts with (barium, strontium) dopants to form M-type barium and strontium ferrites. Moreover, the decomposition of CF_2 explains not only the absence of CF_2 in the CF_2 system, but also the invariant amount of the M phase for different amounts of dopants, due to the existence of the same amount of F. (Note that these amounts are more than 2 wt % of La_2O_3.) As for the results of the Y^{3+} doped calcium ferrites, Braun *et al.* [16] have reported that C_4F_7 could be synthesized by mixing a specific proportion of $CaCO_3$, Fe_2O_3 and Y_2O_3 and calcining at 1180° C, which explains why C_4F_7 appeared in this system.

These doped CF_2 specimens were inserted into a furnace at 1180° C for 4 h and quenched in water because of the instability of CF_2 and in order to investigate the real role of these dopants in the CaO–Fe_2O_3 system. For Y_2O_3 doped CF_2 (Fig. 4), M phase and C_4F_7 did not occur independently of the amount of Y_2O_3, and though CF_2 still maintained most of its structure, the double peaks at $d = 0.2628$ and 0.2605 nm merged. It is interesting to note that it becomes magnetic but pure CF_2 phase does not. This phenomenon was also observed in CF_2 doped with a smaller amount of La_2O_3. It is thus evident that Y^{3+} ions should substitute the ionic sites in CF_2 as La^{3+} ions do, but they can not induce the M phase.

For $BaCO_3$ and $SrCO_3$ doped CF_2, the obtained phases seem to be the same as samples calcined in furnace using slow heating and furnace cooling, but the formation mechanism is different and could be distinguished by comparing the results shown in Fig. 5. In Fig. 5, three points should be noted when comparing the CF_2 system in Table I. First, the amount of the M phase increased with increasing dopants, (Figs 5a and b). Second CF_2 existed at the lower doping level (Fig. 5a). Third, these two differently prepared M phases are different, i.e., the samples using slow heating and furnace cooling, contained mostly M-type barium ferrite, but the samples using very fast heating and quench, consisted mostly of an M-type calcium ferrite, because the lattice constants are slightly different. Inferring from the results mentioned above, it not only further supports the mechanism proposed by the authors, [8] but could also draw a conclusion that the ionic radius might be the most important factor to induce the M phase in CF_2, which also suggests that these dopants (Ba^{2+}, Sr^{2+} and La^{3+}) should substitute the Ca^{2+} sites.

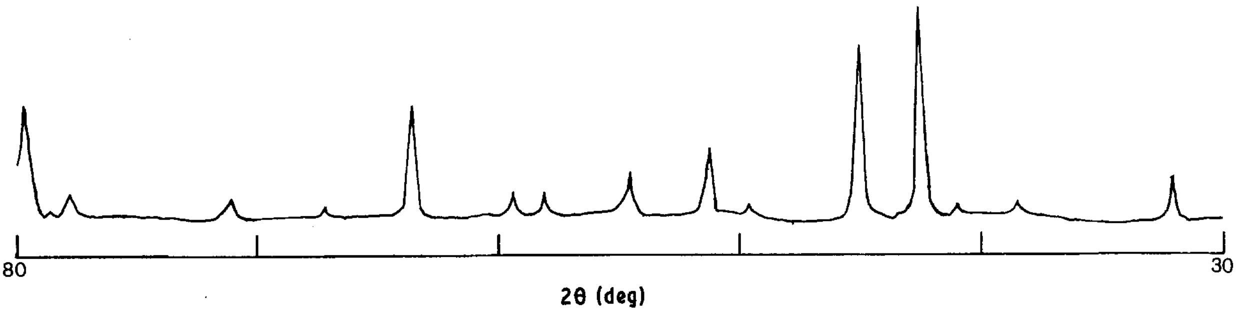

Figure 3 An X-ray pattern of CF doped with 1 wt % $BaCO_3$, fired at 1180° C for 4 h, showing that CF did not react with $BaCO_3$ to form the M phase.

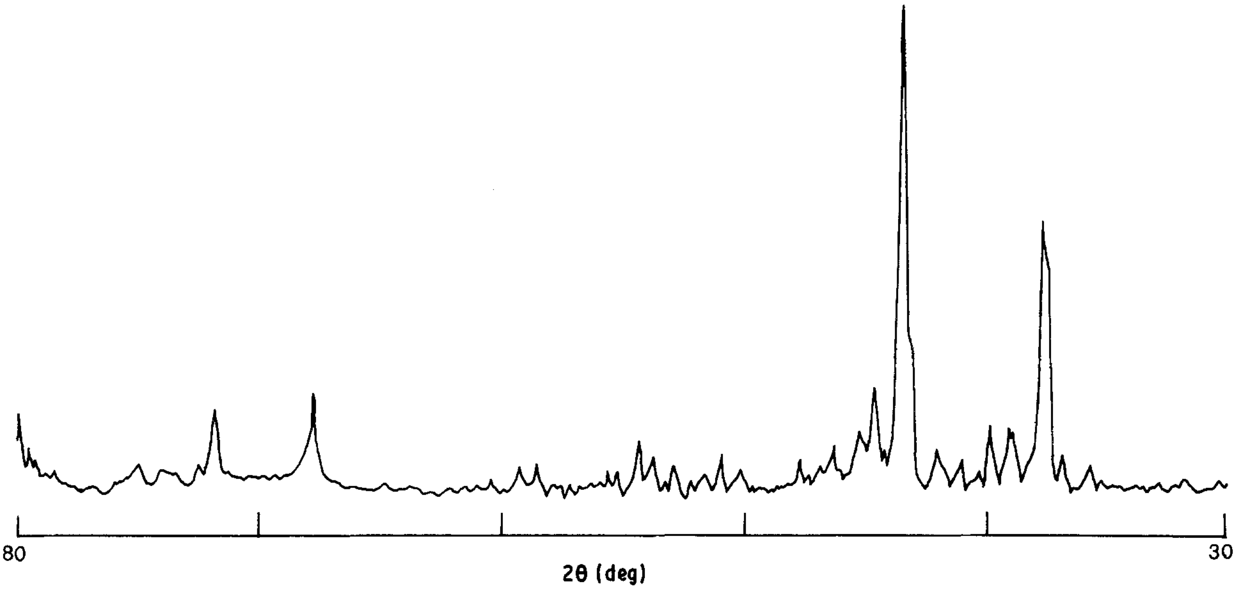

Figure 4 An X-ray pattern of CF_2 doped with 2.8 wt % Y_2O_3, inserted directly into a furnace at 1180° C for 4 h and then quenched in water. (All peaks are CF_2)

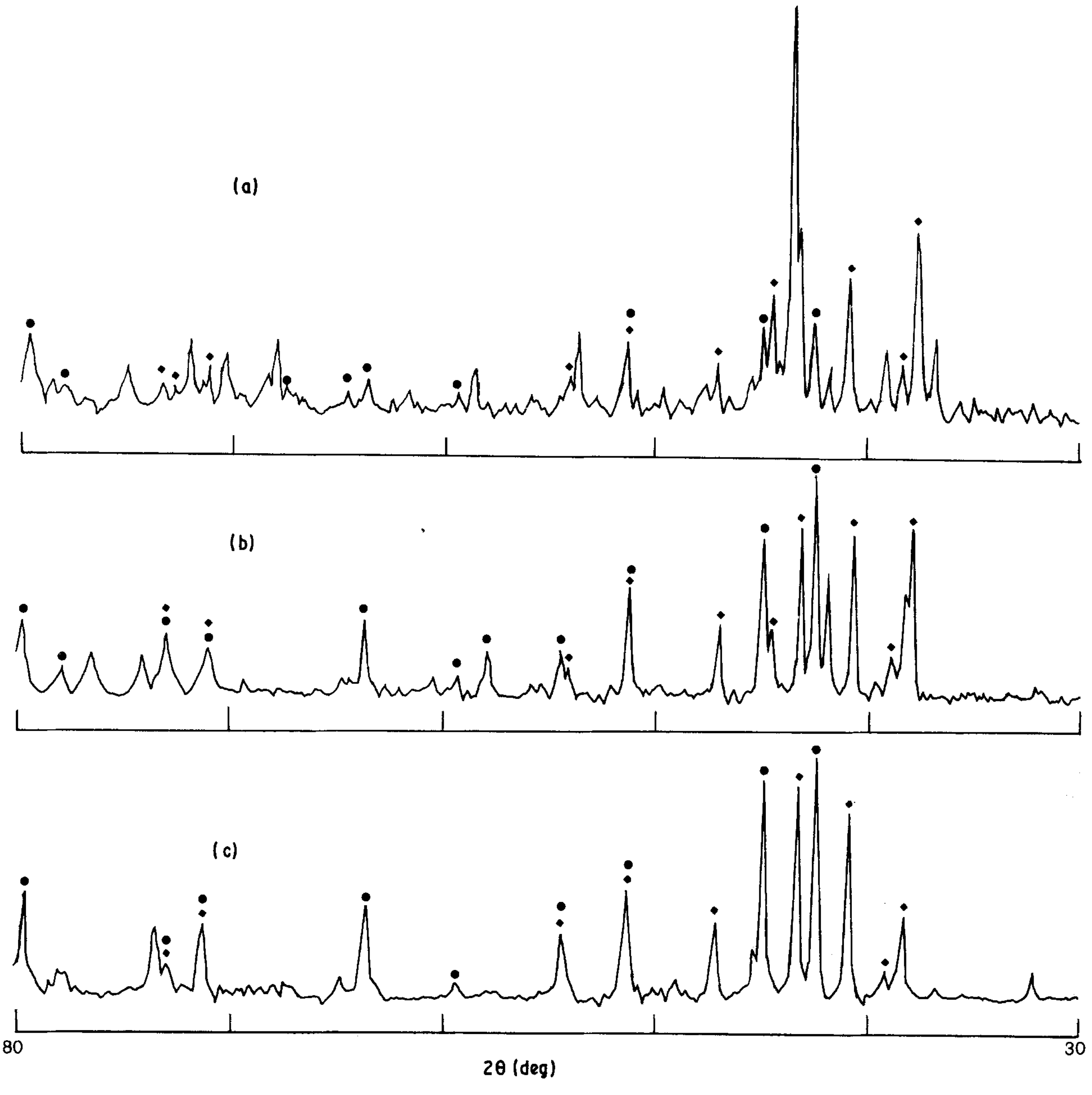

Figure 5 X-ray patterns of CF_2 doped with (a) 1 wt % and (b) 10.9 wt % $BaCO_3$ and (c) 2.7 wt % $SrCO_3$, inserted directly into a furnace at 1180° C for 4 h and then quenched in water. (●: CF, ◆: M and the peaks not marked are CF_2)

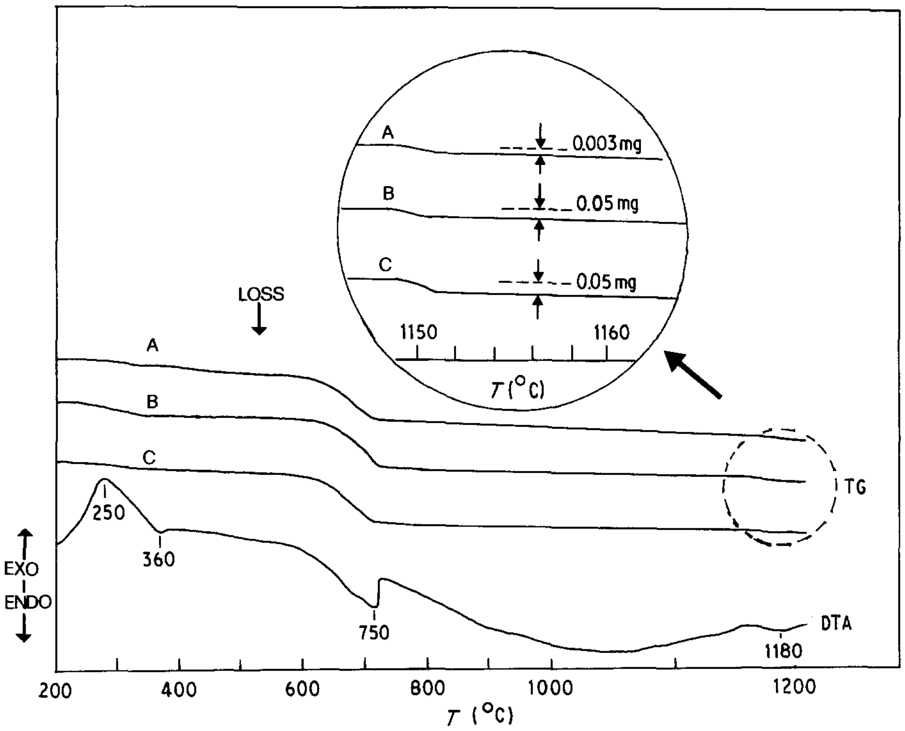

Figure 6 DTA–TG diagrams for $(CaO \cdot 6Fe_2O_3)_{100-x}(La_2O_3)_x$ samples showing the weight loss during the formation of the M phase (A) $x = 2$, (B) $x = 3$ and (C) $x = 4$. (Note: the heating rate before 1000° C is $10° C\,min^{-1}$ but after that is $5° C\,min^{-1}$).

3.2. Defect structures in forming the M phase

It is important to investigate the defect structures in developing the M phase, which would provide deep insights about the sites substituted by the dopants. In view of the occurrence of the M-type barium (or strontium) ferrite, mentioned above, La_2O_3 was selected as a dopant. Four possible mechanisms can be envisioned for the incorporation of La_2O_3 into the M phase, which include

$$3La_2O_3 \rightarrow 6La^{\circ}_{Ca} + 2V'''_{Fe} + 9O^{x}_{0} \quad (1)$$

$$La_2O_3 \rightarrow 2La^{\circ}_{Ca} + V''_{Ca} + 3O^{x}_{0} \quad (2)$$

$$La_2O_3 \rightarrow 2La^{\circ}_{Ca} + 2e' + 2O^{x}_{0} + \tfrac{1}{2}O_2 \quad (3)$$

$$Fe_2O_3 + La_2O_3 \rightarrow 2La^{\circ}_{Ca} + 2Fe^{2+'}_{Fe^{3+}} + 5O^{x}_{0} + \tfrac{1}{2}O_2 \quad (4)$$

As far as these four mechanisms are concerned, only reactions (Equations 3 and 4) are accompanied by evolved gas. Moreover, the latter two reactions have not only evolved gas but also good electrical conductivity.

Fig. 6 shows the DTA–TGA diagram of $(CaO \cdot 6Fe_2O_3)_{100-x}(La_2O_3)_x$, in which the heating rate has been changed from 10 to $5° C\,min^{-1}$ at 1000° C. The thermal behaviour of these specimens is quite similar, thus only the specimens doped with 4 wt % La_2O_3 are plotted in the figure. The mechanisms of the first two peaks, one exothermal peak at 250° C and another endothermal peak at 360° C, are not clear. The endothermal peak at 750° C is the decomposition of $CaCO_3$. Moreover, the broad endothermal range from 750 to 1120° C might be the gradual formation of CF. Finally, around 1180° C, the endothermal peak might arise from the formation of the M phase. There was weight loss accompanying the formation, which starts at the beginning of the endothermal peak. It is implied that gas will evolve when the M phase begins to develop. It can be seen in Fig. 7 that the conductivity at 33° C increased with the increasing amount of La_2O_3, which suggests that the possible mechanism is either Equation 3 or Equation 4.

The conduction behaviour of these two mechanisms, however, (Equation 3 and 4) is quite different: the former belongs to the brand model, in which the conductivity will decrease with increasing temperatures as a result of lattice scattering; the latter should be attributed to the hopping model, in which the conductivity increases with temperature. As can be seen in Fig. 8, the conductivity increased with increasing temperatures for different amounts of La_2O_3. Thus, it seems to the authors that Equation 4 might be the most probable mechanism, which is also supported by the results that Fe^{2+} ions exist in this system analysed by the chemical method [3, 7]. It should be noted that the conductivity of Ba^{2+} and Sr^{2+} doped calcium ferrite was much lower than that of the La^{3+} doped system, which might arise from the absence of Fe^{2+} in the former system and further supports that

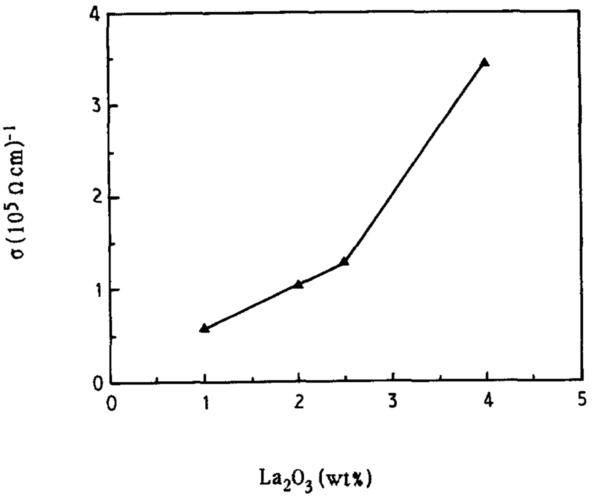

Figure 7 The conductivity at 33° C increased with the amount of the La_2O_3.

these dopants all substitute calcium sites in forming the M phase, attributable to the factor of ionic radius.

Furthermore, according to the defect structures described in Equation 4, the dissolved La_2O_3 content could be estimated from the weight loss. It can be seen in Fig. 6 that the dissolved La_2O_3 content estimated from the weight loss was 1.98, 2.8 and 3.21 wt % for the dopant amounts 2, 3 and 4 wt %, respectively. The larger difference between estimated dissolved La_2O_3 content (3.21 wt %) and doped amount (4 wt %) was attributed to the heating scheme of DTA, which explained the incomplete formation of the M phase of the X-ray pattern. The results suggest that the weight loss does relate to the amount of dissolved La_2O_3 content, depending on the temperature and time, which in turn, further supports the conclusion about the dependence of the solid solubility of La_2O_3 in inducing the M phase [8, 17].

3.3. Conductivity behaviour

It has been reported [18] that the great majority of transition metal oxides are semiconductors in that the temperature variation of their conductivity σ may be described by an equation

$$\sigma = A/T^{\beta-1} \exp(-E/kT) \qquad (5)$$

where β is 1 or 2, A a constant, E the activation energy, and k and T have their usual meanings. As can be seen in Fig. 8, these data are fitted quite well by Equation 5 with $\beta = 2$ at high or low temperature region. The values of the pre-exponential factor A and activation energy E are summarized in Table II. It is quite important to point out that the values of the activation energy in each region were consistent for different amounts of the M phase though they were different in these two regions. The transition temperatures for different amounts of the M phase were also summarized in Table II and these values were also in agreement. In view of the consistency of the activation energy and transition temperature are ferent amounts of the M phase, the influence of other phases on the conductivity could be neglected though it is known that other phases might exist when the amount of La_2O_3 is lower than 4 wt % [8] in which CF_2 might contain a small number of Fe^{2+} ions [15]. Furthermore, it should be pointed out that the activation energy and transition temperature are in good agreement with those obtained from the coprecipitated method [17].

Miyata [21] has observed that the pre-exponential factor A in Equation 5 depends almost entirely on the ferrous content and is practically independent of the remaining composition of the ferrite. Moreover, A has been described explicitly as [22]

$$A = gNc_0(1 - c_0)e^2a^2\nu_0/k \qquad (6)$$

where g is a geometric factor; N the total density (cm^{-1}) of conducting ions, a fraction (c_0) of which is Fe^{2+} and a fraction ($1 - c_0$) of which is Fe^{3+}; a the jump distance (cm); ν_0 the lattice vibrational frequency (sec^{-1}) associated with conduction; and e and k have their usual meanings. Equation 6 usually is employed to investigate the materials with composition close to stoichiometric ferrites MFe_2O_4, however, in this investigation, the amount of the M phase varied with La_2O_3 content. It has been shown in Section 3.1. that the ionic radius is the most important factor, therefore, the fraction of the M phase could be proportional to the dissolved La_2O_3 content. As evidenced in Fig. 9, the relationship between the roughly estimated fraction of the M phase and the added weight per cent is quite

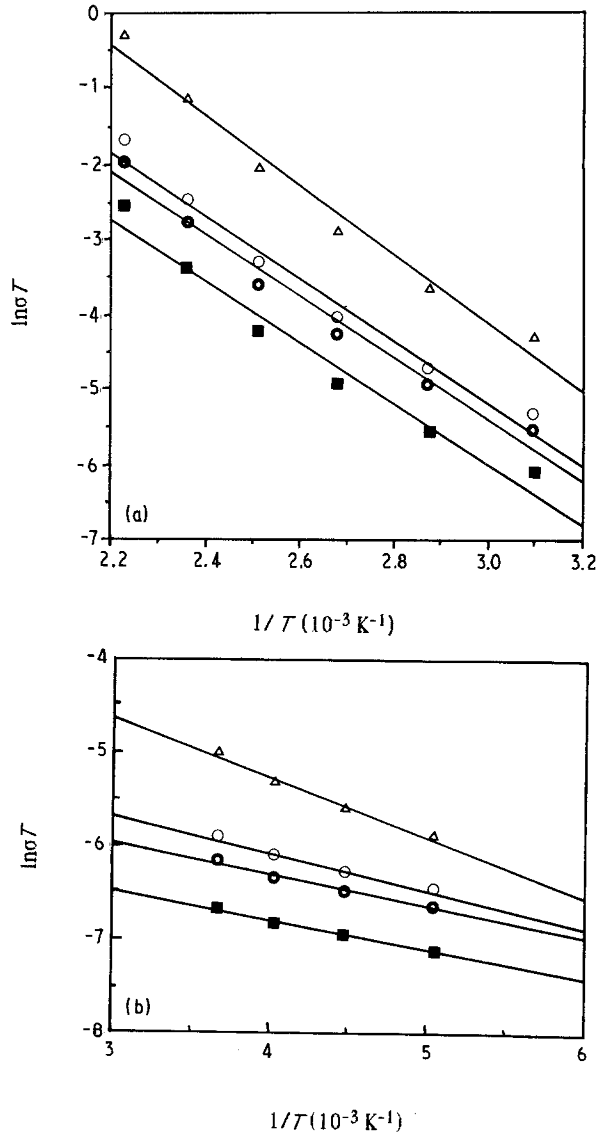

Figure 8 Activation energy plot for small-polaron conduction in La^{3+} doped calcium ferrites: (a) at high temperature region and (b) at low temperature region. (■: 1 wt %, **o**: 2 wt %, ○: 2.5 wt % and △: 4 wt %)

TABLE II Electrical conduction analysis of experimental results

	Parameters	x of $(CaO \cdot 6\,Fe_2O_3)_{100-x}(La_2O_3)_x$			
		1	2	2.5	4
(HT)	E(eV)	0.35	0.35	0.36	0.40
	A	531	914	1542	17649
(LT)	E(eV)	0.027	0.028	0.033	0.054
	A	0.0038	0.0067	0.0109	0.0649
	T_t (°C)	46	42	45	47

HT high temperature, LT low temperature and T_t transition temperature.

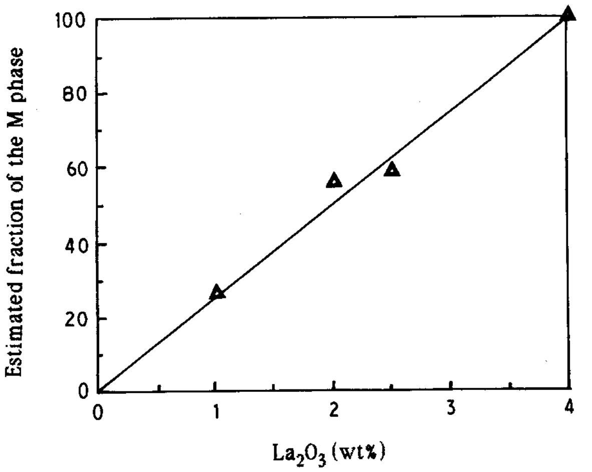

Figure 9 The proportional relationship between estimate of the fraction of the M phase and the doped amount of La_2O_3.

proportional. The peak (107) with the strongest intensity was used to estimate the fraction of the M phase on the basis of the specimen doped with 4 wt % La_2O_3, which has formed a complete M phase, i.e. 100%. This relationship was also found for the coprecipitated method [14].

The proportionality shown in Fig. 9 implies that every certain number of unit cells of the M-type calcium ferrites should be stabilized by a La^{3+} ion, e.g., if 4 wt % La_2O_3 is the minimum requirement to form M phase completely shown in the previous work, [8] there would be about one La^{3+} ion in every two unit cells. In this case, $c_0(1 - c_0)$ would be the same in these systems independent of the amount of the M phase, which, however, can not be applied to the amount of dopants larger than the minimum requirement. Therefore, the parameters considered in the Equation 6 should also be the same, i.e., A is a constant in these systems. Table II shows, however, that A values in these systems are different. It is suggested that A should be a function of some parameter other than those considered in Equation 6. Fig. 10 shows an exponential function of A and the fraction of the M phase. Equation 6 could, therefore, be modified as $A' = A \exp M$, where M is the fraction of the M phase. The intercepts (≈ 98 and 0.0011 for high and low temperature regions, respectively) are in reasonable agreement with that obtained from coprecipitated method (≈ 81 and 0.002). The intercept now represents the value of the parameters considered in Equation 6, thus the presumption that the value of $c_0(1 - c_0)$ is the same in these systems is further justified.

4. Conclusions

The conclusions are as follows.

(1) The stability of CF_2 decreases with the elapse of time, i.e. if reheated at temperatures below 1155° C a few days after preparation, it will decompose.

(2) CF_2 playing a precursor role has further been verified.

(3) The ionic radius is the most important factor in inducing the M phase of calcium ferrite.

(4) The mechanism of defect structure in La^{3+} doped calcium ferrite could be described as follows

$$Fe_2O_3 + La_2O_3 \rightarrow 2La'_{Ca} + 2Fe^{2+'}_{Fe^{3+}} + 50^{x}_{0} + \tfrac{1}{2}\,O_2.$$

(5) The conduction behaviour might be dominated by the hopping mechanism and the activation energy estimated is 0.35 to 0.40 eV in the high temperature region and 0.027 to 0.054 eV in the low temperature region.

(6) The pre-exponential factor A of Equation 5 is an exponential function of the fraction of the M phase in the specimen.

Acknowledgements

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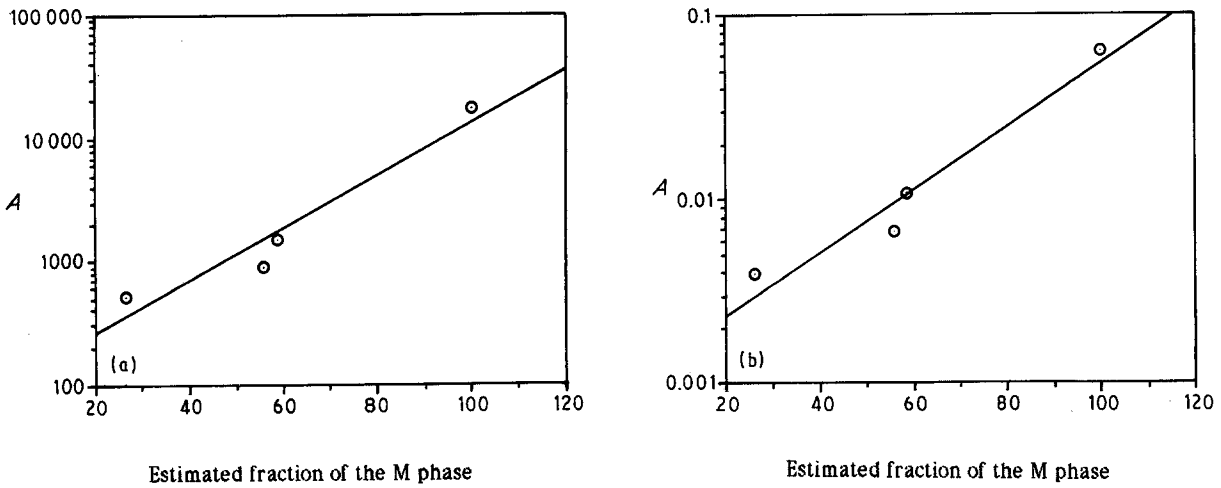

Figure 10 Pre-exponential factor A of different amounts of La_2O_3 plotted against the fraction of the M phase in La^{3+} doped calcium ferrites: (a) at high temperature region and (b) at low temperature region.

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