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Solid state reactions in the Fe_2O_3–$CaCO_3$–In_2O_3 system

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The kinetics of solid-state reactions of powdered reactants were investigated by X-ray and by differential thermogravimetry in a magnetic field. Measurements revealed mutual diffusion of the Fe^{3+} and In^{3+} ions in the Fe_2O_3–In_2O_3 system heat treated for 3 h at 700 to 1400° C. Diffusion of indium into the Fe_2O_3 lattice caused a shift of the Curie temperature of the antiferromagnetic iron oxide towards lower temperatures. Only $CaIn_2O_4$ was found between $CaCO_3$ and In_2O_3 up to 1400° C. Also, in the Fe_2O_3–$CaCO_3$–In_2O_3 system, the reaction started with the mutual diffusion of iron and indium and the forming of $CaFe_2O_4$. End-products were the magnetic α–$Ca_4Fe_{14}O_{25}$ and $CaFe_4O_7$, and the non-magnetic $CaFe_5O_7$, depending on the In^{3+} concentration. Indium stabilized the magnetic calcium–iron oxide structures, shifting their Curie temperatures towards lower values.

1. Introduction

The polycrystalline garnet system of $\{Y_{3-2x-z}Gd_zCa_{2x}\}[Fe_{2-y}In_y](Fe_{3-x}V_x)\ O_{12}$ is potentially useful for microwave device applications, because of the simultaneous occurrence of low-temperature dependence of saturation magnetization and low dielectric and magnetic losses. However, the structure and formation of these yttrium–iron garnet ceramics have been studied mostly in connection with their behaviour in microwave applications. Only a few investigations have been carried out on the kinetics of garnet formation starting from the oxides. Using the standard ceramic technology for preparing the polycrystalline garnets, the circumstances of presintering and sintering have to be very carefully chosen as many intermediates form with different reactivities and temperature stabilities.

For this purpose, a systematic study has been started to clarify the role of each component in the kinetics of garnet-forming solid-state reactions.

In the $Y_2O_3 - Fe_2O_3$ system, YIG formation has been found by an orthoferrite intermediate [1]. The reaction between CaO or $CaCO_3$ and Fe_2O_3, studied by ourselves and in other laboratories [2–5] resulted in the antiferromagnetic $CaFe_2O_4$ followed by the formation of ferrimagnetic $CaFe_4O_7$ at higher temperatures [6]. No chemical reaction could be found between the Y_2O_3 and $CaCO_3$ up to 1200° C.

In the Y_2O_3–Fe_2O_3–$CaCO_3$ system, the addition of low concentrations of Y_2O_3 promoted the diffusion of iron into the CaO lattice. Thus the formation of the orthorhombic $CaFe_2O_4$ had already begun at lower temperatures. At higher temperatures, the formation of a hexagonal $Ca_4Fe_{14}O_{25}$ (T_c 113 to 125° C) was favourable to $CaFe_4O_7$. At 900° C an orthorhombic calcium ferrite, $Ca_3Y_2Fe_{19}O_{30}$ appeared (T_c 85 to 90° C). The garnet formation was also taking place by an orthoferrite intermediate. The Curie temperature of this orthoferrite phase with a perovskite structure was found to decrease from 370 to 328° C with the increase of sintering temperature, due to the incorporation of Ca^{2+} ions into the orthoferrite lattice. No similar change of T_c was found in the garnets. As the amount of the garnet phase increased, the yttrium concentration of this calcium ferrite showed a decrease correlated to its T_c. In samples with an yttrium content above that of $CaCO_3$ (1 : 1 mol fraction) preference was given to the formation of orthoferrite and garnet. At the same time, the starting temperatures for the formation of the calcium–iron compounds, and their amount, decreased.

Here another three component systems of these garnet materials, the Fe_2O_3–$CaCO_3$–In_2O_3 mixture are investigated.

2. Experimental procedure

2.1. Samples

Mixtures were prepared of Fe_2O_3–In_2O_3 and In_2O_3–$CaCO_3$ with the composition given in Table I, and of Fe_2O_3–In_2O_3–$CaCO_3$ with the composition in Table II. Raw materials were used with different purity levels (99.5% purity of Fe_2O_3; 99.99% purity of In_2O_3 and *pro analysi* purity of $CaCO_3$). After ball-milling of the mixtures of the raw materials in acetone media for 5 min, sintering was carried out in a tube furnace at

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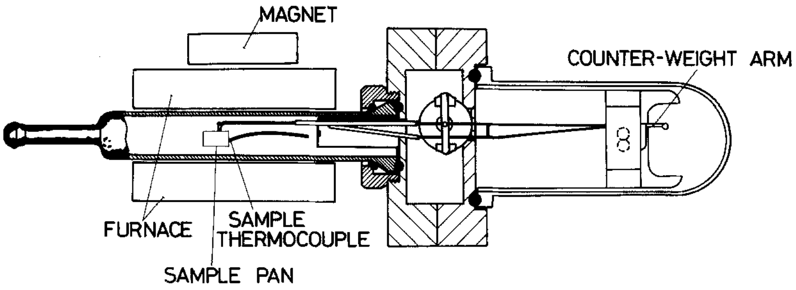

Figure 1 Sketch of the DTG(M) measuring system.

temperature from 700 to 1400° C for 3 h in air. The heating rate was $200° C h^{-1}$, and the cooling rate $80° C h^{-1}$.

2.2. Measuring methods

The samples were studied by the X-ray diffraction method and by differential thermogravimetry in a magnetic field, DTG(M). X-ray diffraction investigations of the sintered samples were carried out in a Guinier–de Wolff focusing camera at room temperature using CuK_α radiation. The Curie temperature of the magnetic phases was determined by the DTG(M) method. The essence of this method is the investigation of the interaction between the samples and a weak magnetic field, as a function of temperature, with a micro-thermal analyser (Du Pont 990). Besides the thermal decomposition, the DTG(M) curves show peaks at the Curie temperature of the magnetic constituents with an estimated error of ± 15° C. The DTG(M) measurements were established for temperatures from room temperature to 720° C, using a heating rate of $20° min^{-1}$ (Fig. 1).

DTG(M) is more sensitive than the X-ray diffraction, but the former is applicable only to magnetic phases in the samples. DTG(M) is a semiquantitative method because the T_c peak amplitudes depend not only on the quantity of the phases but also on the grain size and the magnitude of the magnetic moment. The X-ray diffraction method is less sensitive but identifies all phases. It is also semiquantitative but gives the lattice parameters of the component phases, thus indicating the contraction or expansion of the lattices due to mutual diffusion.

TABLE I Chemical compositions of the investigated two-component system

Fe_2O_3 (mol)	In_2O_3 (mol)	$CaCO_3$ (mol)	In_2O_3 (mol)
4.54	0.32	0.80	0.16
4.10	0.50	0.80	0.25
4.00	0.50	1.00	0.25
0.50	4.00	–	–

TABLE II Chemical composition of the investigated three-component systems

Fe_2O_3 (mol)	$CaCO_3$ (mol)	In_2O_3 (mol)
2.0	1.0	0.025
2.0	1.0	0.05
2.0	1.0	0.10
2.0	1.0	0.15
2.0	1.0	0.20
2.0	1.0	0.25
2.0	1.0	0.50
2.0	1.0	1.00
2.0	1.0	1.50

3. Results and discussion

3.1. $CaCO_3$–In_2O_3 and Fe_2O_3–In_2O_3 system

In the mixtures of $CaCO_3$ and In_2O_3, only $CaIn_2O_4$ was formed from 800° C, and DTG(M) measurements did not reveal any characteristic peak except that of the thermal decomposition of $CaCO_3$.

In the Fe_2O_3–In_2O_3 mixtures, diffusion of Fe^{3+} ions into the In_2O_3 and that of the In^{3+} ions into the Fe_2O_3 lattices was revealed by the X-ray diffraction method, (Fig. 2). The expansion of the Fe_2O_3 and the contraction of the In_2O_3 lattice caused a shifting in the diffraction lines. These changes were also observed in the DTG(M) curves; the Curie temperature of the antiferromagnetic Fe_2O_3 at 690° C was shifted to lower temperatures when increasing the temperature of the heat treatment. Changes can be divided into two groups, one occurring in the system below 1000° C, and the other between 1000 and 1300° C. In samples heated above 1300° C, magnetic and structural disorders were observed (Fig. 3).

3.2. Fe_2O_3–$CaCO_3$–In_2O_3 mixtures

The Fe_2O_3–$CaCO_3$–In_2O_3 mixtures could be investigated up to 1200° C, as above this temperature the samples melted. With X-ray diffraction investigations the similar mutual diffusion of Fe^{3+} and In^{3+} ions was found, as in the case of the two-component system. Formation of the hexagonal α–$Ca_4Fe_{14}O_{25}$ was observed in amounts increasing with the increase in indium content of the mixtures. Indium seems to stabilize this structure, which was only found in traces in the pure calcium–iron oxide system (Fig. 4).

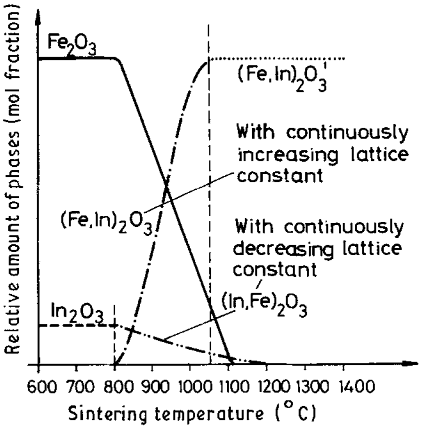

Figure 2 Phases present in the Fe_2O_3–In_2O_3 system after heat treatment at 700 to 1400° C for 3 h in air.

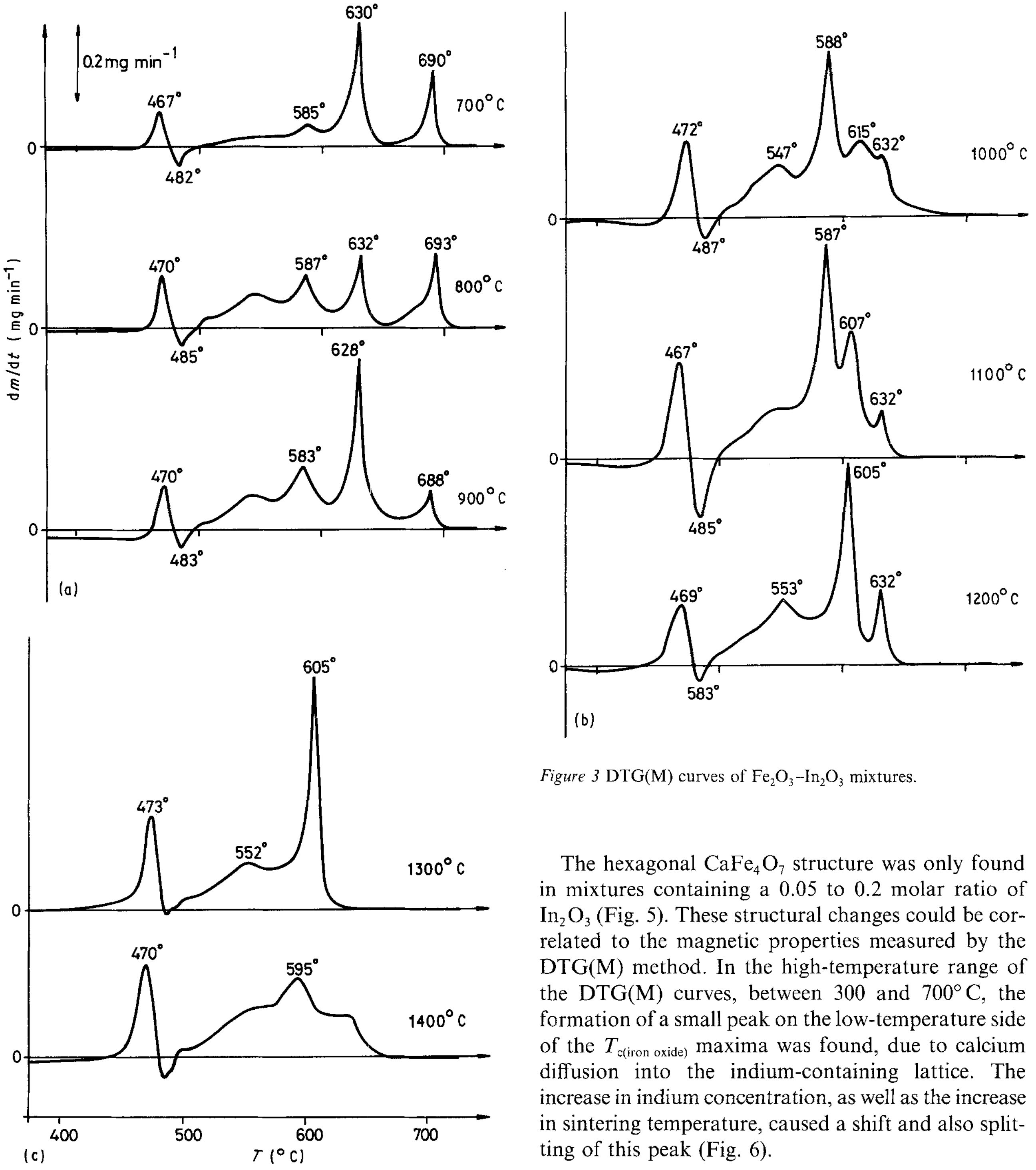

Figure 3 DTG(M) curves of Fe_2O_3-In_2O_3 mixtures.

The hexagonal $CaFe_4O_7$ structure was only found in mixtures containing a 0.05 to 0.2 molar ratio of In_2O_3 (Fig. 5). These structural changes could be correlated to the magnetic properties measured by the DTG(M) method. In the high-temperature range of the DTG(M) curves, between 300 and 700° C, the formation of a small peak on the low-temperature side of the $T_{c(\text{iron oxide})}$ maxima was found, due to calcium diffusion into the indium-containing lattice. The increase in indium concentration, as well as the increase in sintering temperature, caused a shift and also splitting of this peak (Fig. 6).

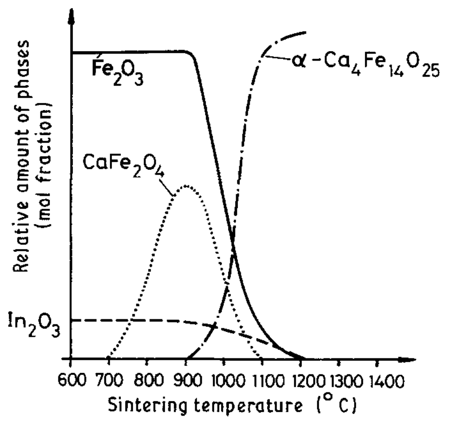

Figure 4 Products of solid-state reaction in the 2.0 Fe_2O_3 + 1.0 $CaCO_3$ + 0.25 In_2O_3 system.

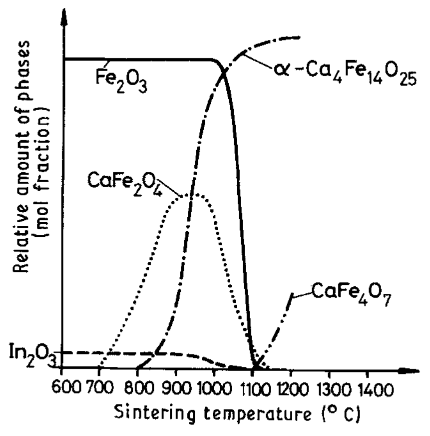

Figure 5 Products of solid-state reaction in the 2.0 Fe_2O_3 + 1.0 $CaCO_3$ + 0.1 In_2O_3 system.

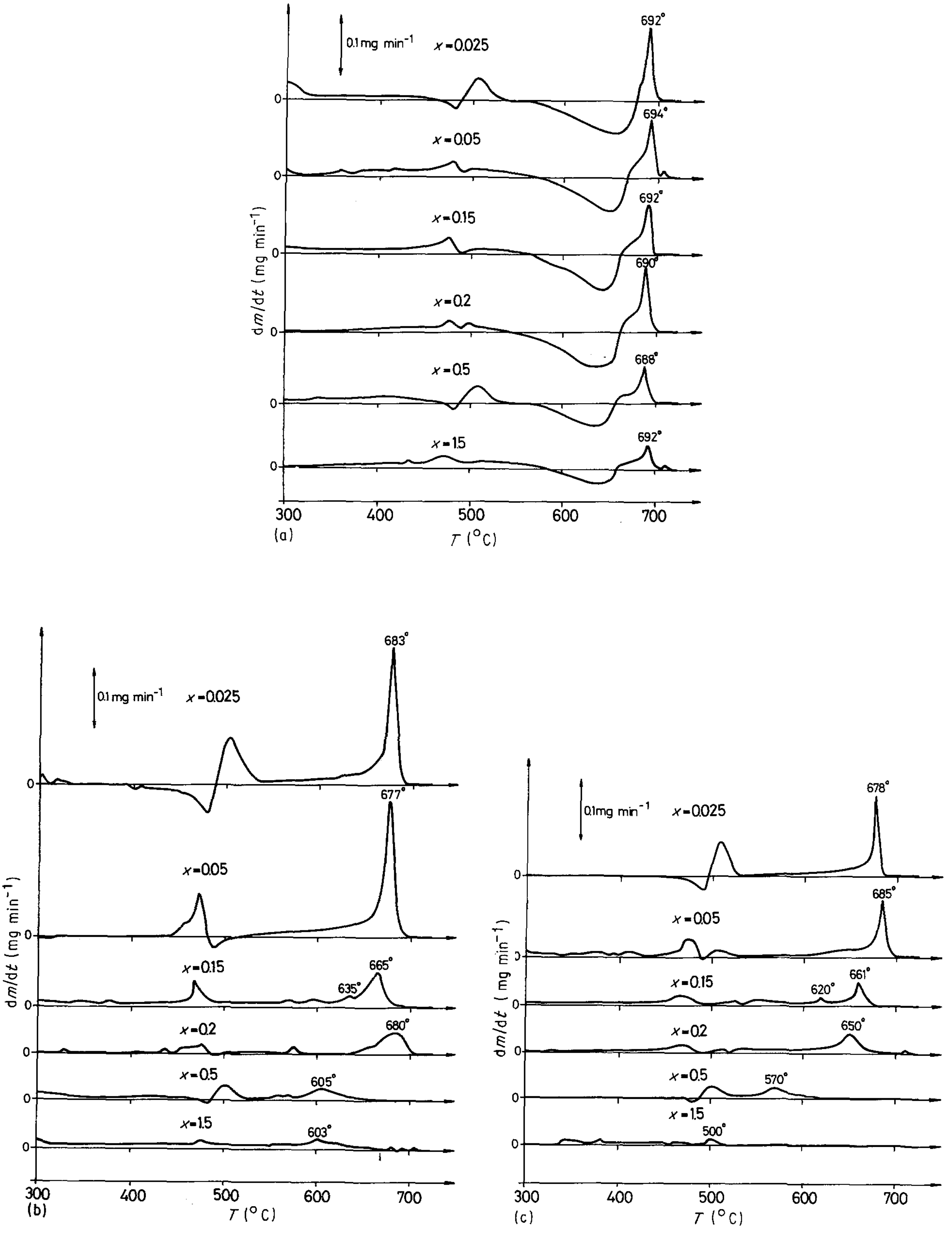

Figure 6 DTG(M) curves of mixtures of composition 2.0 Fe_2O_3 + 1.0 $CaCO_3$ + x In_2O_3, sintered at (a) 800° C; (b) 1000° C; (c) 1100° C.

In the low temperature range of the DTG(M) curves, the peak around 40 to 50° C is correlated with the presence of the In^{3+} stabilized hexagonal α-$Ca_4Fe_{14}O_{25}$ (Fig. 7).

The Curie peak around 110° C, appearing only in mixtures containing 0.05 to 0.2 molar ratio of In_2O_3 and shifting towards lower temperatures with increasing indium content, can be connected with the appearance of the hexagonal $CaFe_4O_7$ structure. Above a molar ratio of 0.5 for In_2O_3, non-magnetic $CaFe_5O_7$ with an orthorhombic structure was formed.

4. Conclusions

In every composition of Fe_2O_3-In_2O_3 and Fe_2O_3-In_2O_3-$CaCO_3$ systems, the first step leading to a solid-state reaction was the mutual diffusion of the Fe^{3+} and In^{3+} ions into the In_2O_3 or Fe_2O_3 lattices, respectively. An In^{3+}-rich iron oxide reacted with the $CaCO_3$ at

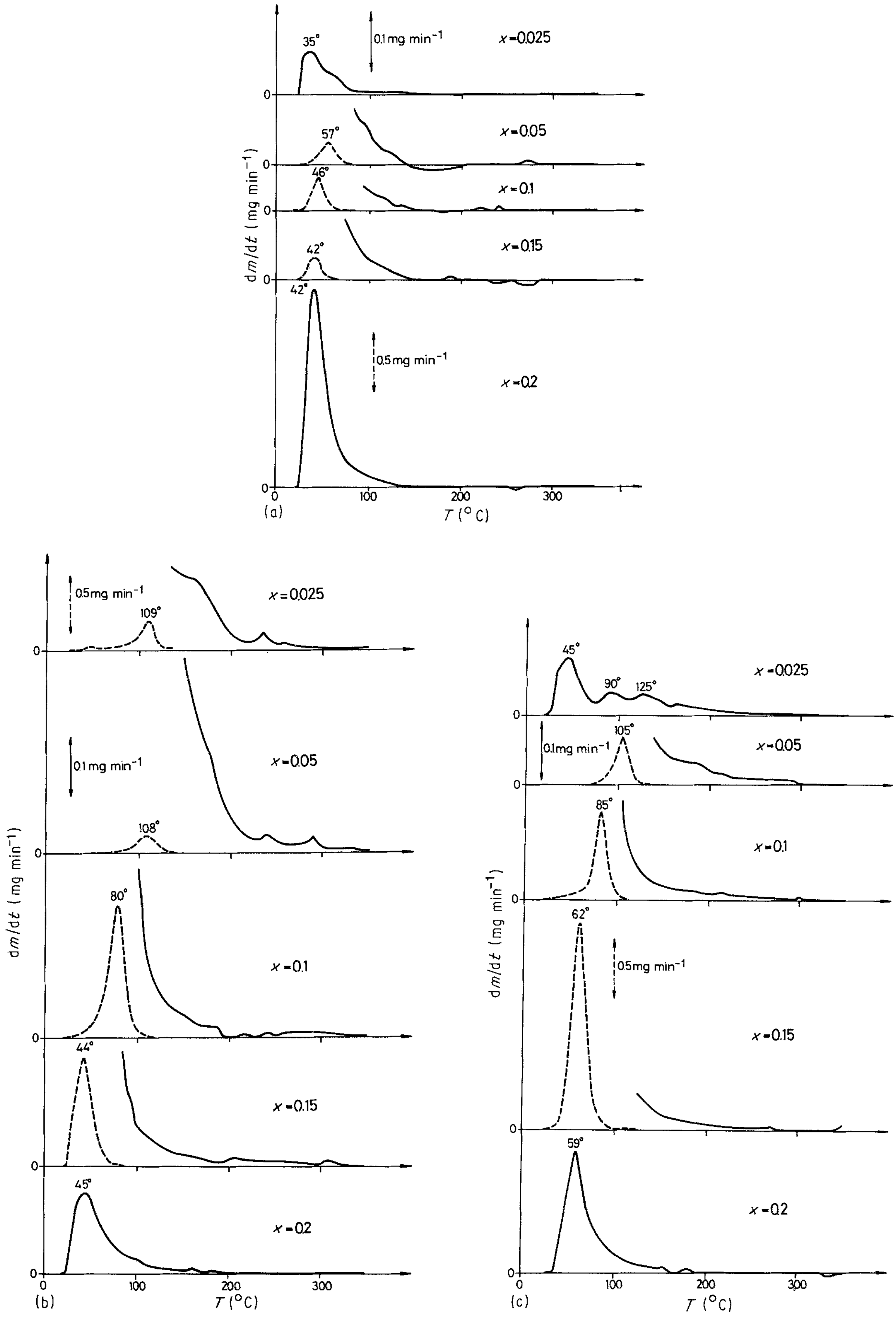

Figure 7 DTG(M) curves of mixtures of composition 2.0 Fe_2O_3 + 1.0 $CaCO_3$ + x In_2O_3, sintered at (a) 1000° C; (b) 1100° C; (c) 1200° C.

higher temperatures. Several calcium–iron oxides with different temperature stability range and magnetic properties were formed, depending on the In^{3+} ion concentration. The stabilizing effect of In^{3+} found in our investigations is already known for Y^{3+} and Mg^{2+} ions [7].

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