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SOLID-STATE REACTIONS IN THE SYSTEM TALC–$CaCO_3$ DOPED WITH Ni(II) AT HIGH TEMPERATURES

M HASSANEIN

Department of Inorganic Chemistry, National Research Centre, Dokki-Cairo (Egypt)

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ABSTRACT

The system talc–$x CaCO_3$–0 $2NiCl_2$ $6H_2O$ in the molar ratio 1 x 0 2 ($x = 1$, 2, 3 and 4) was studied at two different temperatures, viz, 1000 and 1200 ° C The quenched, coloured reaction products at room temperature were identified using X-ray diffraction and absorption spectrum techniques X-ray results revealed that the main constituent or constituents of the reaction products obtained after firing at 1000 ° C were (I) enstatite–diopside at $x = 1$, (II) enstatite–diopside and monticellite at $x = 2$ and (III) monticellite and akermanite at $x = 3$ and 4 At 1200 ° C the main phases identified at $x = 1$ and 4 were the same as in case of firing at 1000 ° C, whereas the phases enstatite–diopside and akermanite at $x = 2$ and ákermanite at $x = 3$ were characterized On the other hand, absorption spectra of the resulting Ni^{2+}-containing silicate phases after the firing process at the two working temperatures showed characteristic absorption bands of tetrahedrally as well as octahedrally coordinated Ni^{2+}, in confirmation with the formation of akermanite and enstatite–diopside, monticellite, which offer tetrahedral and octahedral lattice positions for Ni^{2+}, respectively Generally, it was observed that the concentration of some resulting Ni^{2+}-containing phases increased or decreased with increasing firing temperature, depending on the formation tendency of other silicate phases at varying x

INTRODUCTION

Thermal reactions of talc, $Mg_3Si_4O_{10}(OH)_2$, as one of the most important raw materials for many industries, have been extensively studied, in contrast little information is available on such reactions of talc–coloured metal oxides Recently, a study of solid-state reactions occurring on heating talc with two transition metal chlorides, MCl_2 $6H_2O$, M = Co(II) and Ni(II), revealed distinguishable differences between the two systems with respect to the nature of the observed phases and their further reactions, saturation limit of Co(II) and Ni(II) in the enstatite phase as well as the effect of their concentrations [1,2] A further thermal study of the talc–$CaCO_3$ system containing the coloured cation Co(II) at a constant low concentration [3] indicated the formation of some silicate phases normally existing at equilibrium conditions at elevated temperatures within the three-component

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system CaO–MgO–SiO_2 The presence of Co(II) in such reactions was found to increase the formation tendency of akermanite at lower temperature, for example In the light of previous results of the systems talc–Co(II) and talc–$CaCO_3$–Co(II) on one hand, and talc–Ni(II) on the other hand, it seems to be preferable to investigate further the system talc–$CaCO_3$–Ni(II), which is the aim of the present work

EXPERIMENTAL

Talc, $CaCO_3$ and $NiCl_2 \cdot 6H_2O$ used for the preparation of the reaction samples as well as the experimental conditions (thermal treatment including firing temperatures, period of heating and cooling procedure) were the same as reported earlier [1–3] The X-ray diffractometer and automatic Carl Zeiss DMR 21 spectrophotometer were the tools used for the characterization of the resultant phases

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption spectra of the quenched, coloured reaction products of the studied system fired at 1000 and 1200 °C, respectively Absorption spectra of pure synthesized Ni(II)-diopside and Ni(II)-akermanite are shown in Fig 3 Table 1 includes data of some known related silicate compounds By taking one of the changeable parameters,

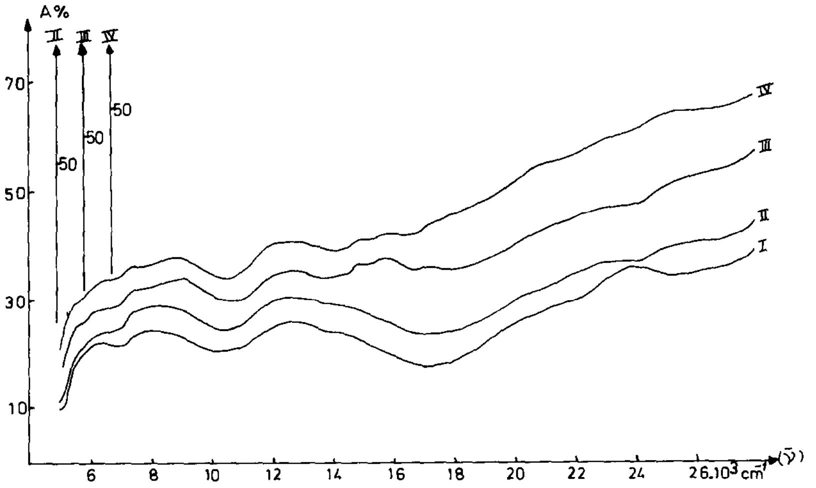

Fig 1 Electronic absorption spectra of the reaction products in the system talc–$x$$CaCO_3$–0 2$NiCl_2$ $6H_2O$ treated at 1000 °C $x = 1$ (I), 2 (II), 3 (III) and 4 (IV)

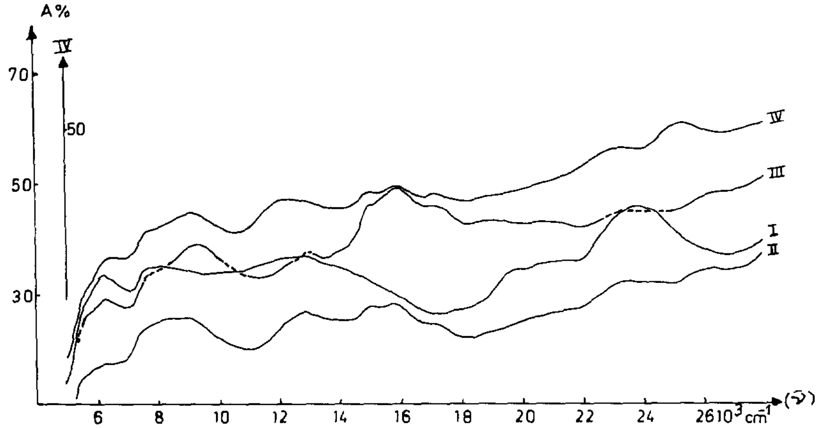

Fig 2 Electronic absorption spectra of the reaction products in the system talc–$x\mathrm{CaCO_3}$–0 2$\mathrm{NiCl_2}$ 6$\mathrm{H_2O}$ treated at 1200 °C $x = 1$ (I), 2 (II), 3 (III) and 4 (IV)

namely temperature, at a constant molar ratio of $\mathrm{CaCO_3}$ (talc and Ni(II) concentrations being kept constant) into consideration, the results of thermal reactions present could be grouped and discussed in the following manner

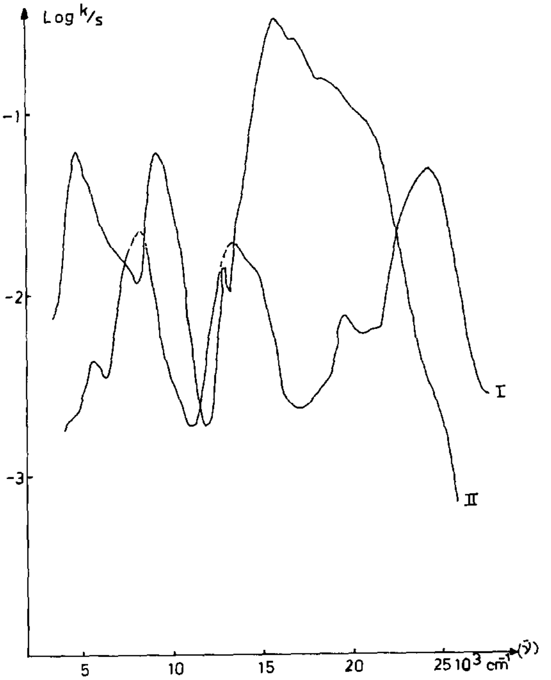

Fig 3 Electronic absorption spectra of synthesized $\mathrm{CaNi_{0\,1}Mg_{0\,9}Si_2O_6}$ (I) and $\mathrm{Ca_2Ni_{0\,1}Mg_{0\,9}Si_2O_7}$ (II)

TABLE 1

General view of some silicate phases in tertiary system CaO–MgO–SiO$_2$

Silicate phase	Cell dimensions (Å)			ΔH_f (kcal mol^{-1})			Mixed crystal formation ▨ Immiscibility gap ☐
	a	*b*	*c*	298 K	965 K	1173 K	
Enstatite ($Mg_IMg_{II}Si_2O_6$)	18 21	8 81	5 20 [6]	−8 12	−8 68	−8 15 [12]	Enstatite ▨ Diopside [4]
Diopside ($Ca_IMg_{II}Si_2O_6$)	18 68	8 89	5 24 [7]	−35 25 [13]			Diopside ☐▨ Wollastonite [4]
Monticellite ($Mg_ICa_{II}SiO_4$)	4 82	11 11	6 38 [8]	−27 56 [14]			Monticellite ▨☐ Forsterite [4]
Forsterite ($Mg_IMg_{II}SiO_4$)	4 77	10 26	6 00 [9]	−14 19	−15 44	−14 86 [12]	Forsterite ☐▨ Calcium-olivine [17,18]
Akermanite ($Ca_2MgSi_2O_7$)	7 84	–	5 02 [10]	−43 83 [13]			
Merwinite ($Ca_3MgSi_2O_8$)	–	–	–	−57 02 [14]			
Wollastonite ($CaSiO_3$)	–		–	−21 25 [15]			
Calcium-olivine (Ca_2SiO_4)	5 08	11 23	6 76 [11]	−30 19 [16]			

Reactions with 1 mol $CaCO_3$

The X-ray diffractogram of the reaction product obtained on firing the corresponding mixture at 1000 °C showed a pattern of diffracted lines of different intensities, whereas, at 1200 °C, the same pattern of lines, but of relatively higher intensity and at lower 2θ, were observed Interplanar distances of lines of strong and medium intensities taken as a base of the identification process were found to coincide with those of enstatite and diopside phases which were known to form a continuous mixed crystal (Table 1) The increase of intensity of diffracted lines and their shift towards lower 2θ as a result of a firing temperature at 1200 °C may be attributed to a seemly complete formation of crystalline enstatite–diopside mixed crystal phase Partial exchange of Mg(II) by Ca(II) within the enstatite lattice during enstatite–diopside mixed crystal formation would lead, therefore, to an increase of lattice dimensions (Table 1), and hence to larger interplanar distances as observed.

Absorption spectra of the same reaction product obtained at 1000 and 1200 °C show broad bands at (I) 6600–6200, (II) 8750–7800, (III) 15000–12500 (shoulder at 20000), (IV) 24000 cm^{-1} and (I) 6250, (II) 8000, (III) 12750 (shoulder at 19750), and (IV) 24000 cm^{-1}, respectively (Figs 1 and 2, curve I) Analysis of these bands, characteristic of octahedrally coordinated Ni(II) (intensity increased relatively with increasing firing temperature), showed some differences (e g broadness and number) in comparison with those of pure Ni(II)-diopside (Fig 3), pure Ni(II)-enstatite [5] and Ni(II)-talc [2] The presence of bands I, III and IV, related to Ni-enstatite, together with bands II, III and IV, related to Ni-diopside, may lead to the conclusion of Ni-enstatite–diopside mixed crystal formation, in confirmation with X-ray results Moreover, the assumed $2(Ca_{0.5}Mg_{1.5})Si_2O_6$ mixed crystal (talc $CaCO_3 = 1$ 1) provides formally three differently distorted octahedral configurations around Ni^{2+} $Mg_IO_6 > Mg_{II}O_6$ (enstatite) $\simeq$ $Mg_{II}O_6$ (diopside) Previous studies on single systems showed that Ni^{2+} substituted Mg_I as well as Mg_{II} positions in enstatite and diopside, respectively [5] It could be expected, therefore, that Ni^{2+} would distribute over (at least) two lattice positions in the mixed crystal enstatite–diopside, a behaviour which is in fair agreement with the spectral findings As suggested before [3], the formation of $CaSiO_3$ at lower temperature and its solid-solution reaction $CaSiO_3$–$MgSiO_3 \rightarrow (Ca, Mg)Si_2O_6$ as well as the formation of other related silicate phases seems to be a question of formation tendency rather than stability, which agrees with the relatively high formation enthalpies of the corresponding silicate (Table 1)

Reactions with 2 mol $CaCO_3$

Spectra and X-ray diffractograms of the reaction products obtained in this range of $CaCO_3$ concentration differ to some extent from those obtained at 1 mol $CaCO_3$ At 1000 °C, the spectrum showed some IR-shift of the lower energy located absorption maxima, together with the appearance of a broad band at 26000 cm^{-1} (curves I and II in Fig 1) Such a small change in the spectrum of octahedrally coordinated Ni(II) may be attributed to the greater presence of Ni^{2+} in a distorted lattice position of an additional phase than that identified in the system with 1 mol $CaCO_3$ Probably, the monticellite phase $MgCaSiO_4$ may be additionally formed according to the reaction

$$3MgSiO_3 + SiO_2 \text{ (talc dissociation products)} + 2CaO \xrightarrow{1000\,^\circ C}$$

$$Mg_2Si_2O_6 + MgCaSiO_4 + CaSiO_3$$

As is known, Mg_IO_6 polyhedra in the monticellite lattice are distorted, thus providing a preferred lattice position for Ni^{2+} to occupy However, it seems very probable that such phases (enstatite, monticellite and wollastonite) would take a different percentage of Ca^{2+} (or Mg^{2+}) ions into their lattices, leading, therefore, to their known corresponding mixed crystal $(Ca, Mg)_2Si_2O_6$, $(Mg, Ca)SiO_4$ and $(Mg, Ca)SiO_3$ (Table 1)

At 1200 °C, the appearance of a new group of absorption bands at 12900, 15000, 15800, 17200 and 23250 cm^{-1}, which are not characteristic of octahedrally coordinated Ni^{2+}, in addition to a broadening and some shifting of the others, was observed (curve II in Figs 1 and 2) An alternative geometrical arrangement for Ni^{2+} is the tetrahedral configuration (MgO_4), present in the akermanite $Ca_2MgSi_2O_7$ lattice Actually, a close similarity in positions of the new bands and some of those of pure 0 1 Ni-akermanite [5] was found (curve II in Figs 2 and 3), if we only consider the main absorption bands of synthesized Ni-akermanite and their assignment according to electronic transitions scheme of Ni^{2+} in tetrahedral coordination

$$^3T_1(F) \rightarrow {}^3T_2(F)\ 4700\ cm^{-1} \qquad \text{(I)}$$

$$^3T_1(F) \rightarrow {}^3A_2(F)\ 9150\ cm^{-1} \qquad \text{(II)}$$

$$^3T_1(F) \rightarrow {}^3T_1(P)\ 15850\text{–}12900\ cm^{-1} \quad 18700\text{–}17000\ cm^{-1} \qquad \text{(III)}$$

The observed broadness and shift of some absorption bands may be regarded as a result of an absorption overlapping of tetrahedrally and octahedrally coordinated Ni^{2+} According to shape and positions of the octahedral absorption bands, the phase containing enstatite–diopside mixed crystal could probably exist Thus, the reaction product at 1200 °C may be described as largely Ni^{2+}-containing $(Ca, Mg)_2Si_2O_6$ and $Ca_2MgSi_2O_7$ phases. The formation of the akermanite phase at 1200 °C may be due to a further reaction which seems to be thermodynamically possible, with the assumption that significant changes in formation enthalpies due to the presence of low Ni^{2+} concentration

$$MgCaSiO_4 + CaSiO_3 \xrightarrow{1200\,^\circ C} \quad Ca_2MgSi_2O_7$$

$$(-27\ 36) \ + (-21\ 25) \xrightarrow{+4\ 77} \quad (-43\ 83)\ \Delta H \text{ kcal}$$

X-ray analysis confirmed the presence of the enstatite–diopside mixed crystal and monticellite phases in the reaction product obtained at 1000 °C on one hand, and the enstatite–diopside, together with akermanite, phases at 1200 °C on the other Diffracted lines were observed to be shifted towards greater 2θ (smaller d Å) on increasing the temperature from 1000 to 1200 °C, in agreement with the formation of akermanite, which has smaller lattice dimensions, comparable to the coexisting phases (Table 1)

Reactions with 3 mol CaCO$_3$

Spectra of reaction product obtained at 1000 °C showed a number of absorption bands related to Ni^{2+} in both octahedral and tetrahedral coordinations (curve III in Fig 1) Therefore, silicate host lattices containing differently coordinated Mg^{2+} ions, and able to be substituted by Ni^{2+} ions, could be formed by assuming the reaction

$$3MgSiO_3 + SiO_2 + 3CaO \xrightarrow{1000\,^\circ C} Ca_2MgSi_2O_7 + (Mg, Ca)SiO_4 + (Mg, Ca)SiO_3$$

At 1200 °C the spectrum showed mostly absorption bands of tetrahedrally coordinated Ni^{2+}, with relatively higher intensity than previous spectra discussed, together with some Ni^{2+} octahedral bands and shoulders of weak intensity (curve III, Fig 2) According to these results, the incomplete formation of akermanite at 1000 °C seems obviously to be shifted towards an increase of its formation via a secondary reaction

$$(Mg, Ca)_2SiO_4 + (Ca, Mg)SiO_3 \xrightarrow{1200\,^\circ C} Ca_2MgSi_2O_7$$

The formation of the assumed phases formed at 1000 °C, as well as akermanite as a main constituent of the reaction product at 1200 °C, were confirmed by X-ray analysis

Reactions with 4 mol CaCO$_3$

In this range of $CaCO_3$ concentration and at the two firing temperatures 1000 and 1200 °C, the tendency of formation of Ni^{2+}-containing akermanite and monticellite seems to be favoured, as revealed by X-ray (characteristic diffracted lines of both phases) and spectral analysis (absorption bands of both tetrahedrally and octahedrally coordinated Ni^{2+} (Figs 1 and 2, curve IV) Thus a proposed reaction may be formulated as

$$3MgSiO_3 + SiO_2 + 4CaO \xrightarrow{1000\,^\circ C} Ca_2MgSi_2O_7 + 2MgCaSiO_4$$

However, the incomplete formation of Ni-akermanite at 1000 °C may proceed not only through monticellite–wollastonite reaction, as suggested before, but also through different other reactions, such as

$$Ca_2SiO_4 + MgCaSiO_4 + \quad CaMgSi_2O_6 \rightarrow \quad 2Ca_2MgSi_2O_7$$

$$(-30\;19) + (-27\;56) + \quad (-35\;25) \xrightarrow{+5\;34} \quad (-2 \times 43\;83)\ \Delta H \text{ kcal}$$

$$Ca_3MgSi_2O_8 \text{ (merwenite)} + CaMgSi_2O_6 \rightarrow 2Ca_2MgSi_2O_7$$

$$(-57\;02) \qquad + (-35\;25) \xrightarrow{+4\;61} (-2 \times 43\;83)\ \Delta H \text{ kcal}$$

Regarding the intensity of absorption bands (Fig 1, 2 and 3), it is observed that the Ni^{2+}-tetrahedral bands are more intense than the octahedral ones, a fact which is due to the absence of a centre of symmetry in the tetrahedral arrangement Generally, it is obvious that there is a change of band intensity which could be attributed to (a) firing temperature—on increasing firing temperature, the formation of stable Ni^{2+}-containing phases was increased and consequently the intensity of their related absorption bands (curves I and III in Figs. 1 and 2) (b) $CaCO_3$ concentration—on increasing the molar ratio of $CaCO_3$ from 2 to 3, the formation of the phase Ni–akermanite was increased, as deduced from the increase of intensity of its characteristic tetrahedral absorption bands (Fig 2, curves II and III)

The visual colour of 1 mol CaO-containing reaction products fired at 1000 and 1200 °C was beige, whereas those of 2–4 mol CaO-containing products changed their colour from beige to a mixed bluish-green–greenish-blue colour on increasing the firing temperature from 1000 to 1200 °C, respectively

In relation to colour of some pure synthesized 0 1Ni-enstatite (yellowish-green), 0 2Ni-diopside (pale yellowish-green) and 0 2Ni-akermanite (blue) [5], the present visual change of colour, particularly at higher firing temperatures, could be possibly due to the coexistence of Ni^{2+} ions in two different coordinations of different silicate phases as theorized

It is, however, worth noting two general observations concerning the thermal reactions of the present system (a) at 2 mol $CaCO_3$, and a firing temperature of 1000 °C, the phase Ni-akermanite was not detected, whereas Co-akermanite [3] was formed This behaviour may be attributed to the greater preference of Co^{2+} ions for the occupation of tetrahedral positions than Ni^{2+} ions under the given experimental conditions (b) At 3 and 4 mol $CaCO_3$, and the two working temperatures of 1000 and 1200 °C, the tendency of Ni-akermanite formation was increased, whereas that of Ni-enstatite–diopside was diminished In presence of Co^{2+} ions, the analogous two Co silicate phases were identified [3] The lessened Ni-pyroxene formation may be due to the effect of Ni^{2+} ions in lowering the metasilicate formation as reported [19] and observed before [2].

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