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

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ABSTRACT

Four solid reaction mixtures of talc–x $CaCO_3$–0.2 $CoCl_2 \cdot 6\ H_2O$ in the molar ratio $1:x:0.2$ ($x = 1$, 2, 3 and 4) were prepared and thermally treated at 1000 and 1200°C. The resulting coloured reaction products were identified—after sudden cooling to room temperature—by means of X-ray diffraction and ligand-field absorption spectrum methods. Analysis of the reaction products obtained at 1000°C showed diffracted lines as well as absorption bands characteristic of phases (I) Co-diopside Ca(Mg, Co)Si_2O_6 at $x = 1$, (II) Co-diopside, Co-monticellite Ca(Mg, Co)SiO_4 and Co-akermanite Ca_2(Mg, Co)Si_2O_7 varying in concentrations at $x = 2$ and 3, and (III) Co-akermanite and Co-monticellite at $x = 4$. On the other hand, analysis of the reaction products treated further at 1200°C confirmed the presence of the same phases formed in the reaction mixtures at $x = 1$ and 4, whereas Co-monticellite seemed to dissociate where $x = 2$ and 3. However, the intensities of both diffracted lines and absorption bands of the corresponding phases were found to increase on increasing the firing temperature and $CaCO_3$ concentration. Generally, the results are discussed in view of formation enthalpies as well as spectra of differently coordinated Co(II) in silicate structures.

INTRODUCTION

Knowledge of the phases occurring during the thermal reactions of the mineral talc, $Mg_3Si_4O_{10}(OH)_2$, is important since talc constitutes one of the principal raw materials for many of the products of the ceramic industry. This industry, in general, includes the manufacture of all products that are nonmetallic and inorganic in nature and require the application of elevated temperatures at some stage in their production, e.g. porcelains, refractories, pottery, glass, porcelain enamel, abrasives, cements and limes. It was thus necessary to study such thermal reactions of talc alone [1,2] as well as some talc–metal compound systems as reported previously [3]. Recently, a study of the reactions of talc towards Co(II) over a wide range of cobalt molar concentration and two different temperatures showed that firing temperature, rapid cooling and Co concentration greatly affect the nature of the phases formed [4]. However, there are many other less known solid-state

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reactions of talc with other compounds which are of paramount importance to practical use. The present investigation aims, therefore, at narrowing this gap through characterization of phases formed at high temperatures in the system talc–$CaCO_3$ doped with Co(II) as an optical indicator.

EXERIMENTAL

Preparation of reaction mixtures of talc: x $CaCO_3$: 0.2 $CoCl_2 \cdot 6\ H_2O$ in the molar ratio 1 : x : 0.2 (x = 1, 2, 3 and 4) and their thermal treatment were the same as reported earlier [4]. The talc and $CoCl_2 \cdot 6\ H_2O$ were of the same samples used previously [4], whereas $CaCO_3$ (P.A., precipitated) was a Merck product.

X-Ray diffraction and ligand-field spectrum techniques were applied using a Philipps-X-ray diffractometer (Cu K_α radiation) and automatic Carl-Zeiss DMR 21 spectrophotometer, respectively.

TABLE 1

Some experimental data on the system talc–x $CaCO_3$–0.2 $CoCl_2 \cdot 6\ H_2O$ (molar ratio = 1 : x : 0.2)

Reaction mixture	Thermal treatment		Phases identified	Colour
	Temp. (°C)	Time (h)		
$x = 1$	1000	12 + 12	Co-diopside	Rose
2			Co-diopside(increasing) + Co-akermanite + Co-monticellite	Rose-violet with blue hue
3			Co-akermanite(increasing) + Co-monticellite-(increasing) + Co-diopside(decreasing)	Blue
4			Co-akermanite(increasing) + Co-monticellite-(increasing) + probably Ca_2SiO_4 and $Ca_3(Mg, Co)Si_2O_8$	Light-blue
$x = 1$	1200	24 + 24	The same as in the reaction at 1000°C with increase in concentration	Rose
2			Co-diopside + Co-akermanite(increasing)	Light blue with violet hue
3			Co-akermanite(increasing) + Co-diopside	Deep blue
4			Co-akermanite + Co-monticellite (increasing) + probably Ca_2SiO_4	Light blue

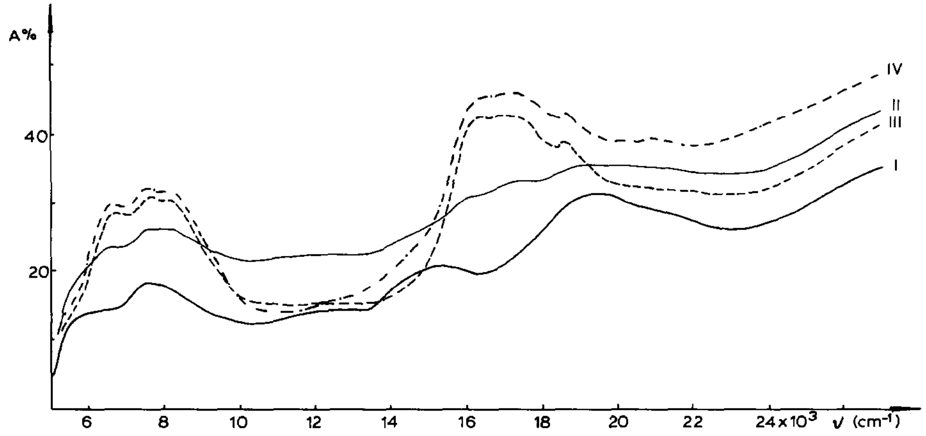

Fig. 1. Electronic absorption spectra of the reaction products in the system talc–x $CaCO_3$–0.2 $CoCl_2 \cdot 6 H_2O$ treated at 1000°C. $x = 1$ (I), 2 (II), 3 (III) and 4 (IV).

RESULTS AND DISCUSSION

Table 1 includes some experimental data on the studied systems. Electronic absorption spectra of the coloured reaction products obtained at 1000 and 1200°C are shown in Figs. 1 and 2, respectively. Figure 3 shows the spectra of some related pure synthesized Co silicate minerals.

It is well known that the solid products of talc on thermal dissociation at 1000°C are magnesium metasilicate $MgSiO_3$ (the ortho form is a main constituent) and amorphous SiO_2, whereas cristobalite SiO_2 together with

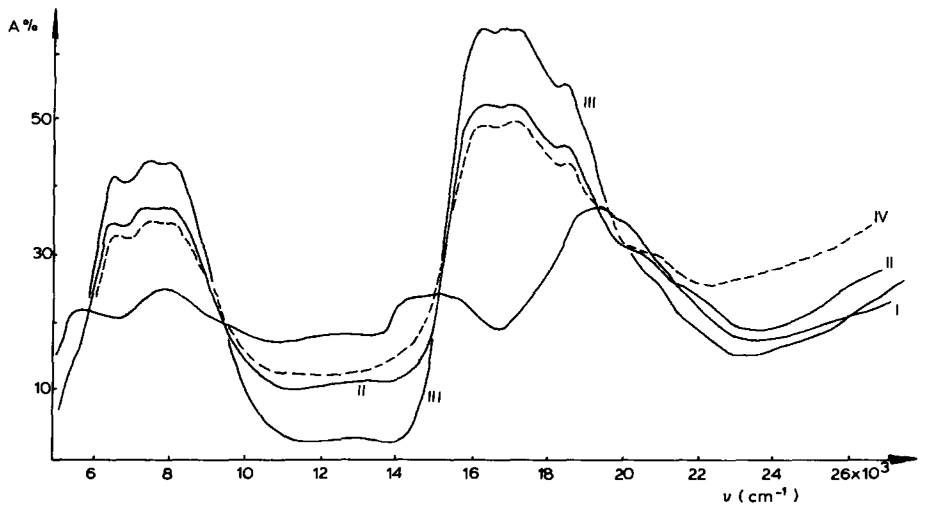

Fig. 2. Electronic absorption spectra of the reaction products in the system talc–x $CaCO_3$–0.2 $CoCl_2 \cdot 6 H_2O$ treated at 1200°C. $x = 1$ (I), 2 (II), 3 (III) and 4 (IV).

$MgSiO_3$ (mainly as the proto form) are the products at 1200°C. It has been realized, however, that the stability range of the three enstatite modifications (ortho, proto and clino) depends both on the firing temperature and the cooling rate [5,6]. In addition, the existence of a further high-temperature modification, named high-clinoenstatite (1130–1250°C), was reported by Schwab [7]. The present results of talc reactions on the addition of $CaCO_3$ show, on the other hand, that a variety of Ca–Mg silicates are formed, which are known to exist within the system Ca–Mg–Si oxides. In general, it is observed that $CaCO_3$ concentration and firing temperature factors affect the nature of the phases produced and consequently their relative concentrations in reaction products. A change of $CaCO_3$ concentration at constant firing temperature (talc and Co^{2+} are kept constant) leads to the formation of phases that fall into three distinct groups according to the $CaCO_3$ mole concentration.

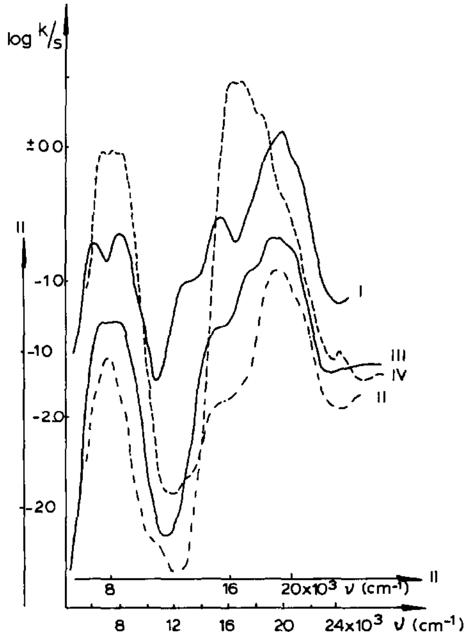

Fig. 3. Electronic absorption spectra of pure synthesized $Co_{0.2}Mg_{1.8}Si_2O_6$ (I), $Co_{0.3}Mg_{0.7}$Ca-SI_2O_6 (II), $CaCo_{0.5}Mg_{0.5}SiO_4$ (III), and $Co_{0.5}Mg_{0.5}Ca_2Si_2O_7$ (IV).

System with 1 mole $CaCO_3$

The visual colour of the reaction products is pale rose which normally originates from *d–d* electron transitions of an octahedrally coordinated Co^{2+} in oxidic host lattices. In relation with the nature of the present reactions, it is desirable to mention the minerals forsterite, Mg_2SiO_4, monticellite, $CaMgSiO_4$, enstatite, $Mg_2Si_2O_6$ and diopside, $CaMgSi_2O_6$, which are known structurally to possess MgO_6 octahedra suitable for isomorphous replacement of Co^{2+} (as a central ion) to form CoO_6 or generally $(Mg, Co)O_6$ polyhedra. Mg^{2+} ions are distributed over two different lattice positions (in the sense of MgO_6 octahedra distortion) in forsterite and enstatite, whereas they occupy only one position in monticellite and diopside. However, MgO_6 octahedra in monticellite were found to be more distorted than those in diopside which are quasiregular. Absorption bands of isomorphously incorporated Co^{2+} ions in such lattices show, therefore, some differences in fine structure and degree of broadness (Fig. 3).

The general feature of the measured spectra of the rose reaction products treated at 1000 and 1200°C is characteristic of Co^{2+} in octahedral coordination (Figs. 1 and 2, curve 1). The location and shape of the three main absorption bands corresponding to the transitions [$^4T_{1g}(F)$ ground state term]

$$^4T_{1g} \rightarrow {}^4T_{2g}(F) \sim 8000\ \mathrm{cm}^{-1} \tag{1}$$

$$^4T_{1g} \rightarrow {}^4A_{2g}(F) \sim 15000\ \mathrm{cm}^{-1} \tag{2}$$

$$^4T_{1g} \rightarrow {}^4T_{1g}(P) \sim 19500\ \mathrm{cm}^{-1} \tag{3}$$

are nearly similar to those of pure synthesized Co-diopside (7000, 15500 and 18500 cm^{-1} for transitions 1, 2 and 3, respectively; Fig. 3, curve II) [8]. It is observed, however, that absorption maxima are relatively broad and cover a wide range of absorption which is due eventually to the presence of Co^{2+} in different phases with different lattice positions, the formation of which might take place via solid-solution reactions. The stable wollastonite, $CaSiO_3$, (formation enthalpy $\Delta H = -21.25$ kcal/mole^{-1} [9]) could be assumed to be formed during reactions between the resulting active CaO and SiO_2 as one of the thermal dissociation products of talc. The second thermal dissociation product, $MgSiO_3$ (3 $MgSiO_3$ per mole talc), would react simultaneously with the formed $CaSiO_3$, thus leading to the formation of $(Ca, Mg)_2Si_2O_6$ diopside pyroxene. This conclusion of such a solid-solution reaction is in fair agreement with previous results on the relation of phases in the system $MgSiO_3$–$CaSiO_3$, where the diopside phase was obtained at higher $CaSiO_3$ concentration [7]. Moreover, the probability of a $Mg_2Si_2O_6$–$CaMgSi_2O_6$ mixed crystal cannot be excluded since a mixed crystal formation with an immiscibility gap is known in this system [10–12]. In addition to the three main absorption bands, a very weak crystal field band appears at ~ 5400 cm^{-1} which may be attributed to Co^{2+} occupying the position of Ca^{2+} ions in diopside, where 6 O^{2-} ligands are octahedrally arranged at a large distance relative to the Mg–O distance (coordination number of Ca in diopside is 8, two ligands are lying at 2.74 Å and six ligands at an average distance of 2.42 Å, whereas the average Mg–O distance is 2.12 Å [13,14]).

The process of Ca^{2+} substitution through Co^{2+} may be understood by assuming that part of the $CaSiO_3$ forms a mixed crystal with $CaMgSi_2O_6$, where Co^{2+} and Mg^{2+} ions occupy Ca^{2+} positions. In fact, a partial wollastonite–diopside mixed crystal is known to exist [10]. This spectroscopic result clearly indicates the indirect formation of $CaSiO_3$ during the present reactions, which agrees with similar spectroscopic evidence previously observed in a system of pure CaO–MgO–SiO_2 oxides [15].

X-Ray diffraction patterns confirm the formation of the diopside phase but it is difficult to identify the presence of $CaSiO_3$ since its characteristic strongest diffracted lines, e.g. at 2.98, 1.83 and 1.71 Å, coincide with those of some Ca–Mg silicates. However, formation of diopside ($\Delta H = 35.25$ kcal mole^{-1} [16]), even at the relatively low temperature of 1000°C, and not other related Ca–Mg silicates seems to be a question of its formation tendency at low $CaCO_3$ concentration.

Systems with 2 and 3 moles $CaCO_3$

The visual colour of the reaction products differs considerably according to $CaCO_3$ concentration and firing temperature. At 2 moles $CaCO_3$ and a firing temperature of 1000°C the colour is rose-violet with a blue hue, whereas it changes to light blue with a pale violet-rose hue at 1200°C. At 3 moles $CaCO_3$ and 1000°C the colour is blue but it becomes deep blue at a firing temperature of 1200°C. It seems from such colour variation that Co^{2+} ions are incorporated in different phases that formed on increasing the $CaCO_3$ concentration other than the diopside phase identified at 1 mole $CaCO_3$. X-Ray analysis reveals that characteristic diffracted lines of diopside, monticellite and akermanite $Ca_2MgSi_2O_7$ phases are present in the reaction products treated at 1000°C. On the other hand, X-ray diffractograms of the reaction products heated further at 1200°C show clearly the absence of lines related to the monticellite phase. Diopside, monticellite and akermanite phases are considered to be stable from the formation enthalpy point of view ($\Delta H = -35.25$, -27.56 [17] and -43.83 [16] kcal mole^{-1} for diopside, monticellite and akermanite, respectively), but since no equilibrium is attained at the relatively low temperature of 1000°C, the formation tendency of such Ca–Mg silicates appears to be the dominant factor rather than stability. Moreover, the Co^{2+} ion seems to stabilize the akermanite host lattice (pure $Ca_2MgSi_2O_7$ is stable in the range 1325–1454°C) due to a pronounced tendency of Co^{2+} ions to occupy tetrahedral coordination more than Mg^{2+} ions do. The formed phase, e.g. $Ca_2(Mg, Co)Si_2O_7$, has, therefore, a wider range of stability than that of Co free akermanite. This conclusion agrees with the fact that the blue phase, $Ca_2Mg_{0.5}Co_{0.5}Si_2O_7$, can be synthesized in a pure state at 1100–1150°C, whereas the host lattice $Ca_2MgSi_2O_7$ is unstable at the same temperature.

The disappearance of the monticellite phase on further heating of the reaction products at 1200°C could be attributed to a secondary reaction taking place according to

$$Ca(Mg, Co)SiO_4 + CaSiO_3 \rightarrow Ca_2(Mg, Co)Si_2O_7$$

As a result of this proposed reaction, the Co-akermanite phase would increase, which is actually the case, in agreement with experimental observation (Figs. 1 and 2, curves II and III). However, phases identified by X-ray analysis offer two different coordination positions for Co^{2+} ions, namely, octahedral configuration as in $Ca(Mg, Co)Si_2O_6$ and $Ca(Mg, Co)SiO_4$, and tetrahedral configuration as in $Ca_2(Mg, Co)Si_2O_7$ lattices. Accordingly, the presence of Co^{2+} ions in these two different coordination states would lead to mixed colours of rose $Ca(Mg, Co)Si_2O_6$ and $Ca(Mg, Co)SiO_4$ together with blue $Ca_2(Mg, Co)Si_2O_7$ phases, which agrees with the visual coloration obtained. The formation of the blue Co-akermanite phase, even at very low concentration, affects the spectra pattern of the other Ca(Mg, Co) silicates (Fig. 1, curve II). Such an effect was previously observed in the case of spectra of rose $CaMg_{1-x}Co_xSiO_4$ mixed-crystal series contaminated with the blue $Ca_2(Mg, Co)Si_2O_7$ phase [15]. As the concentration of the blue phase Co-akermanite increases in the reaction products, the spectra show absorption bands characteristic of tetrahedrally coordinated Co^{2+} (Figs. 1 and 2) corresponding to transitions [$^4A_2(F)$ ground state term]

$$^4A_2 \rightarrow {}^4T_1(F) \sim 6600, 7500, 8250\ \mathrm{cm}^{-1} \tag{4}$$

$$^4A_2 \rightarrow {}^4T_1(P) \sim 16300, 16800, 17400, 18550\ \mathrm{cm}^{-1} \tag{5}$$

which are practically the same as those of pure synthesized $Ca_2Mg_{1-x}Co_x Si_2O_7$ phases (6500, 7400, 8000 and 16100, 16800, 17000, 18350 cm^{-1} for transitions (1) and (2), respectively [8,15]).

System with 4 moles $CaCO_3$

The visual colour of the reaction products treated at 1000 and 1200°C is light blue. X-Ray diffractograms show mainly characteristic lines of akermanite and monticellite phases, together with few additional weak lines which could be related to the phases calcium orthosilicate Ca_2SiO_4 and merwinite $Ca_3MgSi_2O_8$. Formation of such compounds of relatively high calcium content and formation enthalpy ($\Delta H = -30.19$ and -57.02 kcal mole^{-1} for calcium orthosilicate and merwinite, respectively [17,18]) seems to be very probable and is favoured on increasing $CaCO_3$ concentration. Experimental observation (X-ray and spectra results) of an increase in akermanite and monticellite concentrations on heating the reaction products at 1200°C could support the proposed formation of Ca_2SiO_4 and $Ca_3MgSi_2O_8$ which might undergo intermediate reactions as represented by

(1) reaction with a probably formed Co-diopside in traces (not detected by

X-ray diffraction)

$Ca_3(Mg, Co)Si_2O_8 + Ca(Mg, Co)Si_2O_6 \rightarrow 2\ Ca_2(Mg, Co)Si_2O_7$

(2) $Ca_3(Mg, Co)Si_2O_8 \rightarrow Ca(Mg,Co)SiO_4 + Ca_2SiO_4$

Spectra of the reaction products in this range of $CaCO_3$ concentration show, in general, two absorption bands characteristic of tetrahedrally coordinated Co^{2+} ions in $Ca_2(Mg, Co)Si_2O_7$ overlapping those of octahedrally coordinated Co^{2+} ions in $Ca(Mg, Co)SiO_4$ (Figs. 1 and 2, curve IV). Absorption maxima are relatively broad due to the distribution of Co^{2+} ions over two different coordination positions in akermanite and monticellite lattices.

It is perhaps worth noting that neither broad bands associated with amorphous SiO_2 nor the appearance of the strongest reflection of critoballite SiO_2 at about 4 Å are detected during reactions of talc–$CaCO_3$, in contrast to the talc–cobalt chloride system [4]. This observation is understandable if the formation of Ca- and Ca–Mg silicates is taken into consideration. Moreover, well-crystalline phases (as observed from X-ray patterns) result along the whole series of reaction mixtures at the two firing temperatures, indicating that the CaO effect is obviously in favour of increasing maturing temperature.

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