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SOLID-STATE REACTIONS OF TALC TOWARDS Co(II) AT HIGH TEMPERATURES

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ABSTRACT

Solid-state reactions in talc and talc–x $CoCl_2 \cdot 6\ H_2O$ systems (mole ratio $1:x$, where $x = 0.1$, 0.2, 0.4, 0.6, 0.8 and 1.0) were carried out at two different temperatures, viz. 1000 and 1200°C. X-Ray diffraction and ligand-field absorption spectrum methods were applied to characterize the phases in the reaction products after rapid cooling to room temperature. DTA of talc was also carried out and showed an endothermic peak at 960°C (dehydration process) and a broad exothermic band between 1070 and ~1300°C. The results of X-ray diffraction showed, generally, the presence of the three known proto, ortho and clinoenstatite forms in reaction products, together with the appearance of cristoballite SiO_2 at 1200°C. Moreover, the formation of Co_2SiO_4 was detected at higher concentrations of Co^{2+}. The spectra indicated, on the other hand, that the absorption bands within the system talc–Co(II) were characteristic of an octahedrally coordinated Co^{2+} in different enstatite modifications, in confirmation with X-ray data. In general, it was observed that the concentration of phases whose formation was favoured at high temperature increased on increasing the firing temperature, whereas the degree of crystallinity appeared to decrease with increase of the Co concentration.

INTRODUCTION

Talc, $Mg_3(Si_2O_5)_2(OH)_2$, belongs to the layer-lattice minerals of the montmorillonite type, where its basic structure consists of an octahedral layer with Mg^{2+} between two silica tetrahedral layers. Considering talc as one of the principal raw materials for many of the products of the ceramic industry, therefore, the solid-state reactions that occur during heating it are of paramount importance. It is generally known that magnesium metasilicate, $MgSiO_3$, and SiO_2 phases are the solid products of talc on thermal dissociation at relatively high temperature. The nature of such phases concerning modifications, crystallinity and concentration depends greatly on heat treatment. Rieke and Wiese [1] identified the $MgSiO_3$ formed on heating talc at 800 and > 1100°C as protoenstatite, whereas Thilo and Rogge [2] recognised three modifications of $MgSiO_3$ as clinoenstatite (high temperature modification), protoenstatite and enstatite. Recent investiga-

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tions on the polymorphism of synthetic and natural enstatite $MgSiO_3$ [3,4] showed that protoenstatite and clinoenstatite have changed positions regarding their stability ranges, i.e. protoenstatite was the high-temperature modification. However, the principal difficulties are concerned with the identification of amorphous phases that may be formed which the conventional X-ray diffraction techniques cannot discern. The application of another specialized method, such as ligand-field absorption spectra of coloured cations reacting with talc, is necessary to get more information on the phases produced by making use of the fact that a coloured cation shows a characteristic spectrum which is related to a definite structure.

The present investigation aims, therefore, to characterize the phases that occurred during the thermal reactions of talc and the talc–Co(II) system as well as to study the effects of Co concentration, firing temperature and rapid cooling to room temperature.

EXPERIMENTAL

A sample of talc from Hamata, south eastern desert, Egypt, was purified and chemically analysed ($MgO = 31.56\%$, $SiO_2 = 58.12\%$, loss on ignition = 5.34% and impurities as oxides of Al, Ca, K, Na, Fe = 5.0%). The $CoCl_2 \cdot 6\,H_2O$ (P.A.) used was a product of the firm Riedel–de Haen. The different reacting mixtures in the system talc–x $CoCl_2 \cdot 6\,H_2O$ were prepared from solid powders in molar ratio $1 : x$, where $x = 0.1$, 0.2, 0.4, 0.6, 0.8 and 1.0. The well-mixed samples were sintered at two different temperatures (1000 and 1200°C) for a total period of 24 and 48 h, respectively. Every sintering process was repeated after homogenizing the reaction mixtures. The spectra of rapidly cooled rose-coloured reaction products were recorded using automatic Carl Zeiss DMR 21 and Philipps X-ray diffractometer (CuK_{α_1} radiation). The DTA curve for talc was obtained using a Shimadzu apparatus at a heating rate of $10°C\ min^{-1}$.

RESULTS AND DISCUSSION

Talc

The DTA curve of the talc used (Fig. 1) shows that the dehydration process takes place at 960°C in connection with an endothermic peak, whereas a very broad exothermic band is observed between 1070 and ~ 1300°C which is due eventually to a crystallization process. However, there is no detectable heat effect in the range between 960 and ~ 1070°C. An X-ray diffractogram of fired talc at 1000°C after rapid cooling to room temperature reveals, generally, the formation of enstatite phase $MgSiO_3$,

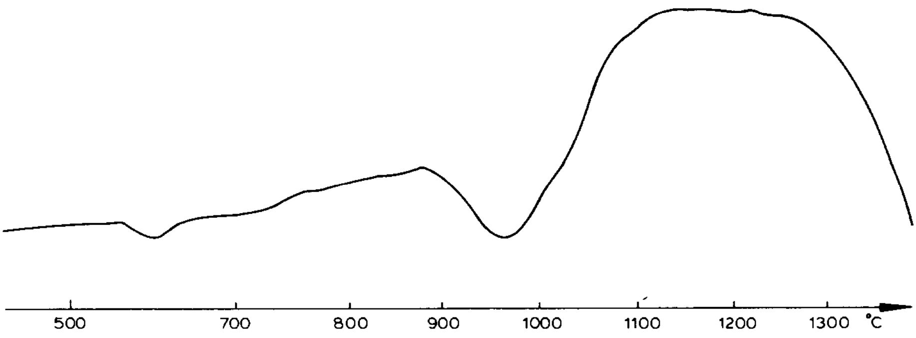

Fig. 1. Differential thermal analysis of talc at a heating rate of 10°C min^{-1}.

together with amorphous SiO_2. This finding is in agreement with previous results of the thermal decomposition of talc [5], which showed that the enstatite phase appeared directly on dehydration with no appearance of an exothermic peak on the DTA curve. Evaluation of X-ray results shows that the three known modifications of enstatite phase are present together with SiO_2. The identification is based on interplanar distances and visual intensities of the three strongest peaks characteristic of each modification, according to ASTM cards (proto = 3.16, 1.96, 1.49; ortho = 3.17, 2.87, 2.49; and clino = 2.87, 2.97 and 1.60 Å). It is obvious from such values that certain peaks of proto and ortho have nearly the same interplanar distances (3.16 ~ 3.17 Å) on the one hand, and ortho and clino (2.87 Å) on the other, and hence composite patterns result. However, it should be possible to achieve identification by considering the other strong peaks related to each phase alone. Accordingly, the products of talc thermally treated at 1000 and 1200°C on rapid cooling to room temperature would likely contain a mixture of the three phases proto, ortho and clinoenstatites in varying concentrations, in addition to cristoballite SiO_2 at 1200°C. The main constituent at 1000°C seems to be the ortho form in addition to very small concentrations of the proto and clino phases. In the reaction products at 1200°C, the proto and ortho phases appear to change positions, i.e. the concentration of proto increases rapidly compared with that of ortho, whereas clino still exists in a small concentration.

The present results, indicating mainly ortho formation at 1000°C, increase of the proto concentration on heating ortho-containing reaction products at 1200°C, together with the formation of clino on sudden cooling of these mixtures, agree with previous studies concerning the stability and transition conditions of the three known enstatite modifications. Smyth [4] concluded from his study on the polymorphism of enstatite $MgSiO_3$ that proto was the stable phase from above 1000°C and ortho was stable below about 1000°C, whereas clino and twinned clino resulted on rapid cooling [3] and quenching [4], respectively, of proto. Moreover, transition of ortho to proto was found to require up to several days at 1200°C [4]. It should be pointed out, however, that the crystallinity of the different phases present in the reaction products increases markedly with increase of firing temperature.

The talc–$CoCl_2 \cdot 6\ H_2O$ system

The present X-ray results are, generally, similar to those to pure talc in revealing the presence of different enstatite phases together with amorphous and crystalline SiO_2 (cristoballite) phases at 1000 and 1200°C, respectively. No metal oxide (CoO) is detected. The identification process of phases is largely based on the strongest peaks, since many peaks in the patterns of reaction products with a high Co concentration (0.6–1.0 mole %) tend to become diffuse. However, four remarkable effects are observed on increasing the Co concentration: (a) an irregular shift in interplanar distances of enstatite phases relative to those of pure talc reaction products, (b) a decrease in cristoballite concentration, (c) the formation of Co_2SiO_4 (olivine structure) in two ranges of Co concentration (0.4–1.0 and 0.8–1.0 mole %) at 1000 and 1200°C, respectively, and (d) a general decrease in crystallinity of the resulting phases.

The decrease in SiO_2 concentration can be discussed on the basis that the very reactive CoO formed may react with free SiO_2 (as one product of the thermal dissociation of talc) leading to the formation of a $CoSiO_3$ phase which reacts simultaneously with the second talc thermal dissociation product, $MgSiO_3$, to give (Co, Mg)SiO_3 solid solution. A similar reaction was previously suggested with powdered enstatite heated to approximately 800°C with metal chloride under oxygen exclusion conditions, where a definite exchange of cations, Mg^{2+} and Fe^{2+}, took place to give mixed crystals of enstatite structure [6].

The present assumption of a (Co, Mg)SiO_3 solid solution in the case of talc–CoO reactions could be supported by the fact that a $CoSiO_3$ phase is known (phase diagram of the system CoO–SiO_2 [7]) and as is the $Co_xMg_{2-x}Si_2O_6$ mixed-crystal series [8].

The appearance of another free phase, namely Co_2SiO_4 in very small concentrations at 1000°C in the range 0.4–1.0 mole % Co^{2+}, may be due to its thermal stability as well as to the provision of insufficient energy to promote further reactions. As the energy increases, the reaction

$$Co_2SiO_4 + SiO_2 \xrightarrow{1200°C} 2\ CoSiO_3$$

at the two concentrations 0.4 and 0.6 mole % Co^{2+} may take place. The equilibrium of such a reaction is obviously shifted towards the formation of $CoSiO_3$ so long as its saturation limit in the $MgSiO_3$ host lattice is not reached. At higher Co concentrations (0.8 and 1.0 mole % Co^{2+}), the case seems to be different where the phase Co_2SiO_4 is still present in reaction products, together with cristoballite. This result of incomplete cobalt meta-

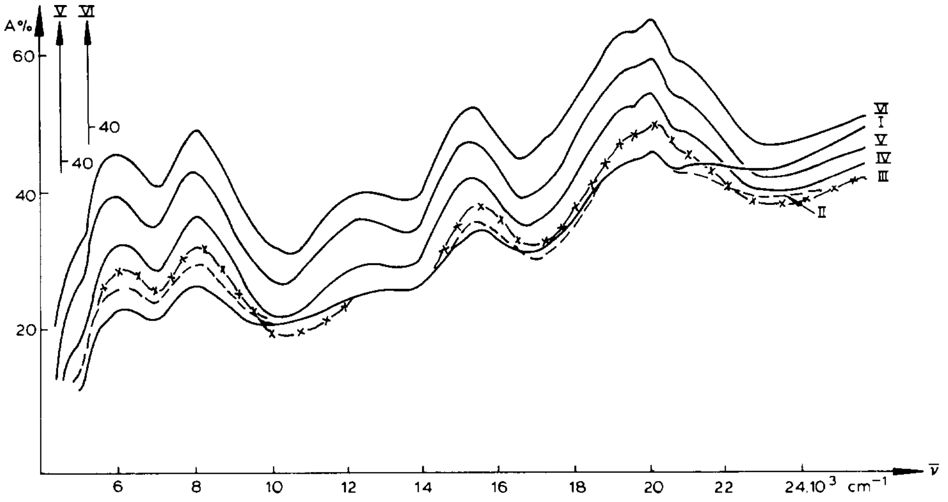

Fig. 2. Electronic absorption spectra of the rose-coloured reaction products in the system talc–x $CoCl_2 \cdot 6\ H_2O$ treated at 1000°C. I, $x = 0.1$; II, $x = 0.2$; III, $x = 0.4$; IV, $x = 0.6$; V, $x = 0.8$; VI, $x = 1.0$.

silicate formation may be attributed to (1) the $MgSiO_3$ lattice is probably saturated with $CoSiO_3$ (at about 0.6 mole % Co^{2+} per one mole talc) and (2) the thermal instability of free $CoSiO_3$ under the experimental conditions used. The found saturation limit of $CoSiO_3$ in the $MgSiO_3$ lattice appears to agree with the relatively low limit of isomorphous replacement of Mg^{2+} by Co^{2+} (20 at. %) in enstatite lattice [8]. As a result of such solid solution, one would expect some shifts in interplanar distances of different enstatite phases and these are, in fact, observed. The obvious decrease in crystallinity of the reaction products on increasing the Co concentration could be related to the CoO effect, which might reduce the maturing temperature and thus act to promote vitrification. Similar effects produced by other different oxides as mineralizers in different systems were reported earlier [9,10].

Analysis of the electronic absorption spectra of the same rose-coloured reaction products indicates that Co^{2+} is apparently coordinated in a Mg silicate host lattice at the two reaction temperatures. The absorption bands obtained are charactertistic of octahedrally coordinated Co^{2+} distributed over two different lattice positions. A careful comparison between the spectra of Co^{2+} in two known host lattices, $Mg_2Si_2O_6$ (ortho and clinoenstatites) and Mg_2SiO_4 (forsterite) [8,11], satisfying this condition on one hand, and the present spectra on the other (Figs. 2–4, Table 1) shows clearly that a Co-enstatite phase (Co_I, Mg_I) $(Co_{II}, Mg_{II})Si_2O_6$ is formed. However, the presence of Co_2SiO_4 in very small concentrations (as revealed by X-ray analysis) seems to have no clear effect on the spectra. Since the three different enstatite modifications are structurally closely related

TABLE 1

Absorption maxima positions (cm^{-1})[a] of the system talc–x $CoCl_2 \cdot 6\ H_2O$ and $Co_{0.2}Mg_{1.8}Si_2O_6$

Temp. (°C)	x 0.1	0.2	0.4	0.6	0.8	1.0	$Co_{0.2}Mg_{1.8}Si_2O_6$	Band assignment	
1000	6000	6100	6200	6150	5900	6000	6050	I → Co_I^{2+}	${}^4T_{1g}(F)$
	8000	8100	8200	8150	8000	8100	8200	I → Co_{II}^{2+}	${}^4T_{2g}(F)$
	12400	12500	12700	12700	12500	12550	13400	II → Co_I^{2+}	${}^4A_{2g}(F)$
	15500	15500	15600	15400	15300	15300	15500 } →	III → Co_I^{2+}	${}^4T_{1g}(P)$
	(17500)	(17500)	(17500)	(17500)	(17500)	(17500)	(17500)		
	(19400)	(19400)	(19500)	(19350)	(19250)	(19300)	(19600) } →	III → Co_{II}^{2+}	
	20200	20150	20150	20000	20000	20000	20150		
	(21500)	(21400)	(21300)	(21250)	(21250)	(21100)	(21200)		
1200	5700	5800	5800	5850	5850	6000			
	8050	8000	8100	8100	8050	8100			
	12350	12200	12300	12500	12400	12500			
	15400	15300	15400	15400	15400	15400			
	(17500)	(17500)	(17500)	(17500)	(17500)	(17500)			
	(19400)	(19350)	(19350)	(19350)	(19350)	(19400)			
	20200	20100	20150	20100	20100	20100			
	(21300)	(21100)	(21200)	(21100)	(21150)	(21250)			

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[a] Figures in parentheses indicate shoulders.

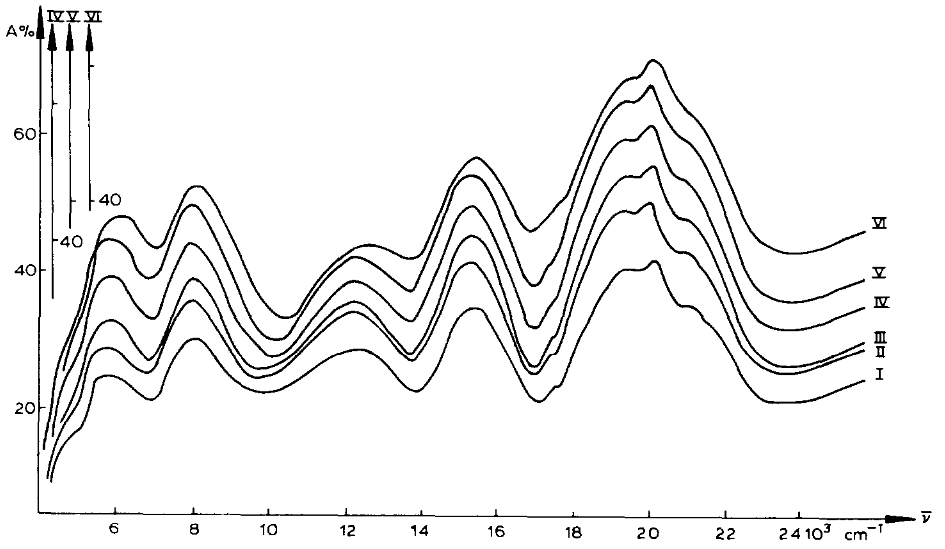

Fig. 3. Electronic absorption spectra of the rose-coloured reaction products in the system talc–x $CoCl_2 \cdot 6$ H_2O treated at 1200°C. I, $x = 0.1$; II, $x = 0.2$; III, $x = 0.4$; IV, $x = 0.6$; V, $x = 0.8$; VI, $x = 1.0$.

[proto(orthorhombic), $a = 9.25$, $b = 8.92$, $c = 5.25$; ortho(orthorhombic) $a = 18.20$, $b = 8.89$, $c = 5.20$; clino(monoclinic) $a = 9.12$, $b = 8.86$ and $c = 5.24$ Å], small differences in the absorption bands of their Co^{2+}-containing crystals would be obtained, as was found previously in the spectra of pure synthesized Co-clino and orthoenstatites [12]. The broadness of the present

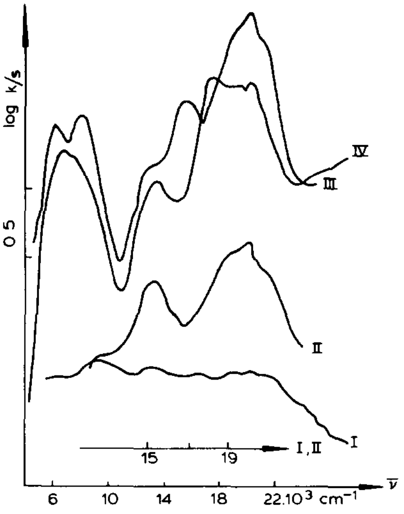

Fig. 4. Electronic absorption spectra of pure synthesized $Mg_2Si_2O_6$ (I), $Co_{0.02}Mg_{1.98}Si_2O_6$ (II), $Co_{0.2}Mg_{1.8}Si_2O_6$ (III), and Co_2SiO_4 (IV).

absorption maxima (Figs. 2 and 3) compared with those of the pure $Co_{0.2}Mg_{1.8}Si_2O_6$ phase (Fig. 4) may, therefore, be due to the coexistence of the three Co-enstatite phases. It is observed, however, that the absorption intensity tends to increase with increase of temperature as well as with Co concentration in the range 0.1–0.6 mole % Co^{2+}, whereas it remains more or less unchanged at 0.8–1.0 mole % Co^{2+}. This behaviour in intensity might support the point of view that the $MgSiO_3$ lattice is saturated with $CoSiO_3$ within the same limit as that suggested by the X-ray results. In conclusion, spectra results confirm, without doubt, the formation of a Co-enstatite phase throughout the whole series of talc–Co(II) thermal reactions, irrespective of the increasing disorder-state of the reaction products, especially at higher Co concentrations.

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