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STABLE Ca_3SiO_5 SOLID SOLUTION CONTAINING MANGANESE AND PHOSPHORUS

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ABSTRACT

The effect of simultaneous addition of varying concentrations of manganese and phosphorus oxides on a $C/S \approx 3$ composition has been investigated. Mineralogical changes on synthesized powders were identified by X-ray diffraction, Infra-red spectroscopy and DTA. M3 polymorph's alite formation with Mn and P inclusions less than 0.69 (wt%) Mn_2O_3 and 0.62 (wt%) P_2O_5 is shown. The Electron Paramagnetic Resonance investigations of synthesized monoclinic C_3S show that Mn ions are in octahedral site as Mn^{2+} oxidation state. The formed solid solutions could be described with the following cationic vacancies formula: $(Ca_{3-5X}\,Mn_{4X}\,\square_X)(Si_{1-2X}\,P_{2X})\,O_5$, with $X \leq 0.005$. © *1997 Elsevier Science Ltd*

Introduction

Tricalcium silicate phase is one of the crystalline phases that constitute the major part of Portland cement clinker. Its structure is built up of Ca^{2+}, $(SiO_4)^{4-}$ and O^{2-} ions and it exists in seven polymorphic modifications; three triclinic forms (T1, T2 and T3); three monoclinic forms (M1, M2 and M3) and one rhombohedral form (R) up to 1100°C (1). The incorporation of foreign ions into the C_3S crystal lattice can modify its energy and one of the polymorphic forms is stabilised at room temperature. The alites in industial clinkers are mainly in active monoclinic forms M1 + M3 (2-4).

The influence of phosphorus element on tricalcium silicate formation has been studied by several authors (5-7); they have shown that the limit of inclusion of phosphate ions in tricalcium silicate solid solution is about 1.1(wt%)P_2O_5. Higher amounts of phosphate inhibit the C_3S crystallization and lead to preferential formation of phosphatic dicalcium silicate solid solution with the stabilization of high temperature polymorphs α' and α of Ca_2SiO_4 (8-11), so the only described mode of substitution in this case is $(PO_4)^{3-} \rightarrow (SiO_4)^{4-}$ substitution.

The inclusion of manganese in tricalcium silicate was also studied and most of the works were aimed to determine the occupancy site and the valence state of manganese ions. Esculescu (12) has found that MnO_2 forms solid solutions based on C_3S up to 1%(wt) and he proposed the substitution of Mn ions conjointly in Ca and Si sites. Knofel et al. (13) have studied the limit of solid solution of Mn in C_3S at 1550°C. They indicate that the limit of single substitution of Si^{4+} by Mn^{4+} is about 0.1%(wt) of MnO_2, from this value up to 2.2%, a double substitution of $Mn^{4+} \rightarrow Si^{4+}$ and $Mn^{2+} \rightarrow Ca^{2+}$ was considered more probable. Puertas et al. (14) have reported, through analytical electron microscopy analysis, the limit of inclusion of manganese in C_3S prepared at 1420°C in oxidizing atmosphere (air); this limit is about 0.72%Mn. These authors indicate that all manganese substituting in the crystal structure of C_3S is virtually as Mn^{4+}, so they propose a formula $Ca_3(Si_{0.954}Mn_{0.036})O_5$ for the monoclinic polymorph of Ca_3SiO_5 synthesized in these conditions.

In the present work it has been studied the effect of combination of manganese and phosphorus elements on the formation of solid solutions, by heterovalent substitution of corresponding ions in tricalcium silicate lattice, at air atmosphere. The synthesized powders were analysed by X-ray diffraction and Infra-Red spectroscopy. Phase transitions were approached by Differential Thermal Analysis. The valence state and lattice site of manganese ions were evaluated by Electron Paramagnetic Resonance.

Experimental

Synthesis of samples was carried out by means of reactions in solid state with high temperature treatment. The used reagent grades are: quartz (SiO_2), calcium carbonate ($CaCO_3$), diammonium phosphate $(NH_4)_2HPO_4$ and manganese oxide Mn_2O_3 (prepared by decarbonation of $MnCO_3$ at 1000°C in oxygen draft (15)).

The mixtures were prepared from stoichiometric quantities of mentioned reagent grades which correspond to weight oxide percentages reported in Table 1. Mixing was accomplished by anhydrous ethanol or acetone to increase homogeneity. The samples were treated slowly at temperatures between 500 and 1000°C with intermediate grinding, then they were compacted in pellets and directly fired at 1500°C for twenty hours and finally quenched in air.

TABLE 1

Chemical Compositions (wt%) of Studied Samples with C/S ≈ 3

Sample	CaO	SiO_2	Mn_2O_3	P_2O_5
S1	73.26	26.08	0.35	0.31
S2	72.84	25.84	0.69	0.62
S3	71.57	25.12	1.73	1.56
S4	69.45	23.92	3.48	3.14
S5	67.30	22.70	5.26	4.73

TABLE 2

Identified Crystalline Phases in Heated Samples (S1-S5)
+++: High amount, ++: Medium, +: Little, -: Nil

Sample	C_3S	β-C_2S	α'-C_2S	2CaO.MnO_2	CaO
S1	+++	-	-	-	-
S2	+++	-	-	-	-
S3	+++	+	-	-	+
S4	-	++	-	+	++
S5	-	++	++	+	++

The samples obtained were analyzed by X-ray Diffraction, IR Spectroscopy, D.T.A. and Electron Paramagnetic Resonance.

Results

X-ray Diffraction. X-ray powder diffraction patterns of the samples were taken using CuKα radiation in a Philips(PW1820) diffractometer. The identified crystalline phases and the semi-quantitative estimation are shown in Table 2; the corresponding patterns are reported in Fig. 1.

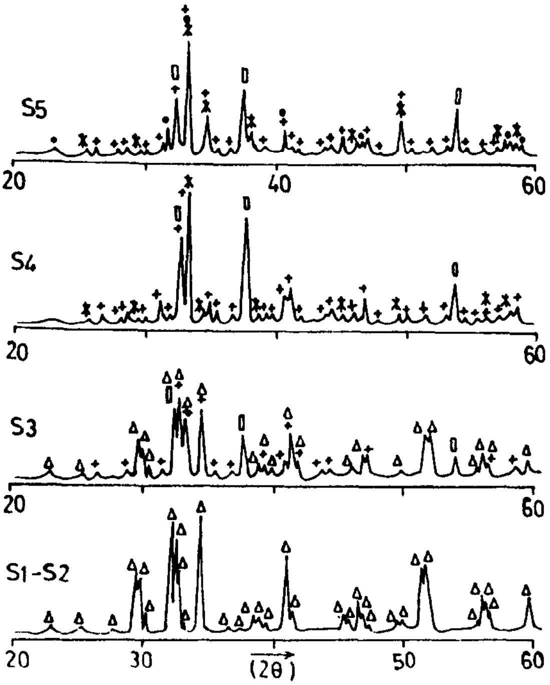

FIG. 1.
X-ray diffraction patterns of samples (S1-S5). Δ: M3 form of C_3S, •: α'-C_2S, +: β-C_2S, *: 2CaO.MnO_2, ▯: CaO.

The samples S1 and S2 have the same diffraction patterns; the only crystalline phase which was identified in these compositions is a tricalcium silicate as the monoclinic polymorph. The observed diffraction lines are similar to the calculated XRD powder pattern of M3 form, assuming the atomic parameters (a = 33.120 Å, b = 7.054 Å, c = 18.550 Å, β = 94.17°) of Nishi et al. for the composition $(Ca_{0.98}Mg_{0.01}Al_{0.0067}Fe_{0.0033})_3(Si_{0.97}Al_{0.03})O_5$ (16,17). The calculated lattice parameters for our solid solution of C_3S containing manganese and phosphorus (samples S1 and S2), from experimental d_{hkl} values, are: a = 33.1163 Å, b = 7.0537 Å, c = 15.5508 Å, β = 94.17°. Sample S3 shows that the complete formation of C_3S phase is not achieved, and traces of β-C_2S phase with remaining quantities of CaO are identified in addition to the same monoclinic C_3S. These quantities of unreacted CaO persisted after heating samples more than 40 hours at 1500°C. At higher added percentage of Mn_2O_3 and P_2O_5 (samples S4 and S5), the limit of solid solution formation was succeeded and $2CaO.MnO_2$ phase was identified with the formation of β-C_2S (sample S4) and α'-C_2S (sample S5). The quantities of formed $2CaO.MnO_2$ increased as the manganese addition increased (sample S5) and it was impossible to develop C_3S phase. The formed phases C_2S, $2CaO.MnO_2$ and CaO persisted after very long heating; more than 60 hours at 1500°C.

Infrared Spectroscopy. Fig. 2 shows the infrared spectra of the same products, obtained after heating the (S1-S5) compositions. Table 3 gives all identified absorption frequencies in these samples. The frequencies of the normal modes of vibration ν_1, ν_3 and ν_4 resulting from the (SiO_4) groups in C_3S and C_2S phases (18,19) are identified. The stretching of P-O bonds in (PO_4) groups occurs normally by the absorption frequencies between 1000 and 1100 cm^{-1} (20,21); we attribute these bands in C_3S and C_2S at observed frequencies between 1065 and 1076 cm^{-1} in all samples (S1-S5). The absorption bands located at 674 and 671 cm^{-1}, in samples S4 and S5 respectively, are attributed to the presence of Mn-O vibrations due to tetrahedral (MnO_4) groups (22), which are present in identified $2CaO.MnO_2$.

Differential Thermal Analysis. D.T.A. tests were conducted on samples S1 and S2 constituted only by C_3S phase. The tests were performed by heating up to 1000°C with subsequent cooling down to 20°C in open air, maintaining the heating and cooling rates at 10°C per minute. The records do not show any thermal effect, neither on heating nor on cooling. This gives proof of the only existence of M3 polymorph of C_3S in treated samples (S1 and S2). The latter form, as mentioned by Taylor (1), does not normally show any thermal effect until more than 1000°C, when transition to R form occurs.

EPR Measurements. The EPR spectra of synthesized powders of monoclinic polymorph Ca_3SiO_5 (samples S1 and S2) are shown in Fig. 3. The observed signals were helpful in determining the valence state and occupancy site of Mn in polycrystalline Ca_3SiO_5. The measurements were carried out at 295°K, using X-band (9.58 GHz) in Bruker spectrometer employing 100 KHz phase-sensitive detection. The original Mn_2O_3 (Mn^{3+}) was also tested; the spectrum obtained, at room temperature, does not show any EPR signal. As a matter of fact, Mn^{3+} has a very short relaxation time and the EPR signal can be observed only at low temperatures (≤10K) (23). This test is used to show non-existent traces of Mn^{2+} or Mn^{4+} in the original used manganese oxide. The latter ions, dissolved in host lattice, are on the contrary easy to identify at room temperature. Some works (24-27) have described the spectrum of these ions in polycrystalline products, further information is given also by several authors on the complete spectrum of Mn^{2+} or Mn^{4+} dissolved in host lattice of single crystals (28-31).

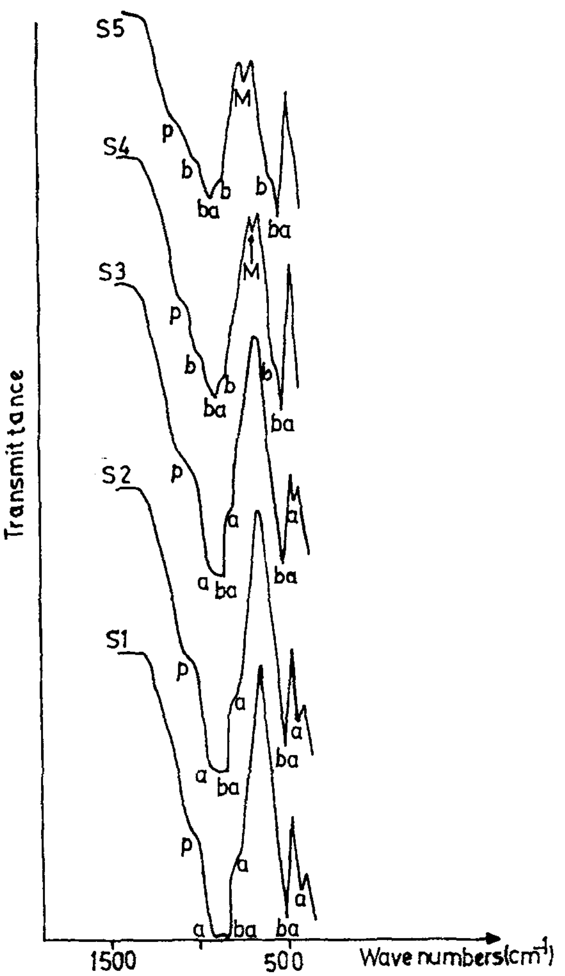

FIG. 2.
IR spectra of samples (S1-S5) p = (PO_4), a = (SiO_4) in C_3S, b = (SiO_4) in C_2S, M = (MnO_4).

The six-line spectrum, of samples S1 and S2, shows a typical six-fold hyperfine splitting ((2I +1) rays), which originates in the nuclear spin moment I = 5/2 of manganese. The corresponding field centers are respectively located at $H_{01} \approx 3372$ Gauss and $H_{02} \approx 3383$ Gauss giving g values at $g_1 \approx 2.0198$ and $g_2 \approx 2.0138$; the observed hyperfine splitting constants /A/ are about 87 Gauss (S1) and 91 Gauss (S2). These values are in agreement with Mn^{2+} centers in octahedral symmetry characterized by a typical hyperfine stucture like arises from allowed transitions between components of the +1/2 and -1/2 Kramers doublet (31-33). The spectrum of sample S1 exhibits also two weak sextets centred at h_1 = 1350 Gauss and h_2 = 2150 Gauss. These signals lead to vanish, in sample S2, from the increased percentage of Mn ions. We attribute these lines to the forbidden hyperfine lines of Mn^{2+}, which can appear sometimes with lower intensities than the allowed lines (34).

In contrast to these results, the resonances of Mn^{4+} ions occur normally towards lower fields (at g ≈ 4) and the corresponding hyperfine splitting constants are about values below

TABLE 3

Observed IR Absorptions (cm^{-1}) in Samples (S1-S5).
(F): very strong, (f): strong, (m): medium, (d): weak

	Samples	S1	S2	S3	S4	S5
Symbol	Vibrations					
p	(PO_4) groups	1076 (d)	1069 (m)	1065 (m)	1062 (m)	1065 (m)
b	$\nu_3(SiO_4)$ in C_2S				1007 (f)	1000 (f)
a	$\nu_3(SiO_4)$ in C_3S	935 (F)	939 (F)	935 (F)		
ba	$\nu_3(SiO_4)$ in C_2S and C_3S	884 (F)	877 (F)	888 (F)	881 (F)	888 (F)
b	$\nu_1(SiO_4)$ in C_2S			830 (f)	848 (f)	844 (f)
a	$\nu_1(SiO_4)$ in C_3S	815 (m)	819 (m)	819 (d)		
M	(MnO_4) groups in $2CaO.MnO_2$				674 (m)	671 (f)
b	$\nu_4(SiO_4)$ in C_2S				558 (m)	555 (m)
ba	$\nu_4(SiO_4)$ in C_2S and C_3S	522 (F)	522 (F)	519 (F)	515 (F)	515 (F)
a	$\nu_4(SiO_4)$ in C_3S	442 (f)	442 (f)	446 (m)		

78 Gauss (23,24,27). These EPR signals are not present in our samples, so there are no traces of Mn^{4+} in our synthesized monoclinic polymorph of C_3S solid solution based on simultaneous inclusion of manganese and phosphorus elements. It appears clearly, after this EPR study, that the only possible substitution site of Mn^{2+} in the host Ca_3SiO_5 lattice in presence of phosphorus elements is the octahedral Ca^{2+} site.

This result does not exclude the possible presence of small quantities of Mn^{3+}, since the latter is observed only at temperatures below 10°K.

More information can be used when examining lines from the obtained spectra. This shows that an increase in concentration of added manganese increases the EPR line width. The increasing rate of lines intensity is identically proportional to increase of manganese concentration. This result can be used to confirm the effective incorporation of manganese ions (Mn^{2+}) in the crystal lattice of samples S1 and S2.

The spectra show another superimposed signal (reproduced by stippled lines in Fig. 3). The signal is constituted by a wide ray at $H \approx 3380$ Gauss. Martins et al. (35) have observed the similar signals which are characteristic from lowly traces of complexed Fe^{3+} ions in phosphate xerogel compounds. We attribute these signals to the presence of iron impurities in reagent grades and to the preparation conditions.

Discussion

The X-ray analysis of several compositions near the $C/S \approx 3$ composition, was carried out and shows that the M3 polymorph of C_3S is undoubtedly formed at Mn and P inclusions less than 0.69 wt%Mn_2O_3 and 0.62 wt%P_2O_5 (samples S1-S2). At higher amounts of these order,

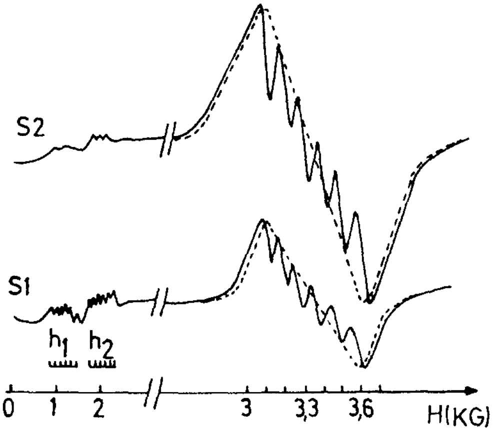

FIG. 3.
EPR spectra of samples S1 and S2.

the alite phase is not formed and solid solutions of C_2S phase take a place with 2CaO.MnO$_2$ and CaO compounds. The observed mineralogical evolution of C_2S phase, on samples (S3-S5), agrees fairly with the reported effect of P_2O_5 (9,36,37); the increasing amount of P_2O_5 leads to the stabilization of C_2S-polymorphs according to the order: $\beta \rightarrow \alpha' \rightarrow \alpha$. The presence of manganese does not influence this stabilization accompanied by the inhibiting effect on C_3S crystallization.

The D.T.A. test, carried out on samples (S1-S2), with the only C_3S constitution, show no thermal effect until 1000°C. The synthesized monoclinic form of C_3S solid solution appears to be stable at ambient, and inversions to triclinic form don't occur even on slow cooling.

The Infra-Red investigations have shown the absorption bands of vibrations resulting from the (SiO_4) and (PO_4) groups in synthesized phases. The localization of the Mn-O vibrations, at 671-674 cm^{-1}, due to tetrahedral (MnO_4) groups in samples containing 2CaO.MnO$_2$ compound gives proof of the non-existence of such groups in samples S1 and S2, since the latters do not show the mentioned vibrations.

EPR data obtained on the same samples (S1 and S2), shows the characteristic field splitting parameters of Mn^{2+} ions in axial symmetry. The location of typical six-fold hyperfine splitting at center fields near the average value of $H \approx 3367$ Gauss with g values near the free spin value $g_e = 2.0023$ show the isotropic character related to the ground therm $^6S_{5/2}$ of Mn^{2+} (d^5 high spin) in octahedral field. The identical proportionality between the intensities of the EPR signals and the concentrations of added manganese constitute a certain proof of the effective inclusion of a proportional quantity of added manganese in the crystal lattice. The identified substitution $Mn^{2+} \rightarrow Ca^{2+}$ in Ca_3SiO_5 lattice seems to be conceivable as regards the Shannon ionic radius of Ca^{2+} (1.00 Å) and Mn^{2+} (0.87Å) (38); the Mn^{2+} ions are able to have a good ability to substitute for the Ca^{2+} ions in octahedral oxygen environment.

All results obtained lead to confirm the inclusion of Mn and P elements in monoclinic M3 polymorph of Ca_3SiO_5. The solid solutions are formed by simultaneous substitutions $Mn^{2+} \rightarrow Ca^{2+}$ and $(PO_4)^{3-} \rightarrow (SiO_4)^{4-}$. So, we propose the following heterovalent substitution:

$$5/2Ca^{2+} + Si^{4+} \rightarrow 2Mn^{2+} + P^{5+} + 1/2\square$$

Considering the compositions S1 and S2, with less than 0.69% Mn_2O_3, the determination of molar ratios corresponding to introduced Mn and P elements, leads to adopt the following formula with cationic vacancies:

$$(Ca_{3-5X}\, Mn_{4X}\, \square_X)(Si_{1-2X}\, P_{2X})\, O_5 \text{ with } X \leq 0.005.$$

The creation of such cationic vacancies in the crystal lattice of this synthesized alite polymorph could explain the hydraulic activity. The presence of crystal defects constitutes one of the important factors to increase the hydraulic activity of clinker phases as has been shown by several authors (39-45).

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