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A NEW ANALYTICAL METHOD FOR SOLID STATE INVESTIGATIONS : "DIFFERENTIAL X-RAY DIFFRACTION".

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ABSTRACT

Recent progress in data treatments allowed by large memory, mass storage and high calculation rates have made possible a new way to improve data obtained with X-Ray analytical technics : differential X-Ray diffraction (DXRD). Use of such differential technics are reported elsewhere as in infra-red spectra domains. Studies of reactions in the solid state are mainly concerned with stable phase transitions as polymorphic, eutectoid, peritectoid reactions or segregations appearing when demixtion lines are crossed, and with metastable transformations of supersatured solids, metastable crystalline compounds and partially crystallized or glassy solids.

X-Ray diffraction and specially the powder method are usefull for such studies, but modifications in the X-Ray spectra obtained when the samples are placed in transition zones are sometimes low enough. Differences can be noticed on Bragg angles, peak intensities, peak width, peak-background ratio and on the combination of those factors. In this paper a new data treatment is proposed to characterize better these differences.

EXPERIMENTAL

X-RAY diffraction investigations at high temperature (20-1300°C) were carried out using an X-Ray generator Siemens K810. A high temperature camera Anton-Paar was attached to a diffractometer Siemens D500 (ref. 1). Powdered samples deposited on the platinum heating ribbon were submitted to a CuK_α radiation isolated by a graphite monochromator, in the range 2θ = 20-40°, with angular step 0.04 and count time 10s. Successive X-Ray analyses were carried out under normal atmosphere. Between each analyse, the temperature was raised - or lowered - at a given rate in steps of 90°C. (Fig. 1).

DATA HANDLING

Each isothermal spectra can be obtained, stored and analysed by means of programmes allowing the smoothing of experimental points, background reduction, peak searching and calculation of the peak intensities. An additive programme

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makes up differential spectra (DS) from two normed X-Ray spectra. The difference between the two spectra (DS) is just an horizontal straight line if two identical files are to be compared. In the contrary DS exhibits peaks with positive or negative intensities in respect to the first or the second spectra (Fig. 2a). When the spectra presents a slight variation in the angular position of one peak, a "double peak" appears on DS. The shift observed between the tops of the peaks corresponds to the angular variation (Fig. 2b).

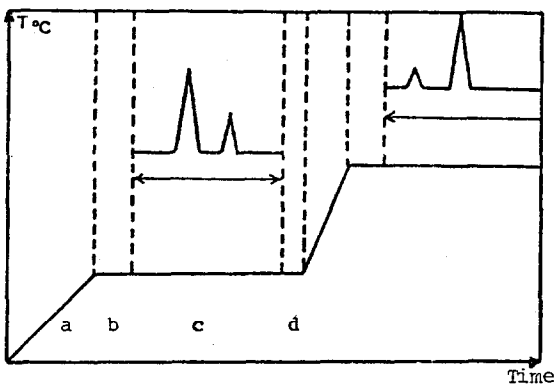

Fig. 1 Timing to obtain successive isothermal spectra a:heating, b:wait for isothermal conditions, c:spectra performed, d:storage

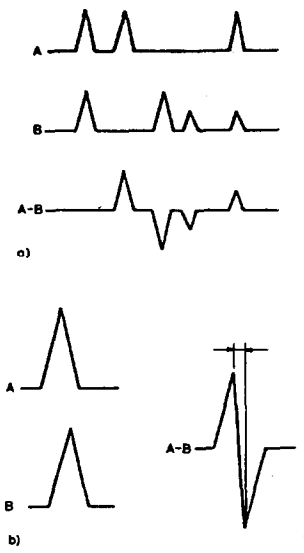

Fig. 2 Principle of D.S.

Spectra obtained after heating are called "C" followed with a number representing the temperature (°C). Rxxx will represent the file corresponding to a spectra obtained after cooling at xxx°C. The differential spectra C1100-R1100 is the file giving the difference between the spectra C1100 obtained after heating at 1100°C and the spectra R1100 obtained after cooling at 1100°C(from room temperature)

THE DXRD METHOD APPLIED TO THE STUDY OF SOLID-SOLID EQUILIBRIA IN THE SYSTEM $CaO-Na_2O-P_2O_5$

The phase diagram obtained by the study of solid-solid transitions in the system $Ca_3(PO_4)_2$-$CaNaPO_4$ (so called C_3P-R) has been drawn up (ref. 2,3,4,5). Differential and direct thermal analysis have been carried on to obtain the diagram of stable equilibria in the system after heating(-). At cooling, thermal analysis results make evidence of two metastable diagram M1(-•-•-) and M2(---).

- for low cooling rate ($v < 450°C.h^{-1}$), the mixture belongs to the stable diagram and then to its metastable continuation M1 ;
- at rapid cooling rate, mixture evolutions are described by M2.

This work is to show how simple and condensed informations supplied with DXRD

can confirms these results. The X-Ray diffraction study have been performed on one melt (composition 17% compound R), in the temperature range indicated on figures 3 and 5 including the most important reactions in the system : transitions between stable solid solution A and metastable A_{M_1} and A_{M_2}.

On the DS C1100-R1100 (Fig. 4) the angular shift between A_{M_1} (R1100) and A(C1100) can be explained by the change in the composition of the stable solid solution A (Fig. 3) which modifies the network parameters. Evidence of βC_3P with A in C1100, and $\alpha C_3P_{M_1}$ with A_{M_1} (R1100) gives a good support for the metastable diagram M_1 validity (-·-·-). The second metastable diagram M_2 (------) is confirmed (Fig. 5) by the last DS (Fig. 6) R_{M_1} 1050 - R_{M_2} 1050.

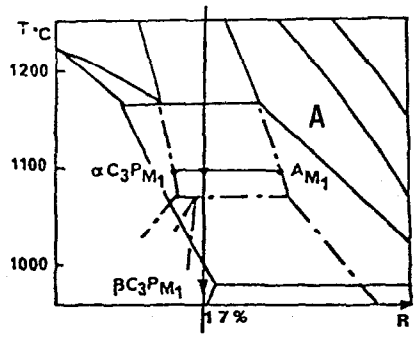

Fig. 3 Phase localization in the diagrams st. and M_1

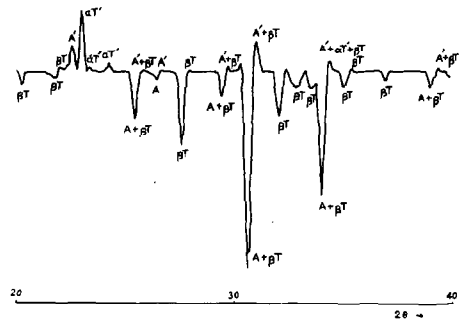

Fig. 4 C1100-R1100

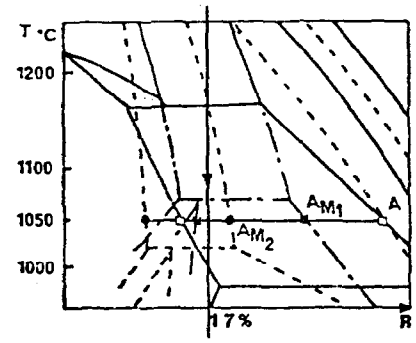

Fig. 5 Phase localization (diagrams M_1 and M_2)

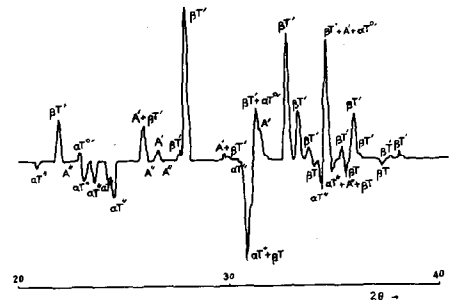

Fig. 6 R_{M_1} 1050-R_{M_2} 1050

CONCLUSION

Thermal analysis allowed us to set up the boundaries of domains where stable phases appear at heating and metastable phases exist at cooling. The corresponding diagram of phases in the system $Ca_3(PO_4)_2$-$CaNaPO_4$ had been drawn.

The characterization of the phases after well defined treatments (heating and cooling rate, highest temperature reached...) has been carried out by means of high temperature X-Ray diffraction experiments. Analyses of the spectra obtained with a new method : the differential X-Ray diffraction (DXRD) confirms the existence, the nature and conditions of formation of the stable and metastable phases A, αC_3P, βC_3P and αR (ref. 6).

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