STRUCTURAL MODIFICATION ON HEAT TREATMENT OF γ-MnO$_2$

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ABSTRACT

The change of structure of γ-MnO$_2$ was studied under heat treatment using neutron powder diffraction in vacuum between 25°C and 600°C and X-ray diffraction in air in the same temperature range. After heating either in air or under vacuum, the final product at 600°C is the well-known Mn$_2$O$_3$. The intermediate formation of the pyrolusite phase depends on the atmosphere in which the sample is heated. Its appearance is connected with the oxidation of the initial Mn(III) contained in γ-MnO$_2$ as MnOOH. Oxidation leads to the formation of β-MnO$_2$ localized as a thin layer on dehydrated γ-MnO$_2$.
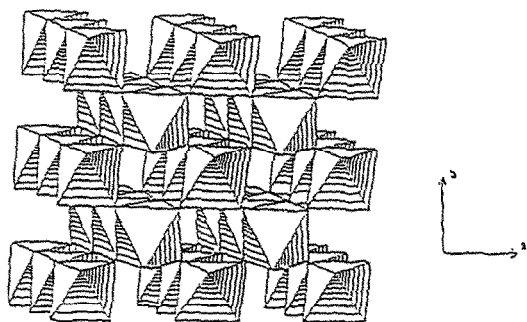
INTRODUCTION

About 20 oxides containing Mn(IV) are recognized and classified as natural minerals. Numerous synthetic isomorphs of each natural group were chemically precipitated and electrochemically deposited.

The basic framework of MnO$_2$ consists of edge-shared [MnO$_6$] octahedra with a corner-shared double chain. The different arrangements of the octahedra lead to different crystal structures, characterized by tunnel size (shown in Fig. 1).

The gamma group is the most attractive as a potential battery material. Its structure is usually recognized as an intergrowth of both ramsdellite (2 × 1 tunnels) and pyrolusite (1 × 1 tunnels) [1–3].

However, the high resolution transmission electronic microscopy results of Turner et al. [4] must be taken into account. Their results demonstrate that tunnels greater than (2 × 1) are observed together with structural defects (Fig. 2).
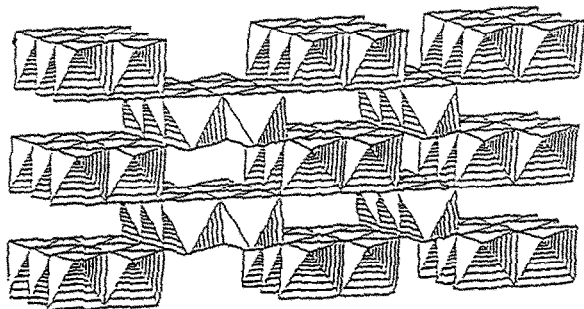
Until now, only X-ray powder diffraction (XRD) has been used to obtain structural information on γ-MnO$_2$. By combining XRD with heating mea-
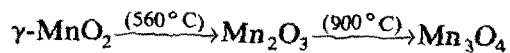
a
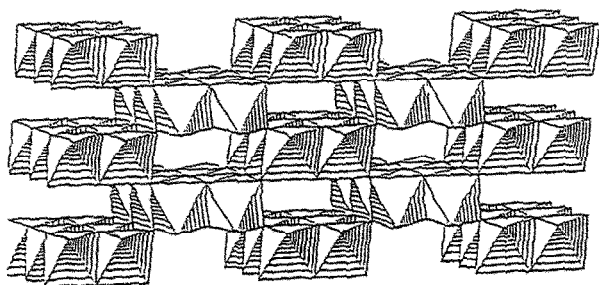
b

c

Fig. 1. Tunnel structures: *chain* of edge-shared MnO_6 octahedra for a, pyrolusite; b, ramsdellite; and c, gamma group.

surements, it has been established that increasing temperature leads to the transitions

$$\gamma\text{-}MnO_2 \xrightarrow{(560\,^\circ C)} Mn_2O_3 \xrightarrow{(900\,^\circ C)} Mn_3O_4$$

It was generally observed that the peaks typical of β-MnO_2 (rutile structure) intensified at 400 °C, before the Mn(IV)–Mn(III) transition, when

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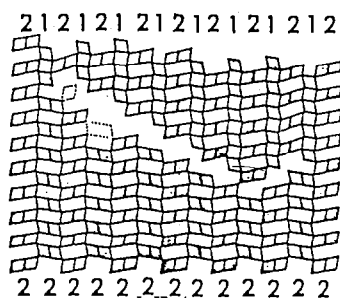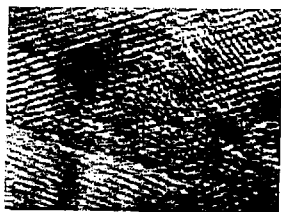
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Fig. 2. High resolution transmission electronic microscopic images obtained for nsutite mineral by Turner et al. [4].

the sample was heated in air [5–8,12,13]. It is generally agreed that this gamma–beta transformation corresponds to a phase transition connected with loss of water [12,13].

In the present work, structural studies on γ-MnO_2 using neutron powder diffraction (NPD) associated with heating the sample under vacuum are reported. The results are compared with those obtained by XRD performed while heating the sample in air.

EXPERIMENTAL

Industrial electrolytic manganese dioxide, deposited electrochemically, with specifications as reported in Table 1, was used as received.

XRD spectra were obtained on a Siemens X-ray diffractometer using Copper Kα radiation. NPD spectroscopy was carried out on the D1B

TABLE 1

Specifications of MnO_2 used

Type	Mn(IV) (%)	Total Mn (%)	Heavy metals (%)	Specific area (m^2 g^{-1})	Crystallo- graphic structure
Deposited on Ti anode	92	59	< 0.01	46	gamma

spectrometer of the Institut Laue–Langevin (ILL) at Grenoble using a wavelength of 2.61 nm.

The structural evolution was studied by heating the sample in air with simultaneous XRD spectra acquisition and by heating the sample under vacuum (10^{-5} mm Hg) during NRD spectra acquisition.

RESULTS

Figure 3 shows the XRD spectra of the γ-MnO$_2$ sample heated from ambient temperature up to 600°C in air. At 400°C the clearly defined pyrolusite structure is observed (Fig. 3c). Below this temperature the gamma structure is stable.

These transformations were also studied using NRD. The sample was heated under vacuum from ambient temperature up to 600°C. We can observe from Fig. 4 the following points.

(i) The heating begins with a notable dehydration detectable by a decrease in the background noise height without important modification of the structure (Fig. 4a, b).
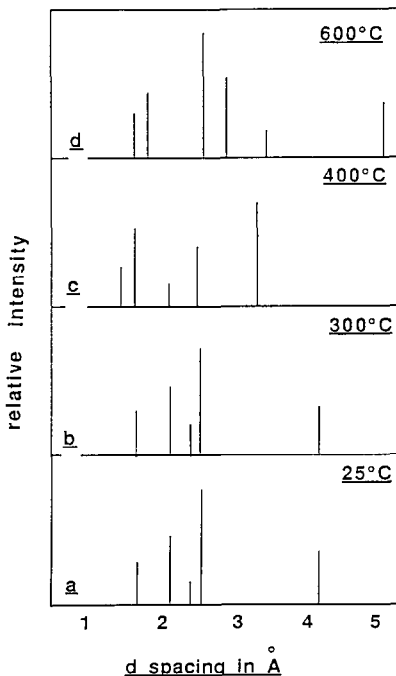

Fig. 3. XRD spectra of γ-MnO$_2$ at a, 25°C; b, 300°C; c, 400°C; and d, 600°C.

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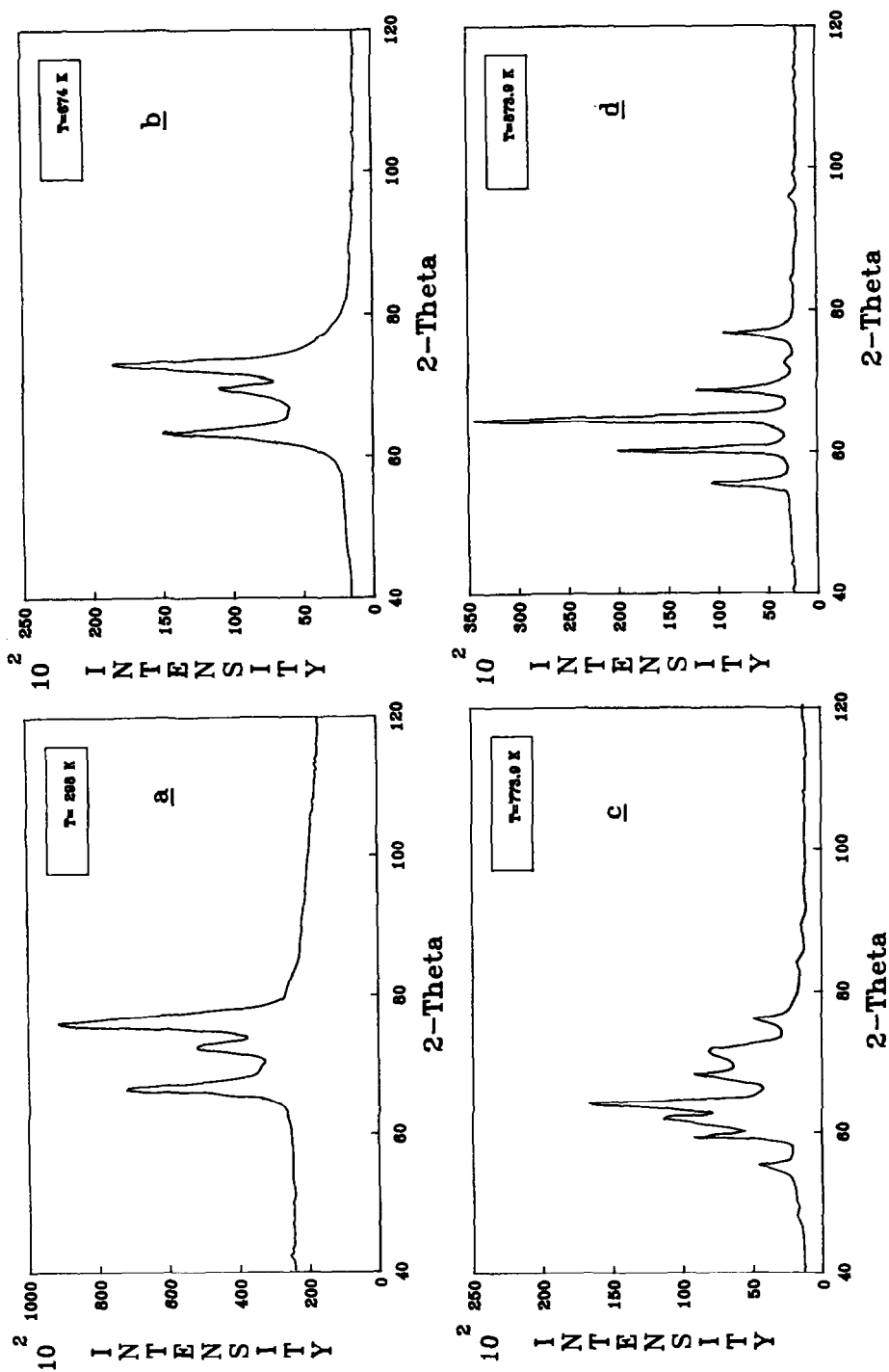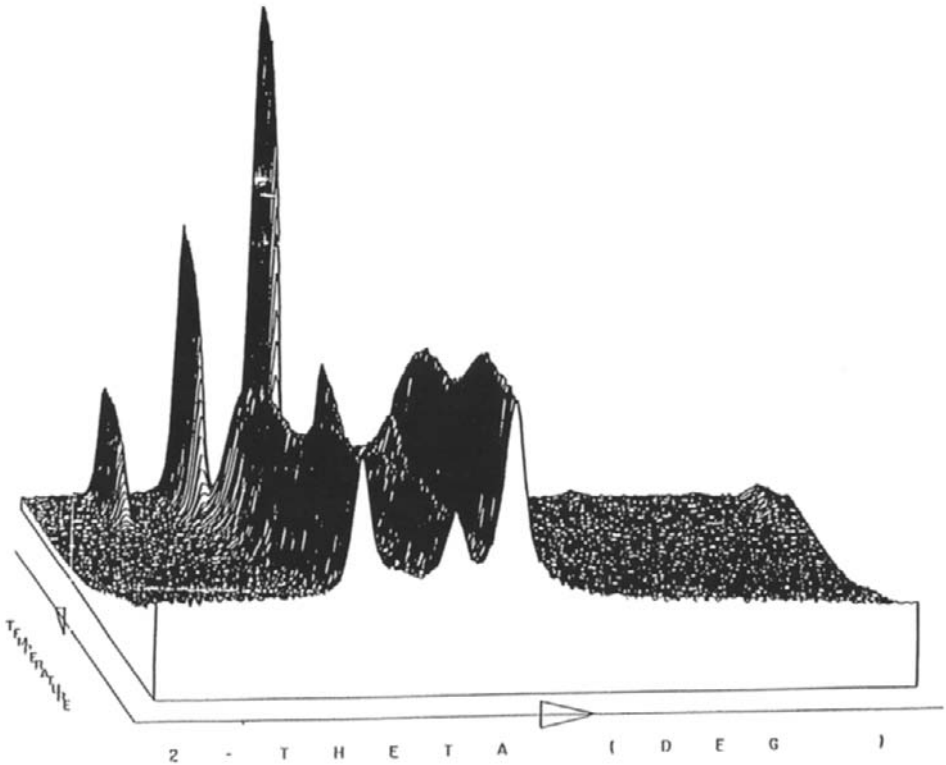Fig. 4. NPD spectra of γ-MnO₂, at a, 298 K; b, 674 K; c, 773.9 K; and d, 873.9 K.

Fig. 5. Three-dimensional NPD spectra between 25 and 650 °C for MnO_2 (the third axis represents temperature).

(ii) For higher temperatures, the structure evolves to yield a compound in which the Mn_2O_3 peaks are present together with the more intense peaks due to γ-MnO_2 (Fig. 4c).

(iii) Above 580 °C only Mn_2O_3 peaks are present.

We can see in Fig. 5 the global evolution of the NPD spectrum during heating. Figure 6 is drawn from the results of Fig. 5; the intensities of diffracted neutrons are transformed into contour lines showing the topography of the transformation. In Fig. 7, the peaks typical of β-MnO_2 are reported and compared with a theoretical plot of pyrolusite generated using a program running on a MicroVAX computer using a β-MnO_2 lattice parameter.

These observations can be summarized.

(i) Heating γ-MnO_2 in air leads to conversion to Mn_2O_3 via β-MnO_2, as confirmed by XRD results.

(ii) When heating γ-MnO_2 under vacuum, β-MnO_2 is not detected at 400 °C as it is when the sample is heated in air.
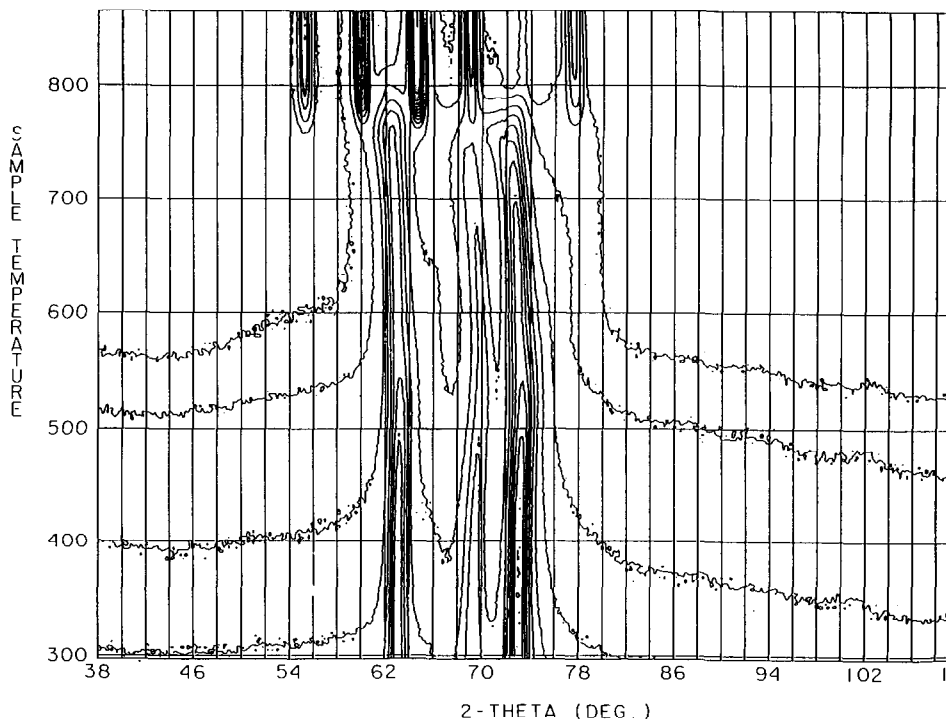
Fig. 6. Contour plot representation of Fig. 5.

DISCUSSION

Many authors have investigated the thermal behaviour of MnO_2 and its water content and have concluded that at $300\,°C$ all water has left the sample. We have explained γ-MnO_2 as a non-stoichiometric and hydrated oxide [9,10] and the thermal and thermogravimetric analysis leads to the following formalism

$$(1 - x)MnO_2, \ x(MnOO^-, H_3O^+), \ y(H_2O)$$

in which the total water is divided into "free molecular water" and water chemically bonded to the Mn(III) fraction, initially present in γ-MnO_2 and noted H_3O^+.
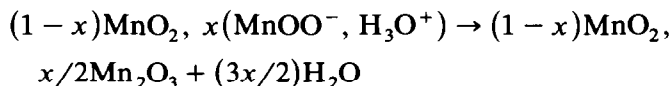
Connecting this formalism with XRD and NPD results allows us to suppose that heating the γ-dioxide leads to the following transformations.

(a) As reported previously [10]
$T < 250\,°C$
The $y \ H_2O$ molecules leave the sample.
$250 < T < 400\,°C$
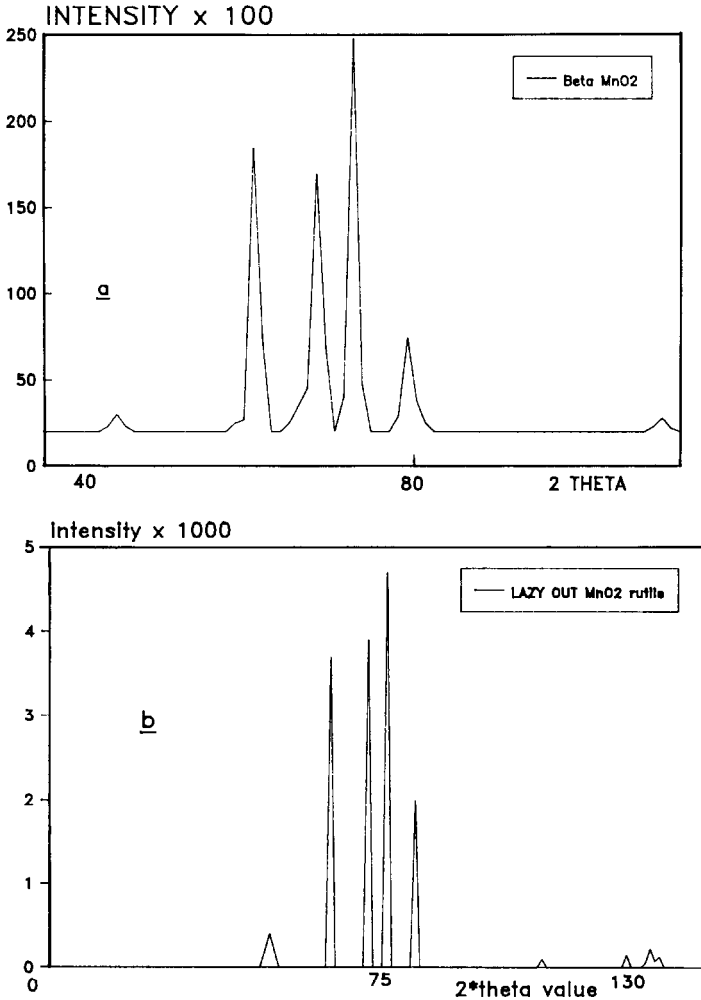
$$(1 - x)MnO_2, \ x(MnOO^-, H_3O^+) \to (1 - x)MnO_2,$$

$$x/2Mn_2O_3 + (3x/2)H_2O$$

Fig. 7. Experimental (a) and theoretical (b) NPD spectra of β-MnO_2.

and the remaining phases MnO_2–Mn_2O_3, although dehydrated, have the same structure as unheated γ-MnO_2 (Fig. 4a, 4b). These two dehydrations can only be explained by the results of Turner [4].

(b) We can now give more details for the other temperature ranges
$400\,^\circ C < T < 500\,^\circ C$
In vacuum no reaction occurs as observed by NRD, whereas in air, oxidation of Mn_2O_3 leads to MnO_2

$$x/2\ Mn_2O_3 + x/4\ O_2 \rightarrow x\ MnO_2$$
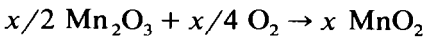
This oxide has a rutile structure as observed by XRD.
(c) $500\,^\circ C < T > 650\,^\circ C$

The sample is transformed into Mn_2O_3, detected by XRD as well as NRD:

$$(1 - x)MnO_2, x/2 \; Mn_2O_3 \rightarrow 1/2 \; Mn_2O_3 + (1 - x)/4 \; O_2$$

In conclusion we can say that β-MnO_2 detected just after reaching $400\,^{\circ}C$ when the sample is heated in air [12,13] is the product of the oxidation of Mn(III) initially present in the γ-structure. (This observation has been made by Matsuki and Kamada [11] who observed the XRD pattern of β-MnO_2 when MnOOH was heated in air.) As no typical β-MnO_2 peaks are observed by NPD at this temperature, this initial transformation does not correspond to a rearrangement connected with the loss of structural water [7].

Note that Mn_2O_3 resulting from the dehydration of $x(MnOO^-, H_3O^+)$ is not observed at $400\,^{\circ}C$ by either XRD or NRD. This means that at this temperature Mn_2O_3 does not form an individual phase: only heating in air can reveal it by oxidation as β-MnO_2. However, it must be kept in mind that the dehydrated γ-MnO_2 contains only about 8% Mn(III). Then this oxidation reaction cannot completely transform γ-MnO_2 to β-MnO_2. The total transformation of γ-MnO_2 to β-MnO_2 requires at least a few days at $400\,^{\circ}C$ in the presence of air. This method is usually used to prepare β-MnO_2 [14,15]. Because no transformation to β-MnO_2 is observed under vacuum, we may suppose that this transformation (which is for 92% a ramsdellite–pyrolusite transition) is made possible by the nucleating effect of the 8% β-MnO_2 produced by the oxidation of the initial Mn(III). The fact that the γ–β transition seems to be immediate and total at $400\,^{\circ}C$ when observed by
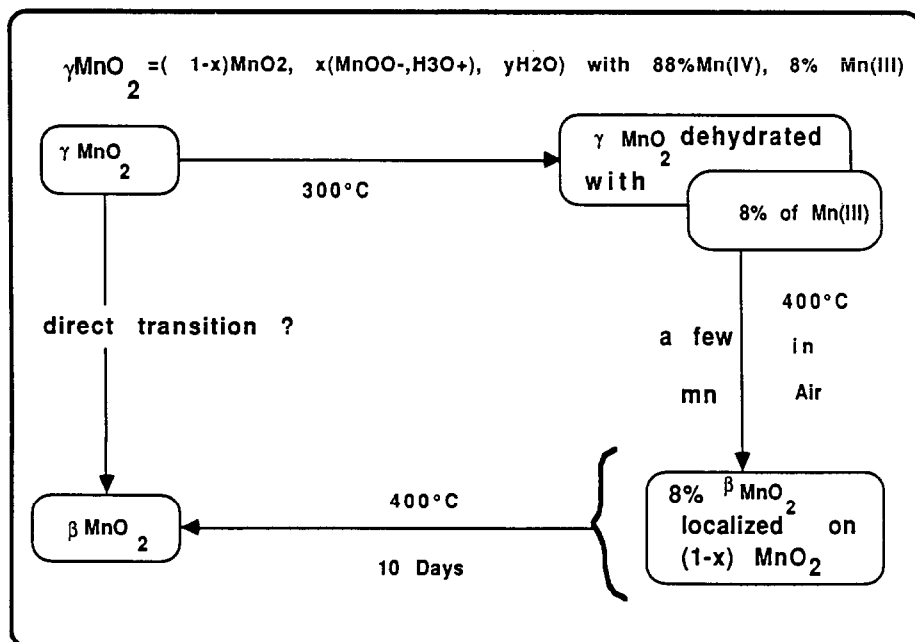
Scheme 1.
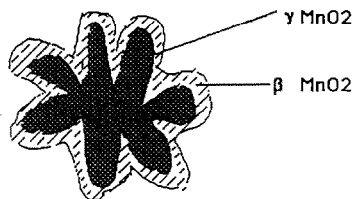
grain composition at 400°C in air

Fig. 8. Schematic diagram of the beginning of the gamma–beta transition at 400 °C in air.

XRD is a consequence of the technique, which is sensitive only to the surface layers: after a few minutes of heating the oxidation of Mn(III) is probably localized at the surface (Fig. 8), but it induces the $\gamma \rightarrow$ gb transition in the majority of the grains.

ACKNOWLEDGEMENTS

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