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X-RAY DIFFRACTION OF POLY CRYSTALLINE TITANIUM OXIDE

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Abstract

X-ray powder diffraction of poly crystalline and sintered Titanium Oxide is reported. The patterns show clearly two phases in both forms of the material. Its concentration was determined from the integrated intensity ratios of the plane (101) vs (101) the (121) vs (121)a nd the (206) vs. (208) lines of Ti_4O_7 vs Ti_5O_9, respectively. For samples taken from one batch, the powder form of specimen contains 45% of Ti_5O_9 while the sintered form contains about 65%. Samples from another batch, prepared under improve process control showed 35% of Ti_5O_9 in the powder form of the material. Both forms contain small traces of some other phases as well, e.g., Ti_3O_3 in the powder form Ti_6O_{11} in the sintered material.

Introduction

The class of rutile derived materials belonging to the homologous series Ti_nO_{2n-1} (so-called Magneli phases) and in particular $_4Ti_7O$, have attracted much attention due to many interesting transport and magnetic properties and to various metal-semiconductor phase transitions (1). Potential applications such as stable electrode materials for fuel cells and electrolysis are also of much interest. Investigation with these materials (e.g., Optical studies) have to some extent been limited by the small size an availability of single crystals. Recently, polycrystalline sintered plates and powder of Ti_4O_7 prepared presumably by a process of hydrogen reduction of rutile (TiO_2), have become commercially available. However, ESR measurement on this material by Polock et al (2) showed a line -width broadening of about 80% in the g=1.762 line, indicative of the possible coexistence of several Magneli phases in this material. They suggested that commercially available titanium oxide consists of Ti_4O_7. Ti_5O_7. Ti_5O_9 and Ti_6O_{11} all of which have longer broader ESR line width. In this report we report X-ray powder diffraction measurements on commercially available titanium oxide. The results clearly indicate coexistence of two Magneli phases, the majority of which consists of Ti_4O_7 while the other is Ti_5O_9.

Experimental Results

The x-ray powder diffraction measurement were performed using conventional techniques. The as-obtained fine powder (P-A) was applied onto a glass

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micro slide forming a smooth non-reflecting layer. Sintered samples (S-B) ground into a fine powder and resulting in a smooth layer similar to the (P-A) sample were also used. The starting material was obtained from two different batches, hereafter referred to as I and II (the later considered on a higher quality reduction process control). The X-ray set-up consisted of Ni filtered Cu target, 0.5^{o} divergence slit and a 0.1mm wide receiving slit. The pattern, which consisted of a scan in the angular range $13^{o}<2\theta<55^{o}$, was obtained in a continuous run. The intensities of the lines used in the concentration determinations were obtained in a step-scan using step-size of 0.01^{o}, a time constant of 4 seconds and a dwell time of 20 seconds / step. We obtained all resolvable lines for Ti_4O_7 in the angular rage $42^{o}<2\theta<55^{o}$. In addition, we obtained lines which could not be associated with those of Ti_4O_7. Some of these lines probably overlapped those of Ti_4O_7, yielding an apparent broadening or odd looking line shape. However, 3 pairs of lines, located close to $2\theta = 21.5^{o}$, 29^{o} and 34^{o}, respectively, could be resolved quite easily with one member in each pair identified from the appropriate ASTM card as corresponding to a Ti_5O_9 lines were clearly bigger in (S-B) than in (P-A). The spectra of both forms of the material differed also in the content of other phases. For instance, (P-A) had a small peak at $2\theta = 25.15^{o}$ corresponding probably to the strongest line of Ti_3O_5, and indicative of the existence of this phase in small amounts. on the other hand (S-B) which did not show this line, showed another small peak at $2\theta = 22.7^{o}$ corresponding probably to a strong line of Ti_5O_{11}.

A representative line intensity of the pairs mentioned above is shown in figure 1 for sample 1. Their identifications in terms of the co-ordinate system of the ASTM card are also shown. The integrated intensities were obtained either from the area below the curves or from the count printout available from the diffractometer. The former had to be used in those cases where the lines were not completely separable. Their approximate line shape, obtained by visual separation, is also indicate in the figure. The results for the integrated intensities are given in Table 1. The indicated errors reflect differences among step-scans taken under the same conditions and yield reproducibility of 0.2% in integrated intensity.

Discussion and Conclusion

The atomic-or, more accurately, the molecular-fraction (N) of Ti_5O_9 in powder specimen could be determine from integrated intensity (P^1) ratio of the corresponding lines, from the unit-cell volume (v) and from the triclinic structure factors (F) according to the equation (3).

$$\frac{N_{59}}{N_{47}} = \frac{P^1_{59}}{P^1_{47}} \frac{V_{59}}{V_{47}} \frac{F^2_{47}}{F^2_{59}} \frac{LP(\theta_{47})}{LP(\theta_{59})}$$

Where, $LP(\theta) = \frac{1 + \cos^2(2\theta)}{\sin(2\theta)\sin(\theta)}$

is the Lorentz-polarization factor. Both V and F^2 were calculated using Strobed's unit-cell. The transformation matrices from the ASTM notation to this co-ordinate system are given in the appendix. The primitive volume was determine from the unit-cell dimensions, for n=5 their unit cell is primitive shell, for n=4 it is body centred. Thus, V_{47} = 485 A^3 and V_{59} = 580 A^3. The structure factors were determined ignoring contributions from the Debye-Waller factor, by linearly interpolating the atomic scattering factors (4), and by using weighing factor and the actual atomic co-ordinates of the various Ti and O atoms. Thus, the molecular-fraction ratio is determined and ignoring the small contribution from the other phases, it yields the absolute fraction of unit cells. The results are summarised in Table 1. It was concluded that for sample of the first batch, the powder material contains 30% of Ti_5O_9 (i.e., about 1/4 of the unit cells corresponds to this phase), while the sintered material contains more than 50% of Ti_5O_9. These results agree with the quantitative ESR results (6). Evidently, the manufacturer was able to improve the process control since the second batch of P-A II contained only 10% Ti_5O_9. No sintered material was available from the second batch.

During the course of the measurements some changes were observed in the patterns, particularly in S-B. These corresponds to changes in the intensity ratios in each of the line pairs. For instance, there were intensity changes in two specimens that have been crushed to powder, one several months after the other (i.e. the older sample aged). Likewise changes have also been observed between measurements taken on a freshly crushed specimen and those taken a few weeks later. the trend of these variations as observed in most cases seems to be an oxidation effect, as the Ti_5O_9 to Ti_9O_7 intensity ratio increased i.e. yielding in some cases a molecular fraction of Ti_5O_9 in excess of 60%. In one case, however, this ratio decreased. Since the interpretation of these trends is not unambiguous, more studies concerning the nature of oxidation and other aging effects in both bulk and powder forms will be required in considering the stability of these electrode materials.

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Appendix

The two coordinate systems used in this paper are that LePage and Strobed (P) and that of Anderson nd Jahnberg (A). The transformation of the unit cell in real space is given in ref. (5).

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix}_P = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 2_{n-5} & n-2 & q \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}_A$$

where q=1 for n even and 2 for n odd. This imemdiately yields $Vp = V_A$ for even n and $Vp = 2V_A$ for odd n. The transformation matrix in reciprocal space is found from the above.

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} = 1/q \begin{bmatrix} q & 0 & -(2n-5) \\ 0 & q & -(n-2) \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The correspondence Miller indicates are obtained from the transpose inverse of this matrix, that is.

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}_P = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 2_{n-5} & n-2 & q \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}_A$$

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TABLE - 1

LINE IDENTIFICATION, STRUCTURE FACTOR AND INTEGRATED INTENSITY USED IN THE DETERMINATION OF MOLECULAR FRACTION

Phase	2θ Deg.	LP		(hkl) P	F^2	BATCH 1								Batch II			
						P-A				S-B				P-A			
						P^1		N,%		P^1		N,%		P^1		N,%	
						COUNTS	CHART	CTS.	CH.	CTS.	CH.	CTS.	CH.	Cts.	Ch.	Cts.	C
Ti_4O_7	20.00	29.00	(102)	(101)	3140	119.775	(1023)	75.8	(77.8)	31.835	(143)	46.0	(49.0)	135,765		90.5	
Ti_5O_9	21.00	25.74	(102)	(101)	5140	± 170		± 0.2						15.726		9.1	
						43.175	(342)	24.2	(22.8)	41,460	(166)	53.0	(50.0)				
						± 105		± 0.2									
Ti_4O_7	28.00	13.00	(122)	(122)	6880	104,635	(380)	73.5	(71)						(60.4)	(90)	
Ti_5O_9	27.00	15.48	(121)	(121)	11070	53,265	(220)	26.5	(29)						(94)	(9.9)	
Ti_4O_7	34.00	10.00	(200)	(206)	8550		(333)		(71)		(245)		(49)				
Ti_5O_9	33.43	0.974	(201)	(208)	11170		(147)		(29)		(280)		(51)				

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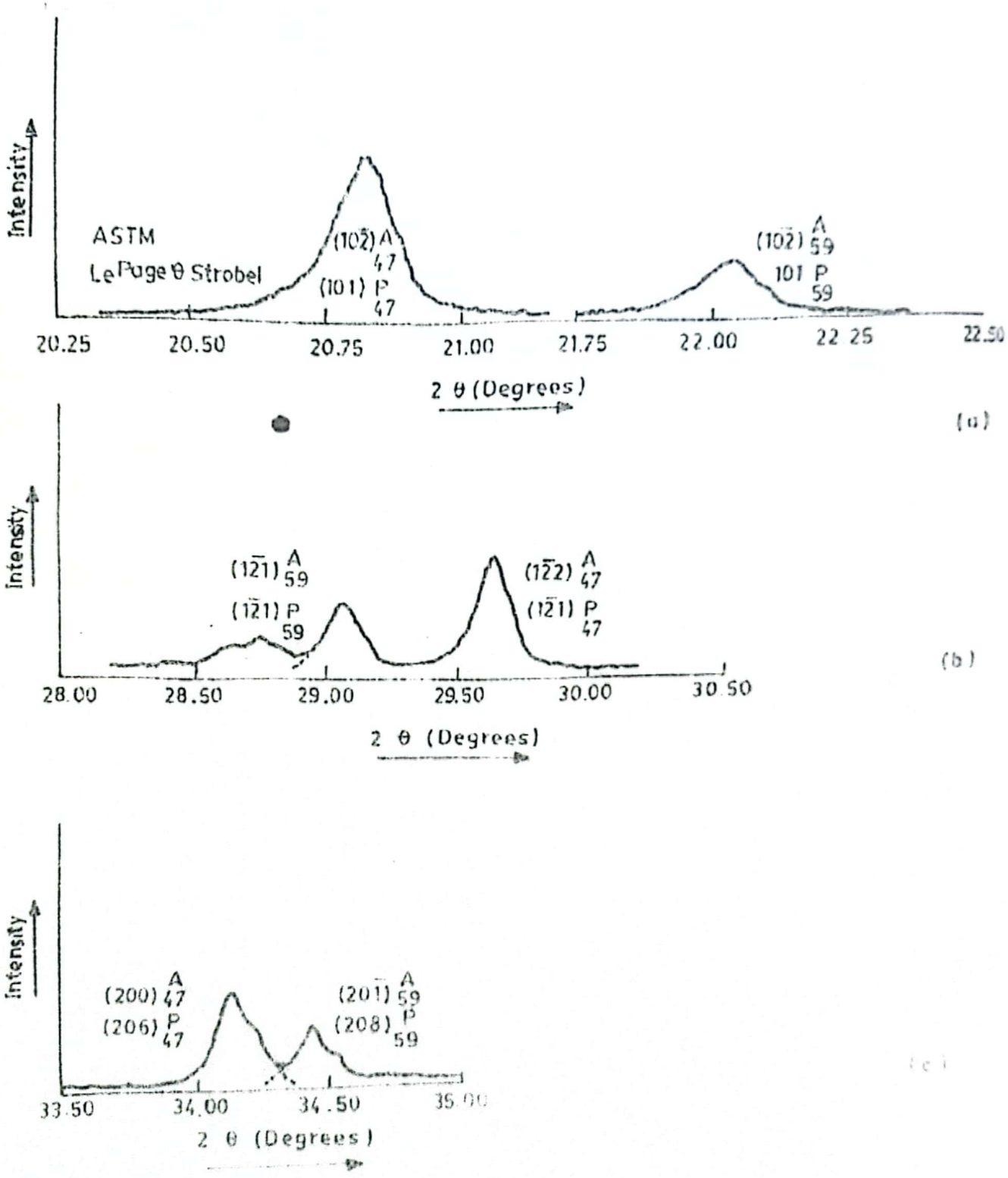


Fig. 1. Line shapes used to determine the integrated intensities