Determination of crystallite size and strain values by fourier method for α - Al_2O_3

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Abstract

The sintering of Al(OH)3 powder for 2 hours each run in the temperature range 1673 K to 1873 K gives rise to the following crystallization sequence:

$$\gamma\text{-}Al_2O_3 \longrightarrow \gamma+\theta\text{-}Al_2O_3 \longrightarrow \theta+\alpha\text{-}Al_2O_3 \longrightarrow \alpha\text{-}Al_2O_3$$

The crystallographic structures of the above products are assessed by x-ray diffraction method . The variation of crystallite size and root mean square (rms) strains in α- Al_2O_3 powder with sintering the temperature range 1673 K to 1873 K are studied by applying Fourier method using Mitra & Misra technique for 3 crystallographic reflections (104),(113) and (116).The results show that the lower temperature α - Al_2O_3(1673 K) derived from $Al(OH)_3$produces lower crystallite size and higher rms strain .

On the other hand ,rms strain decreases with increasing the temperature to 1873K and the differences between the broadening of the above reflections are decreased. Thus, the anisotropy is reduced at higher temperature of sintering (1873K).Lower temperature sintering (1673 K) of $Al(OH)_3$ yield α - Al_2O_3 compacts of higher value of micro hardness number 884 and this value drops to 731 at 1873 K .

Introduction

The structural relations between many crystalline forms of aluminum oxide and hydroxide are exceptional scientific interests and immense technological importance.

α - Al_2O_3 occurs as the mineral corundum (the density ρ = 3.97 $gm.Cm^{-3}$) because of its chemical inertness and good electrical insulating properties, it finds many applications in abrasives

(including tooth paste),refractory and ceramics, in addition to its major use in the electrolytic production of Al metal .Larger crystals when colored with metal-ion impurities .are prized as gemstones,e.g.ruby (Cr^{III} red),sapphire ($Fe^{II/III}$,Ti^{IV} blue ,F^{III} yellow)…..etc.[1] . α - Al_2O_3 is used also as the protective surface layer on the metal. Perhaps the most ingenious and sophisticated development in aluminum technology has been the rest production of Al_2O_3 fibrous which can be fabricated of textile forms:blankets,papers,boards(2).

The thermal analysis of gibbsite [ɣ-Al(OH)$_3$],diaspore[α - AlOOH]and boehmites [AlOOH] have been studied by a number of authors (3-5).ASSIA et al (5) have used Raman and IR spectra to identify α - Al_2O_3 phase obtained from heat –treated of pseudo boehmite [ɣ & α - AlOOH] gel at 1473 K.

A detailed knowledge of crystallite size ,shape and strain in a finely divided powder is required in many fields of materials science .For example .this information is of a fundamental importance in the studies of catalysts or as aid to understanding thermal decomposition and other solid state reactions(6-8).As is well known, an analysis of X-ray diffraction broadening provides a non-destructive method for obtaining the crystallite size and strains.Additionally,if the lines of the pattern are well resolved ,the mean size can be ascertained in different crystallographic directions (9-11).

Throughout this work "crystallite" implies a region over which diffraction is coherent which is normally less than or equal to the volume of the crystal (if it is an individual)or a"grain"if it is composed of one or more crystals .A distinction between crystallite size and "particle size" is important if sizes obtained from diffraction broadening are to be compared with those given by other methods .This crystallite size is preferred ,since individual particle may contains several crystallites, or domains having different orientations.

Apparently and to the best of our knowledge, this work presents for the first time the determination of the crystallite size and rms strain in α - Al_2O_3 powder derived from the thermal decomposition of Al(OH)$_3$ powder for 2 hours at calcinations temperature of 1673 K,1773 K and 1873 K.

Theoretical Consideration

Determination of crystallite size and strain by the method of Mitra & Misra (12)

The Fourier coefficients for pure diffraction line profile (A_L) for each reflection can be determined as:

$$A_L = \sum_{-n}^{+n} f(x)\cos\frac{2\pi nx}{a} \quad \text{.....[1]}$$

where f(x)is the pure diffraction profile which can be expressed as a Fourier series (13).It is well known that (14).

$$A_L = A_L^e . A_L^{l'} \quad \text{.....[2]}$$

Where

$A_L^{l'}$ = nth order Fourier cosine coefficient of the crystallite size line profile .

A_L^e = Fourier cosine coefficient of the line profile due to strain(e) only corresponding to A_L and $A_L^{l'}$,and also :

$$A_L^e = \exp(-2\pi^2 l^2 L^2 \langle e^2 \rangle / d^2) \quad \text{.....[3]}$$

Where

l=order of the reflection =1

$< e^2 >$ =root mean square (r.m.s)strain in the direction normal to the reflecting plane .

L=nd=a real distance in the crystallite ,d is the interplaner spacing and is given by:

$2d(\sin\theta_1 - \sin\theta_0)/\lambda = 2d(\sin\theta_0 - \sin\theta_2)/\lambda = 1/2$ ...[4]

θ_0 is the Bragg angle corresponding to peak position of the intensity distribution .

θ_1 and θ_2 are the Bragg angle corresponding to peak position of the intensity distribution where the tails merge into background.

λ is the wavelength =0.154 nm

P is the size of the crystallite in the direction considered .

The size of the crystallite on the basis of the Gaussian strain distribution hypothesis can be given by the following equation (15):

$$\left\{\frac{dA_L}{dL}\right\}_{L=0} = \left\{\frac{dA_L^{l'}}{dL}\right\}_{L=0} = -\frac{1}{P} \quad \text{.....[5]}$$

In this work, P is determined by drawing a tangent to the (A_L-L) curve at L=0.

As the multiple order reflections are not available root mean square strains were calculated following Mitra & Misra (13) technique by combining[2] and[3] we have :

$Ln2\pi^2 l^2 L^2 \langle e^2 \rangle / d^2$ .....[6]

Where

$$A_L^P = 1 - \frac{L}{P} \text{.....[7]}$$

If "e" is dependent on L, then for a given value of L.the plot of Ln (A_L / A_L^P) against L^2 will be a curve and "e" can be determined from the slope of the curve at L=0.If, on the other hand, "e" is independent of L,the plot will be a straight line passing through the origin ,and the slope of the line will give an estimate of "e" .

Vicker's Micro hardness Test

The hardness test rely upon the slow application of a fixed load to indenter that is forced into the smooth surface of the specimen. Upon removal of the load the depth of penetration is measured as an indication of resistance to the load.Micro hardness testers are commonly used to measure the hardness of individual metallic grains and constituents of alloys.Vicker's hardness test has a fairly continuous scale of hardness (Vicker's hardness number of 5-1500).In Vickers's test a diamond cut of square pyramid having an apex angle of 136°. The Vickers's hardness number (VHN) is defined as the load divided by the surface area of the impression (16).

$$VHN = \frac{Force}{Area} = \frac{2M \sin(\alpha/2)}{Y^2}$$

$$= 1.854 \frac{M}{Y^2} \text{.....[8]}$$

Where :

M=Load applied in Kg .

Y=Length of the diagonal in nm.

α =Angle between opposite faces of pyramid (equal to 136°)

Experimental Considerations

The α -Al_2O_3 powder is obtained from the thermal decomposition of $Al(OH)_3$ AT 1673 K,1773 K,and 1873 K.The sintering time is chosen at2 hours for each run .One gram of $Al(OH)_3$ is placed in an

alumna crucible and the decomposition is performed in static air using thermal furnace incorporated with programmable control and thermocouple type K.This furnace can reach 2273 K and has an accuracy ±5 °C up to 1773K.

A Philips automatic powder diffract meter (PW1820) with flat monochromatic for K line and low background, step rate 0.02° /1.0 sec. Receiving slit 0.2° ,irradiated area 12mm^2 and scan range 10-120° was used to study the broadening of line profiles .The standard was SiO_2 of 99.999% purity supplied by Koch light Ltd. Package allows the selection of conditions for recording the diffraction pattern in addition to the necessary treatment on the scanned peaks such as smoothing, zooming etc.Three well isolated pecks(104),(113) and (116) were used for this study. Correction for instrumental broadening was carried out with Stokes (7)method. Fourier coefficients were calculated by using a personal computer .

Compacts of α -Al_2O_3 derived from thermal sintering of $Al(OH)_3$ at 1673 K,1773K and 1873K,were prepared by pressing powders under 5 tons force using hydraulic press. The thickness and radius of each compact were 100 mm and 50 mm respectively .The test is performed by placing the compact on the anvil and raised till it is close to the indenter point. The load M of 100 gm.Then gradually applied to the indenter and then removed .The diagonal of the square indentation Y is measured to 0.001 mm length by the micrometer eye piece.VHN was calculated in this work by using equation 8.

Results and Discussion

X-ray diffraction spectra

Figure 1(a-j)shows the powder X-ray diffraction (XRD) spectra for the reactant powder $Al(OH)_3$before (fig.1a)and after thermal decomposition at temperature range from 673 K to 1873 K . for two hours .

These spectra indicate that the calcinations of $Al(OH)_3$at the above range give rise to the following crystallization sequence :

$$Al(OH)_3 \longrightarrow \gamma\text{-}Al_2O_3 \longrightarrow \gamma+\theta\text{-}Al_2C_3 \longrightarrow \theta+\alpha\text{ -}Al_2O_3 \longrightarrow \alpha\text{ -}Al_2O_3$$

The temperature range of stability of the various transition alumnus has been determined by using the above X-ray patterns and listed in table 1.0.

The above results confirm the following points:

i) The composition of the reactant material which is $Al(OH)_3$ has Triclinic structures after matching the four lines of the JCPDS card no.24-6.fig.1(a).

ii) γ -Al_2O_3 is stable within a temperature range from 1073 K to 1173 K.

iii) The pure α -Al_2O_3 is obtained after sintering at temperature $\geq$ 1673 K with a Trigonal structure after matching the five lines [(104,(110),(113),(024),and (116)] with the lines of the JCPDS card no. 10-173

iv) fig.1.0(h-g).

v) The decomposition temperature has a significant effect on the height and sharpness of the peaks. As the temperature of decomposition increased up to 1873 K the height of the above lines increased (fig.1.0(I-j)].

F.W.H.M

Figure 2 shows the variation of FWHM with sintering temperature of three selected line profiles 104,113 and 116.These are chosen on the basis of their high intensity which allows an accurate determination of the broadening parameters. This figure shows that the curves have the same behavior which decrease with temperature up to 1873 K.It is apparent that the temperature of sintering hasa significant effect on the FWHM specially above 1673K when the conversion is at its beginning .

Fourier Analysis

Figure 3(a-c) shows the plots of A_L against L in α -Al_2O_3 at 1673 K,1773K and 1873 K for (104),(113) and(116) reflections, respectively .The crystallite size are determined from the initial slopes of the curves A_L-L .For example,at1673 K for (104) reflection is calculated as (-1.0/38) and by using equation 7,P is obtained as 38 nm.and the results are listed in table 2.

The crystallite sizes P at the above temperatures for the 3 reflections were determined by using the above step and the results are listed in table2.

Figure 4(a-c) shows the plot of $Ln\frac{A_L}{A_S^P}$ against L^2 for 104,113 and 116 reflections at 1673 K,1773Kand 1873K on the basis of the Gaussian strain –distribution hypothesis .The r.m.s. strain values are obtained from the slope of these curves at L=0 .

For example the initial slope of $\ln(A_L / A_L^P)$ Vs.L^2 at 1673 K for (104) is calculated as:
$1.9375/6.5*10^2 - 2.9807 * 10^{-3}$ and by using equation 6:
$\langle e^2 \rangle^{1/2} = 3.04*10^{-3}$
$\langle e^2 \rangle^{1/2}$ for the all –3 reflections and at the 1673 K,1773Kand1873K were calculated by the above step ,and listed in table 2.

The previously mentioned above results suggested that the(A_L-$L_)$ curves of 104,113 and 116 reflections in α -Al_2O_3 obtained at 1673 K,1773Kand1873K look different .This means that there is an amount of distortion in directions perpendicular to the previous reflections. Moreover, as the temperature of calcinations increases from 1673K to 1873 K, the crystallite size increases progressively for the above three reflections simultaneously and the broadening between 104 and the other two reflections becom smaller which leads to larger crystallite size. Whereas inverse behavior is observed for r.m.s.strain,(see table 2).The increase of calcinations temperature induces a development of a texture with an increase of the crystallite size .This reordering allows a subsequent relief of the strain and then these samples exhibited a decreasing value of r.m.s.strain .

Vickers's Hardness Number of α -Al_2O_3

The calculated values of Vickers's hardness number (VHN)of α -Al_2O_3 at the end of each calculations run are obtained by using equation (8) and listed in table 3.

Conclusions

1. The pure and stable α-Al_2O_3 phase is derived at temperature ≥ 1673K.
2. The size of crystallites perpendicular to the (104) plan is smaller than these perpendicular to the (113) and (116) planes
3. The growth of crystallites is developed for the three crystallographic directions simultaneously and the differences between the broadening of these reflections decrease with increasing the calcinations temperature.

Thus, the anisotropy is reduced by high temperature of calcinations .

4.An inverse relationship is observed between crystallite size and r.m.s.strain for α-Al_2O_3 at different temperatures.

5. The resistance of α-Al_2O_3 samples against penetration is decreased with increasing the calcinations temperature from 1673 K to 1873 K .Thus VHN is decreased from 884 to 731 .

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Table (1): Temperature range of the various transition alumnu after thermal decomposition of $Al(OH)_3$ at different temperatures.

Temperature (K)	Phases
R.T.=300	$Al(OH)_3$
1073-1173	γ -Al_2O_3
1273-1473	$\gamma+\theta$ -Al_2O_3
1573	$\theta+\alpha$ -Al_2O_3
1673-1873	α -Al_2O_3

Table (2): Crystallite size and r.m.s strain as calculated by Fourier analysis for α -Al_2O_3 yielded from thermal decomposition of $Al(OH_3)$ at 1673,1773Kand 1873K.

Reflection hk1	Temperature (K)	Crystallite size (nm)	r.m.s.strain $*10^{-3}$
104	1673	38	3.04
	1773	52	2.66
	1873	68	2.55
113	1673	43	2.60
	1773	60	2.30
	1873	72	2.16
116	1673	47	1.58
	1773	63	1.25
	1873	73	1.14

Table (3): Vickers's Hardness Number of α -Al_2O_3 Derived from $Al(OH)_3$ at 1673 K, 773K and 1873K.

Temperature (K)	Y(nm)	VHN	Mean VHN
1673	14.0	946	884
	15.0	824	
	14.5	882	
1773	16.0	742	779
	15.5	771	
	15.0	824	
1873	16.0	680	731
	15.5	771	
	16.0	741	

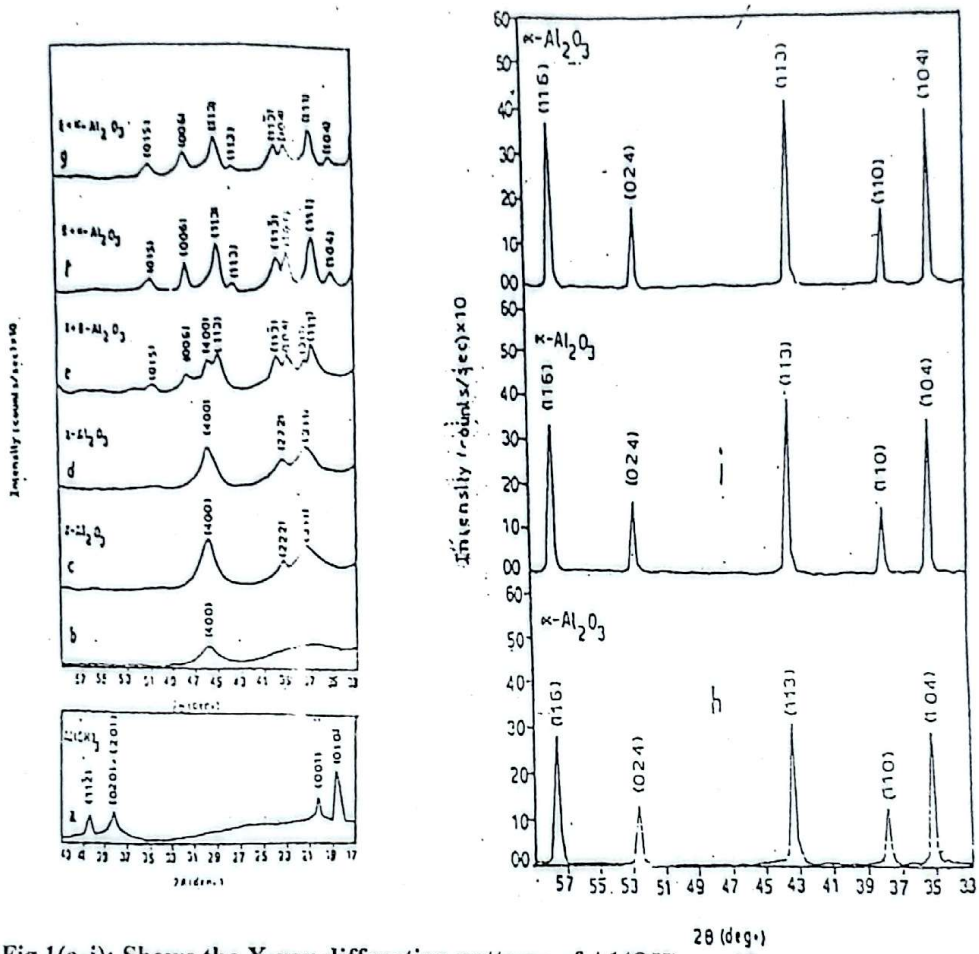

Fig.1(a-j): Shows the X-ray diffraction patterns of $Al(OH)_3$ at 27 °C(a),(b-d) γ-Al_2O_3, (e), $\gamma+\theta$-Al_2O_3, (f,g) $\theta+\alpha$-Al_2O_3 and (h-j) α-Al_2O_3 .

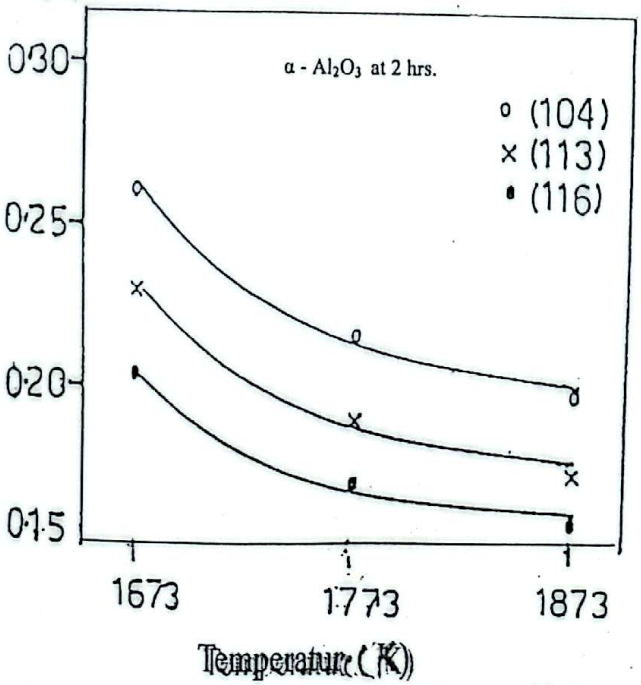

Fig. (2): Variation of FWHM with decomposition temperature of α-Al_2O_3.

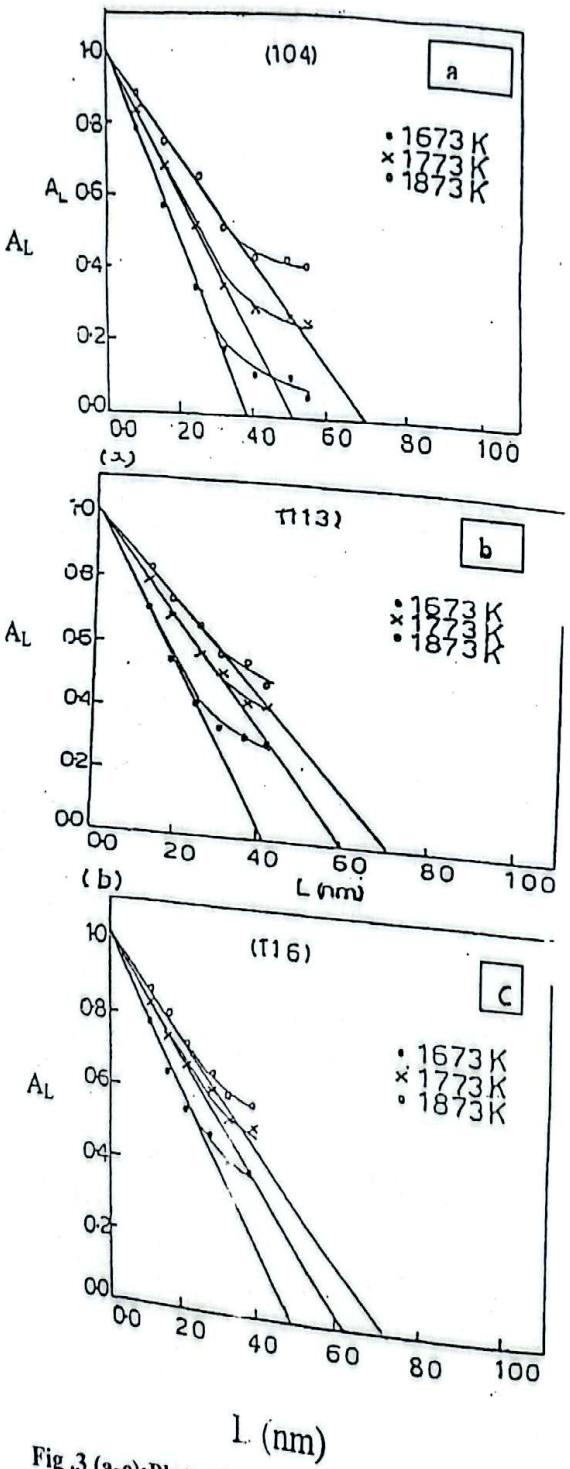

Fig .3 (a-c):Plots of A_L vs . L in α-Al_2O_3 obtained at 1673 K,1773K for reflections (104),(113) and (116).

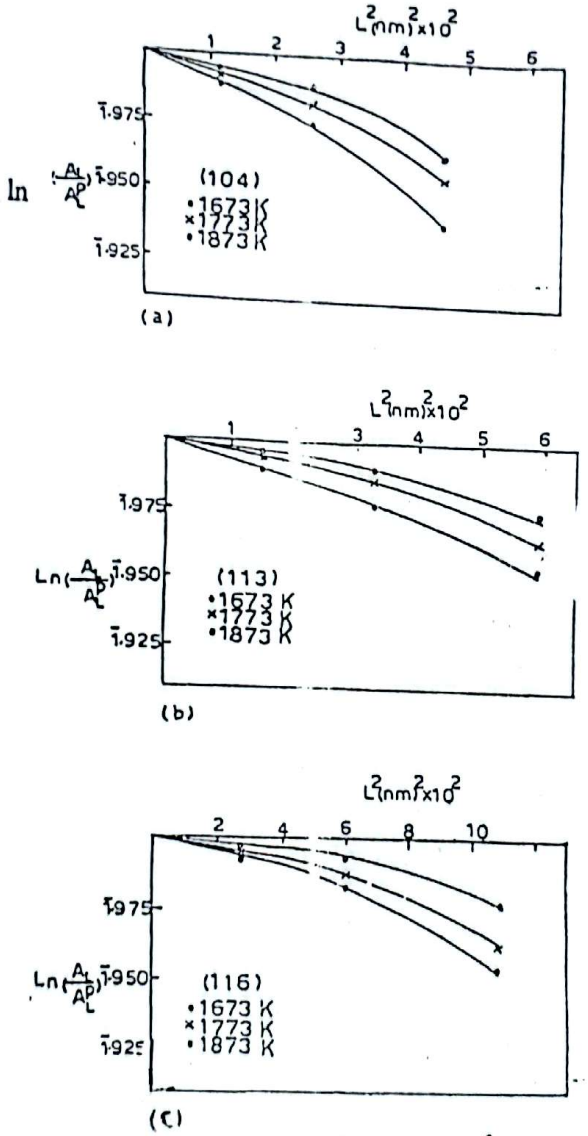

Fig. 4 (a-c):Plots of In ($A_L^I A_L^P$) against L^2 in α-Al_2O obtained at 1673 K,1773K and 1873 for (104),(113) and (116) respectively .

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تعيين مقاس الحبيبة ومقادير الانفعال بطريقة فوريرلـ α-Al_2O_3

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الخلاصة

انتج تحميص مسحوق Al(OH) في مدى درجات الحرارة من 1673 K الى 1873 K لمدة ساعتين في كل درجة تحميص تسلسل التبلورات الاتية :

$$\text{لا-}Al_2O_3 \longrightarrow \text{لا}+\theta\text{-}Al_2O_3 \longrightarrow \theta+\alpha\text{-}Al_2O_3 \longrightarrow \alpha\text{-}Al_2O_3$$

جرى تقييم التراكيب البلورية للمنتجات في اعلاه بطريقة حيود الاشعة السينية ودرس تغير مقاس الحبيبة وجذر متوسط مربع الانفعال لمسحوق α-Al_2O_3 مع درجة حرارة التحميص ضمن المدى من 1673 K الى 1873 بتطبيق طريقة فورير واستخدام تقنية Mitra و Misra للانعكاسات البلورية الثلاث (104) و(113) و(116).

بينت النتائج عند درجة حرارة التحميص الاقل (1673) لـلمركب $Al(OH)_3$ الحصول على مقاس اصغر لحبيبة α-Al_2O_3 ومقدار اعلى لجذر متوسط مربع الانفعال. ومن ناحية اخرى يقل جذر متوسط مربع الانفعال بزيادة درجة الحرارة الى 1873 K ويقل الفرق في عرض الانعكاسات البلورية في اعلاه. ولهذا يقل تباين الخواص عند درجة حرارة التحميص الاعلى (1873 K) . و انتجت درجة التحميص الاوطأ (1673 K) لـ $Al(OH)_3$ منتوجاً من α-Al_2O_3 بمقدار اعلى لرقم الصلادة الدقيقة 884 ويقل هذا المقدار الى 731 عند درجة الحرارة 1873 K.