



Transition alumina phases induced by heat treatment of boehmite: An X-ray diffraction and infrared spectroscopy study

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ABSTRACT

During high temperature oxidation of alumina-forming alloys, various transition aluminas are formed before reaching the most stable α -Al₂O₃ phase. In particular, the γ , δ and θ transition aluminas are concerned. Precise studies on the development, the microstructure and the properties of the oxide layers are not straightforward owing to the difficulty to unambiguously distinguish the various polymorphs by X-ray diffraction (XRD) alone. To remove this difficulty, we propose a procedure which combines XRD and infrared (IR) spectroscopy. γ , δ , θ and α -Al₂O₃ phases, prepared by dehydration of aluminium oxihydroxide AlOOH (boehmite), were measured by XRD and IR spectroscopy on all samples. Thus, reference IR spectra were obtained for all alumina phases, as well as an assignment of the main band in agreement with previous studies, and coherent with the structural evolution of various polymorphs. This precise characterization may constitute a basis for further investigations on thin layers of alumina formed under various experimental conditions (temperature, atmosphere, etc.).

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1. Introduction

Aluminium oxide, alumina (Al₂O₃), is one of the most interesting ceramic materials both for its numerous applications and varied physical properties. It is used for example as a catalyst support, in electronic-device fabrication, as a cutting-tool material, as a protective barrier against corrosion on alumina-forming alloys, or as alternative for surgical material for implants. Alumina has the particularity to exist in a variety of metastable structures, the so-called transition aluminas (such as χ , κ , γ , δ , η , θ) as well as its stable α -Al₂O₃ phase. This polymorphism can be classified in terms of the oxygen sublattice structure and the distribution into this sublattice of aluminium ions in tetrahedral and octahedral interstitial sites [1]. Thus, in α -Al₂O₃, the oxygen sublattice is hexagonal-close-packed (hcp) structured with $\frac{2}{3}$ of octahedral sites occupied with cations, while γ , δ , θ have a face-centred cubic (fcc) arrangement of oxygen atoms and cations present in various proportions in both octahedral and tetrahedral sites.

Our group is particularly interested in the formation of alumina during high temperature oxidation processes of alumina-forming alloys, under various atmospheres (pure oxygen,

water vapour presence, etc.). For these experimental conditions, it seems established that, before reaching the most stable α phase, various transition alumina are formed, principally γ , δ and θ phases and can be simultaneously present [2]. However, the first stages of oxidation and the exact role played by the transition phases on the properties of the final alumina film is not clearly understood. The main reason is the difficulty to precisely characterize the transition alumina structures present at a given time by classic methods [3]. In particular, X-ray diffraction (XRD) provides similar patterns for various aluminas and does not allow to unambiguously characterizing the phases in presence into the film. In contrast, transmission electron microscopy (TEM) has been used to study the oxidation of both intermetallic Fe₃Al and FeCrAl strengthened by yttria nanoparticles [4,5]; the formation of transition alumina for various heat treatments was evidenced and the transformation in α -Al₂O₃ was studied. However, TEM being a demanding technique is not widely available and its spatial resolution is not adapted for providing a general description of a given sample. In this paper, we propose the combined use of both XRD and infrared spectroscopy (IR) and we show that the simultaneous analysis of XRD patterns and IR spectra allows to unambiguously characterizing the transition alumina phases. To achieve this purpose, we studied γ , δ , θ and α alumina phases that can be obtained by heating the oxihydroxide AlOOH (boehmite) at different temperatures. It has been established [6] that boehmite

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transforms into stable α - Al_2O_3 via the sequence $\text{AlOOH} \rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ - Al_2O_3 . In this study, γ , δ , θ and α phases were synthesized by heating boehmite powder in ambient atmosphere at the appropriate temperature (ranging from 873 to 1573 K). XRD pattern and IR spectra were then measured on each sample. Main IR bands were assigned in terms of bending and stretching modes of AlO_4 and AlO_6 units, coherently with the structural evolution of the phases, and in agreement with previous study on alumina. Moreover, a good agreement is found between experimental spectrum and preliminary *ab initio* calculations that we performed for γ and δ phases.

This work provides a suitable and accurate method for future studies on thin alumina films formed in various experimental conditions and substrates.

2. Experimental

Dispal 21N4–80 boehmite powder, AlOOH , from Vista was used. The powder is made of spherical aggregates whose diameter ranges from 3 to 50 μm , as shown in Fig. 1. α alumina powder (99.99% purity) from Alpha Aesar was used as a reference.

The boehmite powder was calcined in ambient atmosphere at temperatures ranging from 873 to 1573 K according to the following heat treatment:

- heating up to the specified temperature at 5 K/min;
- maintaining for the specified time duration (from 1 to 165 h) at the calcination temperature;
- cooling down rapidly to room temperature (air quench).

For temperatures lower than 1323 K, the uncertainty on temperature was $\Delta T = \pm 2$ K, while for temperatures above 1373 K, the uncertainty on the temperature was larger, $\Delta T = \pm 10$ K.

All the samples were then characterised using both X-ray diffraction (XRD) and infrared spectroscopy (IR):

- XRD was performed on powder with a PANalytical X'Pert Pro MRD diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm). Data were collected with steps of $0.02^\circ(2\theta)$.
- IR spectra were obtained using a Perkin-Elmer spectrometer at resolution of 8 cm^{-1} . Fourier transform infrared (FTIR) technique was used in the transmission mode in the 200–4000 cm^{-1} range. For each sample, 120 scans were used. After calcination, 10–100 μg of the powder was grinded. The powder was then

compressed together with 23 ± 2 mg of CsBr in a cold 150 MPa isostatic press (CIP) in order to obtain a 200–250 μm thick pellet. The transmission spectra were obtained by dividing the signal transmitted through the pellet (I) by the signal measured through an aperture of the same dimensions (I_0). All infrared spectra are reporting absorbance ($A = -\ln(I/I_0)$) as a function of the incident wavenumbers.

The apparatus was working in purging mode to minimize the absorption by water vapour and CO_2 gas.

Notice that the NO_3^- anions adsorbed on the surface of the grains are decomposed for temperatures above approximately 600 K.

3. Results

3.1. Boehmite

Boehmite crystallizes as orthorhombic cells and is composed of $\text{AlO}(\text{OH})$ sheets piling up with the oxygen ions located either into the sheets (O_I) or at their surface (O_{II}). The aluminium ions located in the centre of octahedra are surrounded by 4 (O_I) and 2 (O_{II}) [8]. OH groups are binding to the octahedron double layers. In Fig. 2a the XRD pattern obtained on the as received boehmite powder shows a good agreement with the reference XRD pattern (21–1307 JCPDS file). The widths of the X-diffraction peaks are characteristic of crystallographic coherence domains of about 10 nm.

In Fig. 2b, the IR spectrum obtained on the same sample is presented. The two strong and well-resolved absorption bands at 3090 and 3300 cm^{-1} characterize a well crystallized boehmite [8]. The main bands are listed in Table 1, together with their assignment, and compare well with values available in the literature [7–9]. For this material, the Al ions can occupy two sublattices: tetrahedral sites and octahedral sites. Bands extending in the 400–800 cm^{-1} range are due to the stretching and the bending of AlO_6 atomic group, while the 880 cm^{-1} structure results from the stretching of AlO_4 atomic group, for which the Al–O bonds are shorter.

3.2. Alpha alumina (corundum)

α - Al_2O_3 , or corundum, is the most stable phase of alumina. Corundum has a rhombohedral structure in which the oxygen ions

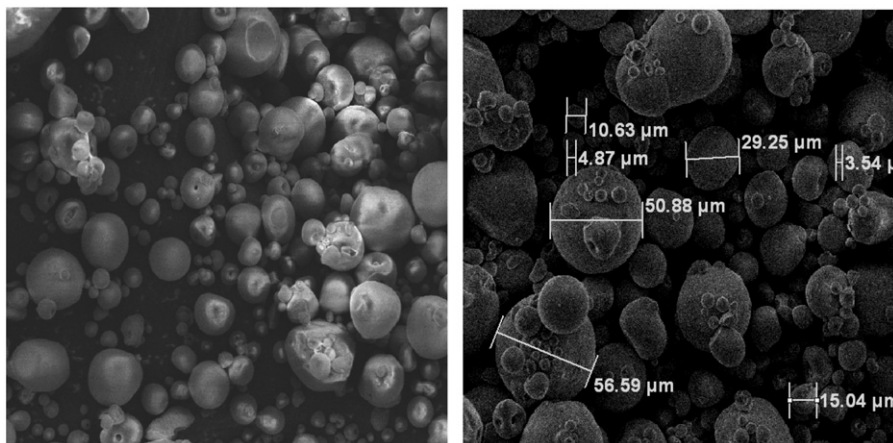


Fig. 1. SEM images of boehmite powder used for forming alumina through calcinations.

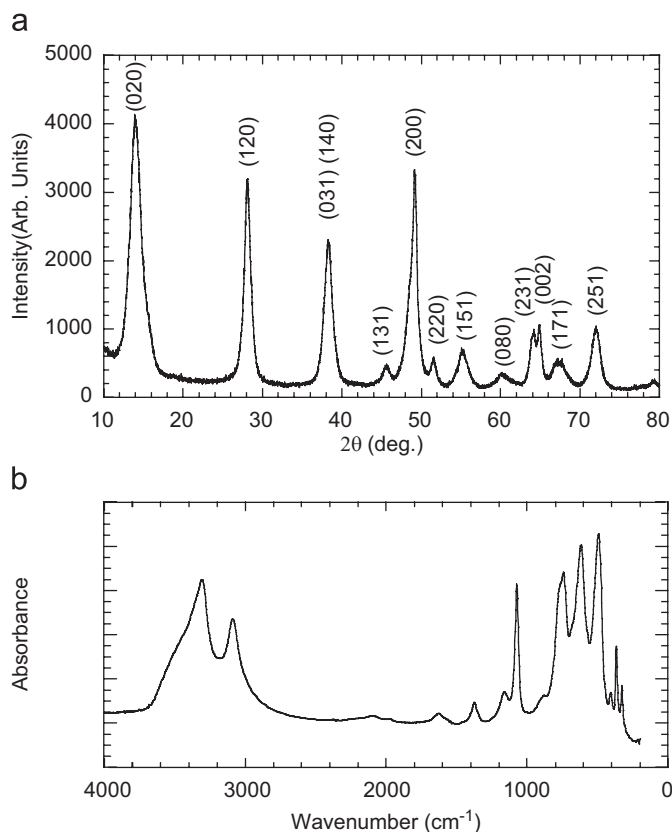


Fig. 2. Boehmite spectral signatures. (a) XRD pattern; (b) IR spectrum.

Table 1

Boehmite IR band positions measured on our powder, together with values and assignment from Refs. [7–9].

Boehmite band position (cm ⁻¹)		Assignment (from Refs. [7–9])
This work	From Ref. [8]	
326	322	Deformations of AlO ₆ and AlO ₄ stretching mode
368	366	
405	395	AlO ₆ bending mode
491	482	AlO ₆ stretching mode
616	610	<i>id.</i>
761	775	OH torsional mode
740	734	
880		AlO ₄ stretching mode
1072		Symmetric and asymmetric bending of AlOH
1160		
1375		H ₂ O deformation vibrations
3090	3090	O–H stretching mode
3304	3295	<i>id.</i>

form a compact hexagonal sublattice in which aluminium ions occupy $\frac{2}{3}$ of the octahedral interstitial sites. The XRD pattern of the as received α -Al₂O₃ powder (Fig. 3a) shows good agreement with the reference XRD pattern (42–1468 JCPDS file).

IR spectrum obtained on the same sample is shown Fig. 3b and the main IR band frequencies are presented in Table 2 together with literature data [10]. Five main structures are visible between 350 and 650 cm⁻¹, the lowest energy results from the bending of Al surrounded by six O, the others resulting from stretchings of Al–O bonds. Note that for the corundum structure, only octahedral Al atoms are present.

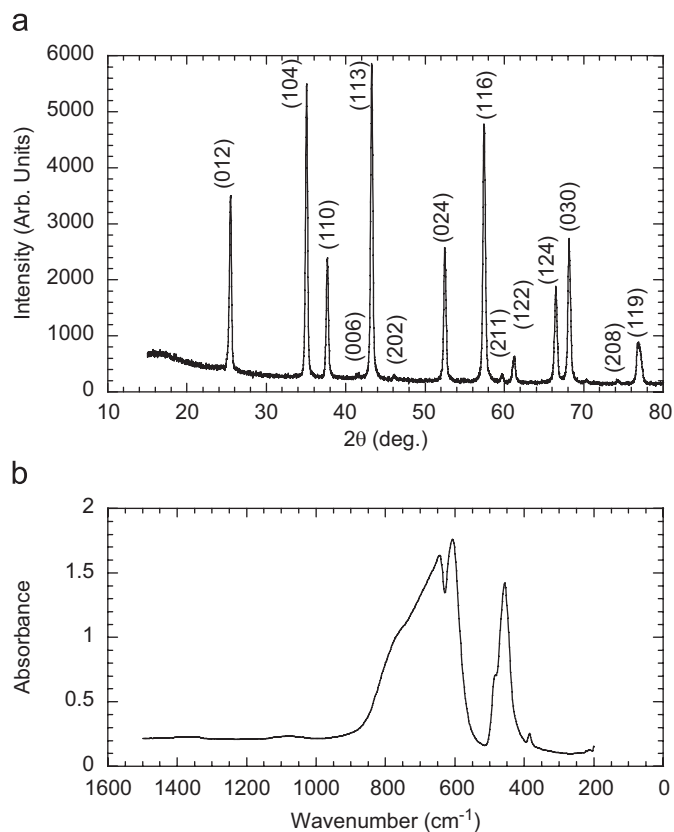


Fig. 3. Alpha alumina. (a) XRD pattern; (b) IR spectrum.

Table 2

α -Al₂O₃ IR band positions measured on our reference sample, together with values and assignment from Ref. [10].

α -Al ₂ O ₃ band positions (cm ⁻¹)		Assignment (from Ref. [10])
This work	From Ref. [10]	
386	385	AlO ₆ bending mode
457	442	AlO ₆ stretching modes
484		
608	569	
645	635	

3.3. Phase transitions induced by heat treatment of boehmite

When heating up boehmite, all OH are eliminated, and various transition aluminas are formed with the sequence $\gamma \rightarrow \delta \rightarrow \theta$ to finally reach the most stable α -Al₂O₃ phase [6,7]. In order to study this sequence, we performed XRD and IR measurements on samples maintained at various temperatures (873, 1123, 1223, 1273, 1293, 1323 and 1573 K) for 24 h and then quenched.

During the dehydration of the boehmite, the spinel structured γ alumina develops first. The initial boehmite orthorhombic structure evolves, the c parameter decreasing [7], while the fcc structure of the anionic sublattice remains [1]. The octahedral Al³⁺ ions are ordered, while the tetrahedral Al³⁺ are disordered and anisotropic, leading to a distortion of the tetrahedron [11–13]. The good agreement between the XRD pattern obtained on samples maintained at 873K during 24 h (see Fig. 4a) and the reference γ pattern (10-0425 JCPDS file) shows that only γ phase is present at this temperature. The IR spectrum of this sample, (Fig. 5a) presents a wide unresolved pattern extending from 350 to 850 cm⁻¹ with maximum absorbance around 380, 600 and

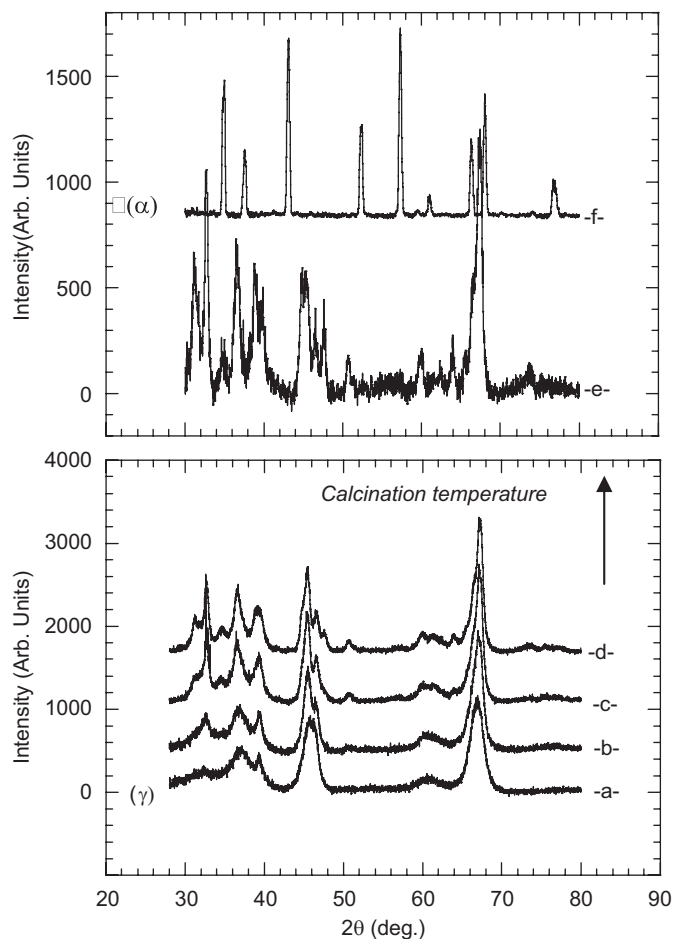


Fig. 4. XRD patterns of boehmite calcined for 24 h at (a) 873 K, (b) 1123 K, (c) 1223 K, (d) 1273 K, (e) 1293 K and (f) 1573 K. The 24 h calcination of boehmite at 873 K forms γ alumina, while calcination at 1573 K forms α alumina.

800 cm^{-1} . This unresolved wide structure is typical of a complex and disordered crystallographic structure. Indeed, the cation ordering leads to a spinel structure with 160 atoms per cell [14], which implies as many as 480 vibration modes. Our measurements are compared in Table 3 with values from literature concerning various alumina [15,16]. This comparison allows to assign the lowest energy band (around 380 cm^{-1}) to both AlO_4 and AlO_6 bending modes, the other two wide structures (600 and 800 cm^{-1}) resulting from AlO_6 and AlO_4 stretching, respectively. Although all the calcinations temperatures are above that of the desorption of water physically and chemically bonded and its of the dehydroxilation (all occurring under 773 K) [15], a small quantity of OH is still present as attested by the presence of small bands above 1000 cm^{-1} assigned to O–H or Al–OH.

For samples prepared at intermediate temperatures (1123, 1223, 1273, 1293 and 1323K), none of the XRD pattern reported in Fig. 4 is specific of a pure alumina phase. Instead, the comparison with reference patterns shows a dominant mix of δ (46–1131 JCPDS file) and θ (35–0121 JCPDS file) phases. Nevertheless, the presence of remnant γ phase cannot be excluded. The δ structure is tetragonal and can be considered as a spinel superstructure built by piling up three spinel units, the Al^{3+} ions occupying $(13+\frac{1}{3})$ out of the 16 octahedral sites and all the eight tetrahedral sites of the conventional spinel structure. θ alumina has a monoclinic structure which is isomorphous of $\beta\text{-Ga}_2\text{O}_3$ with the oxygen atom distribution close to a fcc lattice and the cations distributed in equal number on octahedral and tetrahedral sites. In short, the

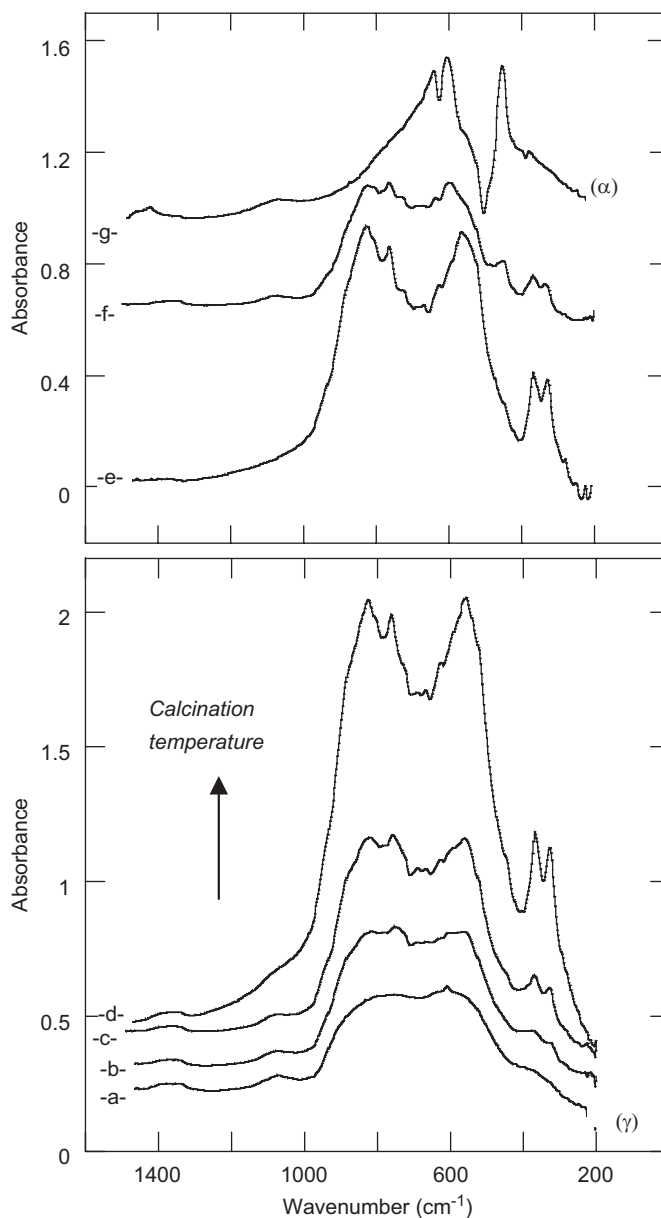


Fig. 5. IR spectra of alumina formed from boehmite calcined for 24 h at (a) 873 K, (b) 1123 K, (c) 1223 K, (d) 1273 K, (e) 1293 K, (f) 1383 K and (g) 1573 K. The 24 h calcination of boehmite at 873 K forms γ alumina, while calcination at 1573 K forms α alumina.

$\gamma \rightarrow \delta \rightarrow \theta$ transformation is accompanied by the cation migration from octahedral to tetrahedral sites, the fcc oxygen sublattice being preserved. IR spectra on the same samples are reported in Fig. 5. One can notice that spectra present better resolved and more intense structures as temperature increases between 1123 and 1293 K. The strong IR bands growing for every temperature and only disappearing when $\alpha\text{-Al}_2\text{O}_3$ develops ($\sim 330, 370, 560, 620, 760, 820\text{ cm}^{-1}$), can be assigned to θ phase. This is coherent with the fact that, as the structure of δ alumina is close to that of γ , it also gives rise to a wide unresolved band. All these peaks, at the particular temperature $T = 1273\text{ K}$, are presented in Table 3 together with their assignment and previous values from the literature. Compared with the γ phase bands (873 K), the bending resulting from AlO_4 and AlO_6 are well resolved, the bands resulting from the stretching of both AlO_6 ($560, 620\text{ cm}^{-1}$) and AlO_4 (760 and 820 cm^{-1}) spanning in the higher energy range.

Table 3

Alumina IR bands positions measured after calcinations of boehmite for 24 h at different temperatures together with values and assignment from Refs. [15,16].

Measured band positions (cm ⁻¹)			From Refs. [15,16]		
T = 873 K	T = 1273 K	T = 1573 K	Band positions (cm ⁻¹)	Unit	Assignment
~380	330	–	250 320	AlO ₄	Bending
	370	380	350	AlO ₆	Bending
		455	450		
600	560	607	500	AlO ₆	Stretching
	620	642	750		
800	760	–	750	AlO ₄	Stretching
	820		850		
~1090	~1090	~1090	1070	Al–O–H groups	Symmetric bending
–	–	–	1166	Al–O–H groups	Asymmetric bending
1370	1370	1420	1355	Al–O–H groups	Stretching vibration

This assignment is supported by calculations by Lodziana and Parlinski [17] suggesting that the phonon states of the α -Al₂O₃ phase (octahedron AlO₆ only) are located in a narrower energy range than the θ phase phonons (both octahedron AlO₆ and tetrahedron AlO₄) spread in a range extending between 130 and 770 cm⁻¹. Moreover, a good agreement is found with preliminary *ab initio* calculations performed in our laboratory [18]: for γ and δ phases, both IR spectra present a wide multiple structure between 300 and 850 cm⁻¹, with maximum absorbance around 400, 605 and 800 cm⁻¹, while equivalent calculations for the θ phase show that the spectrum is dominated by two doublets (at ~300 and 800 cm⁻¹), a peak at ~500 cm⁻¹, and another one at ~650 cm⁻¹.

Finally, for samples prepared at T = 1573 K, XRD pattern (Fig. 4) shows that only α -Al₂O₃ is present. The transformation of θ into α alumina is associated with the migration of ions in both sublattices. Oxygen ion sublattice is modified from an fcc to an hexagonal one, meanwhile tetrahedral Al³⁺ ions are no longer present in α alumina and only AlO₆ units are present. Accordingly, the measured IR spectra corresponding to this temperature (Fig. 5g) shows a similar simple spectrum as its observed on the reference α -Al₂O₃ sample (Fig. 3b), all main bands appearing at energies with a maximum deviation of 3 cm⁻¹ compared to reference spectrum (see Table 3 and 2).

To resume, no characteristic band allows us to distinguish δ phase from γ phase by IR spectroscopy, as opposed to XRD which provides significant different patterns. In contrast, the formation of θ alumina is clearly evidenced by IR spectroscopy, while XRD provides ambiguous answers when several transition aluminas are present. The presence of θ alumina corresponds to the appearance of specific doublets: 330 and 370 cm⁻¹ (first doublet), 560 and 620 cm⁻¹ (second doublet) and 760 and 820 cm⁻¹ (third doublet).

3.4. Kinetic aspects

The results presented in the previous sections obtained for samples submitted to various temperatures applied for 24 h allowed to characterize the various alumina phases present in these samples. It is clear however, that the samples may not be in thermodynamic equilibrium. In the following section we show that indeed, for intermediate temperature (< 1273 K) the samples continue to evolve long after 24 h. For this purpose, Fig. 6 shows IR spectra measured after calcinations of the boehmite at 873 (a), 1273 (b) and 1383 K (c) for different durations up to 165 h.

At 873 K (Fig. 6a), only the intensity is changing from 24 to 120 h, the intensity distribution remaining the same, suggesting that the γ phase is stable at this temperature. Notice that one

cannot exclude a transformation into δ phase as no IR signature of this transformation was evidenced in this study.

Fig. 6b presents alumina resulting from calcinations at 1273 K for 24, 44 and 165 h. For the first two durations, again, only the intensity is changing, the intensity distribution remaining the same. This suggest that after 44 h, only θ phase is present as if the intensity distribution would result from thin θ structures superimposed on a wide unresolved γ - δ band, one would observe an evolution toward a better resolved spectrum as opposed to the present situation in which the shape stays unchanged. In addition, after 165 h calcination, the α phase appears as demonstrated by the growing of peaks at 455, 607 and 642 cm⁻¹.

The observations at T = 1383 K for durations between 1 and 24 h (Fig. 6c) lead to the same conclusions, except that the transformations occur more rapidly at this high temperature.

These evolutions are in qualitative agreement with Wilson and Mc Connell kinetics study [13].

Moreover X-ray diffraction studies aimed at evidencing these kinetics effect were performed. Because of the presence of a very complex and evolving structure, XRD pattern measured for various durations were not exploited in this study as they did not provide extra information compared to the infrared measurements.

4. Conclusions

The aim of this work was to study the alumina phase evolution resulting from thermal treatment of boehmite. Previous studies on this system using XRD technique did not allow to unambiguously characterizing the transition alumina phases. Here, in contrast, the combined use of both XRD and IR spectroscopy allowed to observe the sequence: boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ -Al₂O₃ with increasing temperature from 873 to 1573 K.

The γ phase presents a specific XRD pattern while the IR spectrum is characterized by a broad band between 300–900 cm⁻¹. The transition $\gamma \rightarrow \delta$ is undetectable by IR, while it can be identified by XRD. In contrast, the following transition $\delta \rightarrow \theta$ cannot be probed by XRD as opposed to IR for which some thinner structures develop, in particular three doublets are visible between 300 and 820 cm⁻¹. Through the last transition $\theta \rightarrow \alpha$, all structures of θ associated with tetrahedral sites (AlO₄ sites) disappear which causes a narrowing of the energy range within 380–640 cm⁻¹ giving rise to the characteristic α spectrum dominated by Al³⁺ ions in octahedral sites (AlO₆).

This study provides reference IR spectra for all alumina phases developed from heating up boehmite together with a suggested

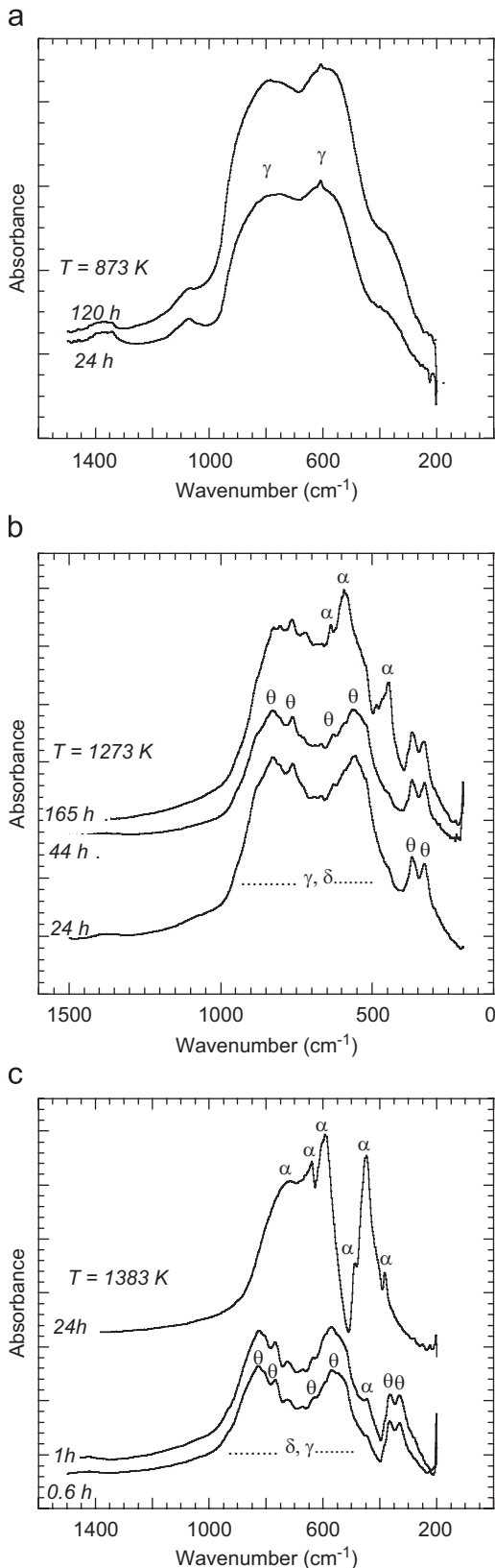


Fig. 6. Evolution with time of the IR absorbance of alumina obtained through calcinations at (a) 873 K, (b) 1273 K and (c) 1383 K.

assignment of the main bands in agreement with previous alumina studies. Moreover, this assignment is coherent with the expected structural evolution for the various phases. This

attribution should be refined in the future thanks to the availability of calculated *ab initio* IR spectra for the various transition aluminas currently under way.

The several heat treatments used in this study suggest that γ , δ , θ transition alumina are formed successively before growing into the α - Al_2O_3 form. Moreover within the time range of the heat treatments, several phases seem to coexist simultaneously. This suggests that the transition kinetics are relatively slow.

Future studies of thin layers of alumina formed on alumina-forming alloys may greatly benefit from this new characterisation and help understanding the great variety in the properties observed for the thin films formed in various conditions (atmosphere, temperature, substrate, etc.).

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- [18] Our preliminary calculations were performed using the Crystal 06 programme with the Hartree–Fock method and DFT correlation energy corrections. The B3LYP DFT correction and 85–11G (*) for aluminium, 88–31G (*) for oxygen atom basis sets were chosen as they give together accurate results for the calculation of vibrational properties on α - Al_2O_3 . It is centre zone calculation, i.e. the frequencies are calculated at the Γ point of the Brillouin zone and the infrared intensities are evaluated through the Wannier functions obtained by localizing the crystalline orbitals.