



Specific signatures of α -alumina powders prepared by calcination of boehmite or gibbsite

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ABSTRACT

The specific signatures of α -Al₂O₃ powders by a combination of X-ray diffraction (Rietveld analysis), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, thermal analysis (TG–DTA) and cathodoluminescence (CL) were investigated. Thus, α -alumina was prepared by calcination of boehmite or gibbsite at 1573 K for 24 h. The size of α -alumina crystallites obtained using boehmite precursor was smaller than that obtained using gibbsite precursor. The difference in oxygen vacancies (F⁺-centers) amount between α -Al₂O₃ powder obtained by calcination of gibbsite and boehmite was confirmed by CL spectra. Furthermore, the Ti³⁺ emission at 1.71 eV is absent in α -Al₂O₃ powder obtained by calcination of gibbsite. CL has been demonstrated as a possible method for differentiation between the various α -alumina powders.

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1. Introduction

The oxides of aluminum have been the subject of many investigations because of their commercial importance and scientific interest. It is important to note that there are many works about alpha alumina using X-ray diffraction, but there is a need for a more detailed structural analysis. To achieve this more exhaustive structural characterization we have used the Rietveld refinement method, FTIR and electron microscopy techniques. Pure α -Al₂O₃ crystal is colorless and shows little absorption in the ultraviolet–visible (UV–Vis) range. But various impurities (Ti, Cr, and Fe) even a trace level causes apparent absorptions which are attributed to various emission centers [1]. In the presence of lattice defects, extra luminescence emissions can be observed in the ultraviolet (UV) region upon highly energetic excitation. The observed UV spectrum in α -alumina can be deconvoluted into two distinct sub-band components: an F⁺-center (oxygen vacancy with one trapped electron) band, located at around 3.8 eV, and a less intense F-center band (oxygen vacancy with two electrons), located at around 3.0 eV [2–5]. The dominate defects for the visible emission might be different for α -alumina powders formed by heating any of the hydrates of aluminum to a sufficiently high temperature. The luminescent characteristics changed with the alumina powder size since the larger powder has less dangling and unsaturated bonds in the surface than the smaller one [6].

In this letter, we present X-ray diffraction (Rietveld analysis), SEM, FTIR, TG–DTA and CL measurements of α -alumina powders formed

by calcination of boehmite or gibbsite. The specific signatures of α -alumina powders are discussed.

2. Experimental procedure

Dispal 21 N4-80 boehmite powder, AlOOH, from Vista was used. The powder is made of spherical aggregates and was composed of 77.4–80% Al₂O₃, 1.6% NO₃, 0.002% Na₂O and max.: 0.25% C, 0.015% SiO₂, 0.015% Fe₂O₃ and 0.15% TiO₂. The sample experienced an ignition loss of 20–22.5% at 1000 °C and had a purity grade of 99.91%. Its average particle size (50 μ m) was due to the agglomeration of smaller crystals. The specific surface area of the original sample was 200 m²/g (after activation at 550 °C for 3 h).

Gibbsite powder, Al₂(OH)₆, from Prolabo (no 20 984.298) was used. The powder is made of platelet aggregates and was composed of 64.5–67% Al₂O₃ and max.: 0.01% Fe₂O₃, 0.02% SO₄, 0.002% heavy metals (as Pb), and 1.0% non precipitable by NH₄OH (as SO₄). The sample experienced an ignition loss of 33–34.5% at 1000 °C and had a purity grade of 99.7%. Its average particle size (20 μ m) was due to the agglomeration of crystallites. The specific surface area of the original sample was 0.5 m²/g. The boehmite powder and gibbsite platelets were calcined in ambient atmosphere (pO₂ = 0.21 atm) at 1573 K. The cycle was as follows: heating up to an isothermal temperature at 5 K/min, maintaining for 24 h at the calcination temperature and fast cooling down to room temperature (air quench). These conditions have been chosen in order to increase the nucleation site density, enhance the particle rearrangement during the phase transformation, to yield a homogeneous distribution of the defects on the surface of the alumina particles and improve the α -alumina phase densification.

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The calcination temperature was maintained for 24 h to obtain a well-crystallised product and without any trace of transitional aluminas. After calcination, 10 to 100 μg of the powder was drawn, then grinded with 23 ± 2 mg of CsBr in order to obtain, a pellet of 200–250 μm in thickness. The FTIR technique was used in the absorbance mode in the 200–4000 cm^{-1} range. The FTIR spectra are obtained using a Perkin-Elmer spectrometer at a resolution of 8 cm^{-1} . The apparatus is equipped with a system allowing the reduction of the optical course in air in order to minimize the perturbations associated with ambient air (water vapour and CO_2). The uncertainty on the position of the various peaks is equal to ± 2 cm^{-1} . The thermogravimetric method (TG) and differential thermal analysis (DTA) data were recorded under a dry air flow with a heating rate of 10 K/min in a SETARAM TGDTA92-16.18 thermal analyser. TG measurements were corrected for temperature-dependent buoyancy by subtracting the data of a measurement carried out on an inert sample. The crystalline structure of the calcined powders was investigated by XRD using a PANalytical X'Pert Pro MRD diffractometer configured as follows: Cu tube operating at 40 kV and 30 mA ($\lambda(K\alpha_1) = 0.15406$ nm, $\lambda(K\alpha_2) = 0.15444$ nm). The scan rate (2θ) was $1^\circ/\text{min}$ at a step size of 0.025° . The data were processed to realize the conditions of the software program FullProf Suite for the structure refinement. The powder morphology was examined using a (Tescan Vega TS5130MM) scanning electron microscope (SEM). The emitted light under electron beam excitation in a UHV system, was analyzed through a quartz window with a Jobin Yvon CP 2000 spectrograph and a CCD detector. The wavelength range of 200–1000 nm was investigated.

3. Results and discussions

Fig. 1 shows the typical TG–DTA curves of the two kinds of samples; gibbsite (blue line) and boehmite (red line). TG and DTA curves are indicated as dotted and solid lines, respectively. Concerning the dehydration–dehydroxylation process of boehmite, three steps can be observed. The first step (297 to 473 K) gives a sharp symmetrical endotherm. It accounts for 5–6% of the mass loss which corresponds to the dehydration of physisorbed water molecules and of part of the chemisorbed molecules. The second step (473 to 773 K) gives a broad endotherm. It represents the major part of the mass loss (about 15%) which is due to the removal of chemisorbed molecules and to the decomposition of boehmite into γ -alumina [7]. The last step (773 to 1273 K) gives no thermal event but appears as a continuous mass loss (about 2%) which corresponds to the elimination of residual hydroxyls. The exotherm, which appears at 1468–1508 K of

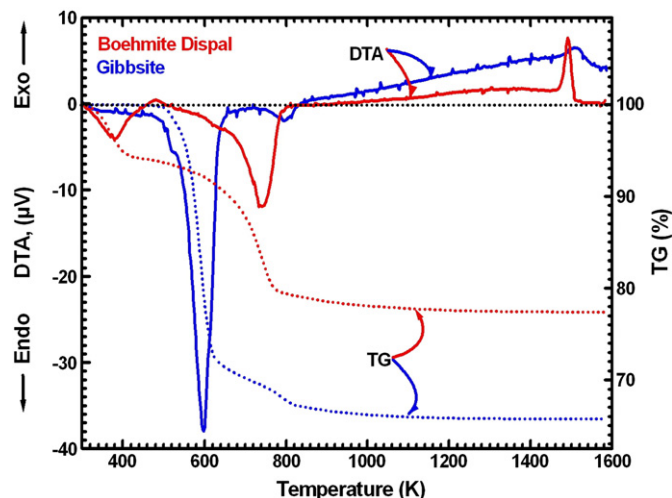


Fig. 1. TG and DTA curves of Boehmite (red line) and gibbsite (blue line).

DTA curve, corresponds to the transformation into α -alumina [8]. For a dry boehmite and without nitrate the theoretical mass loss is 15%. Here, the experimental loss reached 22.5%. The initial loss is likely to correspond to water weakly bound. We also note that the dehydration is complete at more than 1273 K; the transition alumina (γ/δ) most likely contains OH groups.

For gibbsite, the dehydration appears to occur in two steps (around 598 and 803 K respectively) at higher temperature. The expected theoretical loss due to dehydration is 34.6%, the experimental loss is 34.3% a little lower. This difference of 0.3% is a bit larger than the experimental uncertainty 0.1%, the starting gibbsite may be slightly dehydrated. The formation of α -alumina occurs between 1473 and 1533 K [9], it is softer than in the case of boehmite. Finally, the structural transformations to well-crystallised α -alumina are described by nucleation ($T < 1470$ K) and growth mechanisms ($T > 1470$ K).

The Rietveld refinement of the structures was performed using the WinPlotr/FullProf suite package [10]. The peak shape was described by a pseudo-Voigt function, and the background level was modeled using a polynomial function. The profiles were refined using the space group and structure models of Al_2O_3 (R3C, JCPDS 46-1212). The XRD data for the 2θ regions between 20° and 80° was used for the refinement. The observed, Rietveld refined and difference patterns are shown in Figs. 2 and 3. It was obvious that the agreement between the

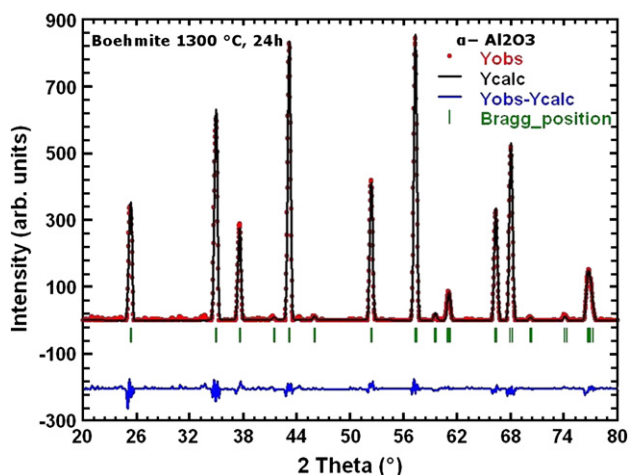


Fig. 2. The observed and calculated diffraction patterns of α -alumina powder prepared by calcination of boehmite. Vertical bars indicate the calculated position of the Bragg peaks. The blue curves in the bottom correspond to the differences between experimental and calculated profiles.

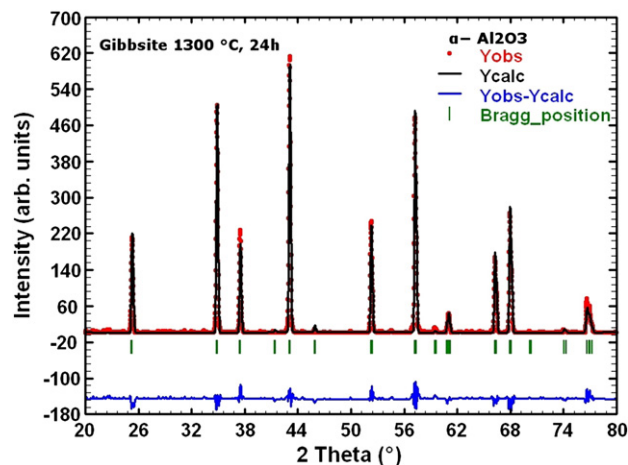


Fig. 3. The observed and calculated diffraction patterns of α -alumina powder prepared by calcination of gibbsite.

experimental data and the simulations was excellent since the R_{wp} (weighted residual error) factor was small ($\leq 7.36\%$). The Rietveld results (cell parameters, atom position, reliability factors and crystallite size (D)) are given in Tables 1 and 2. The size of α -alumina crystallites ($D=31$ nm) obtained using boehmite precursor was smaller than that ($D=43$ nm) obtained using gibbsite precursor. Furthermore, the α - Al_2O_3 from boehmite has a greater lattice parameter ($a=0.4761$ nm, $c=1.3002$ nm) than that of JCPDS file 46-1212 ($a=0.4758$ nm, $c=1.2991$ nm, $c/a=2.730$) and a similar c/a ratio. However, the α - Al_2O_3 from gibbsite has a smaller lattice parameter ($a=0.4752$ nm, $c=1.2972$ nm) and c/a ratio ($c/a=2.729$) than that of JCPDS file 46-1212. Phase transformations are frequently accompanied by microstructural changes. This fact could explain the crystallographic parameters differences between the two α -alumina powders.

Fig. 4 compares the FTIR absorbance spectra of α - Al_2O_3 obtained after calcination of gibbsite and boehmite. For the samples calcined at 1573 K, significant spectroscopic bands at ~ 640 , ~ 594 , ~ 447 and ~ 386 cm^{-1} appear which are identified to be the characteristic absorption bands of α - Al_2O_3 [11]. This is in good agreement with XRD observations. Common bands exist in all cases, such as the broad OH band centered around 3420 cm^{-1} , and the 1640 cm^{-1} H_2O vibration band [12]. The very high surface area of these materials results in rapid adsorption of water from the atmosphere because the FTIR samples were kept and grinded in air. Three peaks of very weak intensities at 2850 cm^{-1} , 2920 cm^{-1} and 2960 cm^{-1} are observed which are due to C–H stretching vibrations of alkane groups. The absorption in ~ 2356 cm^{-1} is due to CO_2 molecular presence in air.

Cathodoluminescence (CL) signal is a good signature of the material qualities and is used in this study to characterize the point defects associated to oxygen vacancies in α - Al_2O_3 powder. The CL spectra of α - Al_2O_3 formed from boehmite and gibbsite are given in Figs. 5 and 6. Titanium and chromium in α - Al_2O_3 lattice gives a luminescence in the visible domain. In CL, the narrow band at 1.81 eV is attributed to chromium impurity, whereas titanium is characterized by a large band centered at 1.71 eV [3,5,13]. The Ti^{3+} impurity emission at 1.71 eV is absent in α -alumina powder obtained by calcination of gibbsite. This can be explained by the structure of first resultant dehydration product of gibbsite. During the dehydration of gibbsite and boehmite the χ - and γ -Alumina develops first, respectively. The structure of γ -alumina has been described as defect spinal structure (fcc) [14], whereas χ - Al_2O_3 has hcp oxygen sub-lattices [15]. A titanium ion is concluded from ODMR (optically detected magnetic resonance) measurement to replace an Al^{3+} ion at the B (spinel cation) site and exist as a Ti^{4+} ion [16]. Whereas in χ - Al_2O_3 , the replacement of Al^{3+} by Ti^{4+} ion is less probable due to the high affinity of aluminum for oxygen in hcp oxygen sub-lattices. The CL

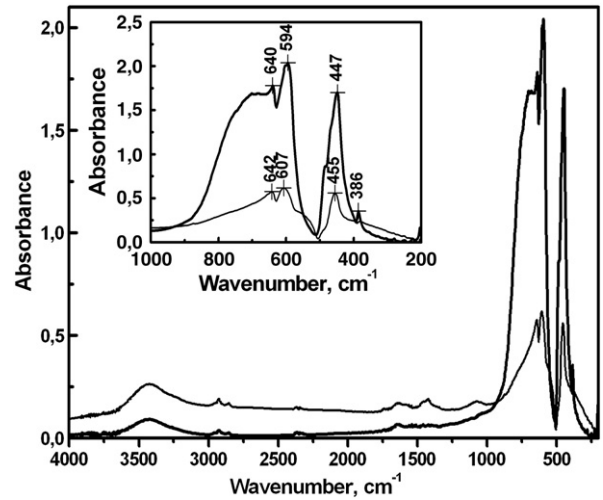


Fig. 4. FTIR absorption spectra of α -alumina powder prepared by calcination of boehmite (fine line) or gibbsite (coarse line).

spectra have shown that wide band over the interval of (2.0–6.0) eV consists of a series of overlapping bands. The main absorption bands located at about ~ 5.03 , ~ 4.42 , ~ 3.91 and ~ 2.42 eV occur in alpha alumina powder, and also do not change with the composition of the starting material. We believe that the observed CL peak at 5.03 eV is related to the interband transitions or to defect that is different in origin to the F- or F^+ -centers in α -alumina. The luminescence band at 4.42 eV is detected only if the excitation density is high and was previously observed in α -alumina by Kortov et al. [17]. Opinions differ on its origin. The emission band at 2.42 eV is attributed to Al_i^+ -centers (interstitial aluminum ions having the charge of +1) [5]. The band of F-centers is absent and less pronounced in α - Al_2O_3 powder obtained by calcination of gibbsite and boehmite, respectively. For instance, the CL intensity at 3.91 eV (F^+ -center) of the α - Al_2O_3 formed from gibbsite (Fig. 6) is approximately 32 times higher than that of the α - Al_2O_3 formed from boehmite measured under the same excitation conditions. It can be observed that the alumina grain morphology of gibbsite (Fig. 6 inset) looks like platelets and differs from that of boehmite (Fig. 5 inset) which are spherical. The O–H stretching mode (Fig. 4) is very low in α - Al_2O_3 powder obtained by calcination of gibbsite. The number of dangling bonds, which are the water-adsorption sites, is extremely reduced. It is possible that

Table 1

The Rietveld refinement results: α - Al_2O_3 from boehmite, $R_p=8.80\%$, $R_{wp}=5.08\%$, $D=31$ nm.

Lattice parameters (nm)	Atom	x	y	z	Biso	Occupancy
$a=0.47615$ $c=1.30024$	Al	0	0	0.3523	0.8129	1.1577
	O	0.3074	0	0.2500	1.2343	1.9076

Table 2

The Rietveld refinement results: α - Al_2O_3 from gibbsite, $R_p=15.3\%$, $R_{wp}=7.36\%$, $D=43$ nm.

Lattice parameters (nm)	Atom	x	y	z	Biso	Occupancy
$a=0.47523$ $c=1.29721$	Al	0	0	0.3525	1.5585	0.7881
	O	0.3183	0	0.2500	3.7937	1.4249

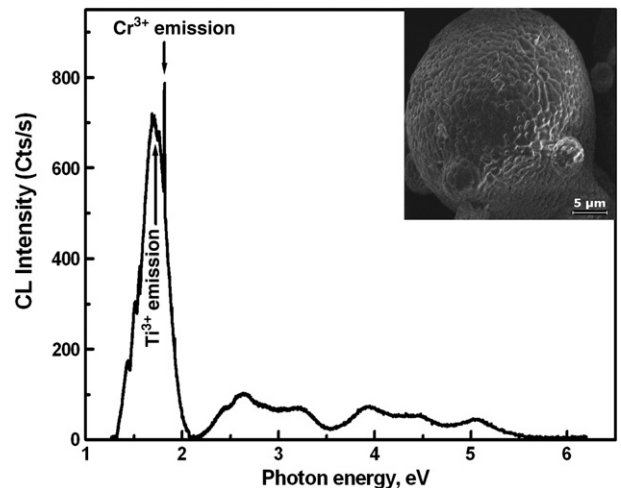


Fig. 5. Cathodoluminescence spectrum and SEM images of α - Al_2O_3 powder obtained by calcination of boehmite powder at 1573 K for 24 h.

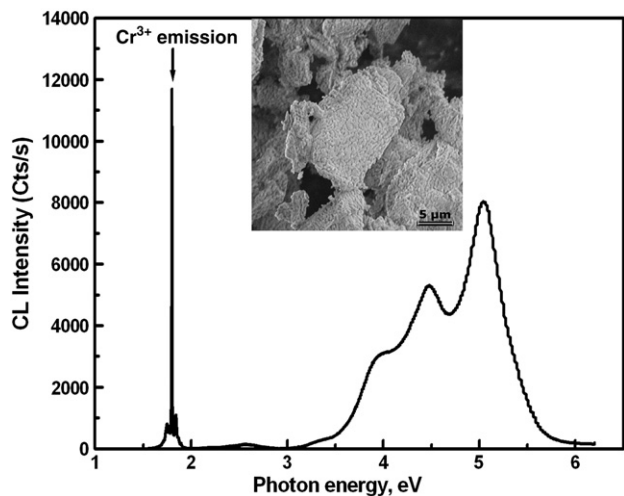


Fig. 6. Cathodoluminescence spectrum and SEM images of α -Al₂O₃ powder obtained by calcination of gibbsite powder at 1573 K for 24 h.

the porosity is too low to allow water absorption during exposure to ambient air. It is well known that the amount of dangling bonds and unsaturated bonds in the powder surface is heavily dependent on the crystallite size and/or on the specific surface area. This is probably the case of alpha alumina samples obtained from gibbsite for which surface effects can be neglected compared to α -alumina coming from boehmite samples. The better the balance between aluminum and oxygen ions according to the alumina formula is, the better the crystallisation at high temperature is, and the smaller the defect amount due to the non-stoichiometry is. It is obvious that the particle morphology has an important influence on the phase transformation of the material, the alpha alumina particles obtained by calcination retaining the starting material morphology as a shape memory effect.

4. Conclusions

α -Alumina was prepared by calcination of boehmite or gibbsite at 1573 K for 24 h. The specific signatures of α -Al₂O₃ powders by a combination of X-ray diffraction (Rietveld analysis), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, TG-DTA and cathodoluminescence (CL) were investigated. The size of α -alumina crystallites obtained using boehmite precursor was smaller than that obtained using gibbsite precursor. The particles

obtained from boehmite have spherical shape, while those obtained from gibbsite have like platelets shape. CL has been demonstrated as a possible method for differentiation between the various α -alumina powders. The Ti³⁺ emission at 1.71 eV is absent in α -Al₂O₃ powder obtained by calcination of gibbsite. The band of F-centers is absent and less pronounced in α -Al₂O₃ powder obtained by calcination of gibbsite and boehmite, respectively. The difference in oxygen vacancies (F⁺-centers) amount between α -Al₂O₃ powder obtained by calcination of gibbsite and boehmite was confirmed by CL spectra.

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