Characterization of a chiastolite-type andalusite: structure and physicochemical properties related to mullite transformation

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Abstract
Chiastolite-type andalusite, whose genesis occurred in the currently unexploited deposit of Sidi Bou Othman (Morocco), has been extensively characterized. The phase composition, microstructure, thermal behavior, sinterability, and evolution of the crystallographic structure associated with the transformation of andalusite to mullite were accurately analyzed. Parallelepiped-shaped crystal grains exhibited off-white X crosses, typical of the chiastolite group. The chemical composition is closely dependent on the crystal size and proportion of alumina. The crystal structure was successfully refined using XRD, and chemical analysis was performed for different crystal sizes up to 30 mm. Powder compacts were prepared from these chiastolites for further characterization after various thermal treatments. According to the Rietveld refinement analysis, the mullization ranges from 1200 to about 1500 °C, and crystallographic parameters have been compared with other andalusites reported in literature. In agreement with this phase transformation, variations related to different material properties such as thermal expansion, pore volume fraction, and mechanical strength were evaluated. These results highlight the potential for further exploitation of the Sidi Bou Othman deposit to produce refractory materials.

1. Introduction
Andalusite which constitutes a trimorphous form of Al₃SiO₅ with both kyanite and sillimanite is a key raw material employed for the production of various ceramics, ranging from refractories to premium high-alumina-content materials dedicated to ferrous and nonferrous industries [1]. As a natural mineral formed under low-grade metamorphism conditions, Andalusite (Al₂O₃·SiO₂) exhibits many interesting characteristics such as a rather high purity, a high melting temperature, low density and rather high creep resistance. Andalusite also differs from other high-alumina-content materials so that it can be used in the fabrication of fired refractories instead of being previously calcined [2]. Moreover, it undergoes a low volume expansion during sintering which opposes to shrinkage, allowing to better control dimensional tolerance [3]. Furthermore, andalusite has an excellent chemical resistance to slag attack and penetration, especially against alkaline species compared to fireclay or bauxite-based materials. This chemical inertia is essentially due to its dense and homogeneous monocrystalline structure almost free of weak channels through which the slag can penetrate [4, 5]. At high temperature, andalusite forms 3:2-mullite defined in the SiO₂/Al₂O₃ phase diagram as 3Al₂O₃·2SiO₂ [6] which

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exhibits remarkable physical and chemical properties suitable for refractory materials, preventing final products from warpage [2].

Andalusite mullitization process is based on a topotactic transition at high temperature but as discussed by many authors, significant variations can occur in relation with fluctuating ore properties of deposits. Wala et al [7] reported the different mullitization processes of andalusite extracted from two separate deposits coming from the Republic of South Africa and France. Namiranian et al[8] studied the particle size influence of Iranian andalusite on the transformation into mullite whereas Taran et al [9] investigated the electronic Fe-Ti charge-transfer processes occurring during the thermal conversion of a Brazilian andalusite into 3:2-mullite.

Due to intrinsic characteristics, andalusite is currently extensively used for several refractory solutions essentially in steel and iron industry. However, the utilization of andalusite is also well developed for brick and castable applications in aluminium, glass, or cement industries, as well as emergent market applications such as coatings on Ni-based alloy substrates and even in calcined Li-ion battery cathode materials [10–12]. From an economic perspective, the demand for andalusite as raw material is still significant and is likely to continue for the predictable future. This is mainly due to the advanced improvements of andalusite quality coming from South Africa combined with the high cost of bauxite [13]. Consequently, production has significantly decreased over the last two decades because of the exhaustion of high-grade reserves. For instance, a supply deficit of andalusite’s mineral was recorded in 2018 both in Peru and in South Africa [14]. For example, Imerys Company through Samrec subsidiary extracts more than 200 000 tons per year which is much more than China whose andalusite based manufactured products are essentially dedicated to domestic use. As a consequence, new alternative andalusite deposits come from other emerging countries, such as Iran, Brazil, India and Australia but they are not abundant enough to meet current consumer demand [10, 15, 16].

Located in the region of Sidi Bou Othman, the Moroccan andalusite deposit considered in the present study is estimated to contain about 22 million tons. The main advantage of this deposit lies in the fact that it is on the soil surface so that it can be readily explored. Arib et al [17] and Sardy et al [18] started to study some physico-chemical characteristics of scattered crystals and the mullitization process. However, a systematic and thorough investigation of Sidi Bou Othman andalusite is yet to be performed.

In this article, Moroccan andalusite chiastolites have been accurately characterized in terms of phase composition, crystal structure, microstructure, pore volume fraction, thermal behavior and mechanical properties associated with the transformation of andalusite to mullite and silica. The approach has consisted to study both (i) andalusite crystal grains directly collected within the deposit and (ii) disc-shaped specimens resulting from a mixture of previously ground powder of various andalusite crystals, during and after thermal treatment at different temperatures. The studied powdered mixture composed of different size fractions of andalusite crystals is statically representative of the natural deposit at the surface soil. As a first approach, both the nature/amount of impurities and the size of crystals are required to be accurately evaluated in regards with other andalusite coming from other deposits: indeed, these two aspects can affect the performances of refractory materials elaborated from these andalusite crystals.

2. Materials and methods

2.1. Geological framework of the Moroccan andalusite deposit

The studied andalusite deposit rock is localized in Sidi Bou Othman, in a close proximity of the Jebilet Palaeozoic massif in the western Moroccan plateau, 25 km west from Marrakech [17]. Large-grained disseminated porphyroblasts constitute 5 to 20% of this rock dating to some 340 million years ago. The andalusite schistose host rock exhibits a grey-black color and a spotted and shiny surface. Moreover, it is affected by a high-grade type of contact metamorphism responsible for developing rich andalusite crystals with an elongated rod-shape and a length ranging from few millimeters to few centimeters (figure 1) [19].

2.2. Organizational chart related to experimental procedure

As the andalusite deposit of Sidi Bou Othman has never been exploited from industrial point of view, both coarse and fine andalusite chiastolites manually collected on soil surface have been investigated. The different steps of experimental procedure are summarized within a flow chart reported in figure 2.

After a preliminary cleaning with distilled water followed by a drying, the collected andalusite chiastolite crystals have been first classified by decreasing size into six different batches (the average length of grains ranging from 0.3 to about 3 cm). Polished sections of these grains have been observed and chemically analyzed. In addition, crystals of these six batches have been mixed together in various proportions, hand crushed and ground in laboratory planetary dry ball mill during 30 min at 350 rpm, and then passed through a 50 μm sieve. Disc-shaped specimens have been finally prepared and fired to analyze the andalusite-mullite transformation. In this way, powder compacts have been uniaxially pressed in a cylindrical die at 20 MPa from the sieved andalusite.
powder mixed with 5% of deionized water. After drying at 105 °C for 24 h, the andalusite-based disc-shaped samples (33 mm in diameter and 8 mm in thickness) have been sintered at various temperatures (1100 °C, 1200 °C, 1300 °C, 1400 °C, 1500 °C and 1600 °C) for 2 h with 5 °C min⁻¹ as heating rate using electrical furnace devoted to laboratory heat treatments (Nabertherm). Each sample was subsequently freely cooled down to room temperature and then analyzed.

2.3. Experimental techniques of characterization
Different experimental techniques have been performed depending on the different state of the andalusite crystals: polished sections, powdered crystals or sintered powders. Note that they are not adapted to adequately detect and quantify carbon.
2.3.1. Sectioned andalusite crystals
To examine the polished sections of andalusite crystals, an optical microscope (DSX1000, Olympus) exhibiting a double lens system has been used. In addition, both cross-sectional and top views have been investigated by scanning electron microscopy (FEI ESEM Quanta 450 FEG, Felmì-Zel Company) operating with a 10–30 kV accelerating voltage. Thanks to an Energy Dispersive Spectrometer, an elemental mapping has been performed to highlight the distribution of chemical elements in the observed cross section. For this, samples have been previously embedded in epoxy resin polished with diamond particles until 1 μm and coated with a platinum layer to ensure the electronic conduction of the surface.

2.3.2. Powdered andalusite crystals
The particle size distribution of the powdered andalusite crystals (before and after sintering) has been obtained using the solid-state method, using a Mastersizer 2000 laser size analyzer (Malvern). Powder density has been estimated using a helium pycnometer (AccuP11, Micromeritics Company). Moreover, an x-ray Fluorescence spectrometer (Malvern Panalytical) has been employed to determine the elemental composition within the overall volume of the tested sample: an intimate mixture of ground and sieved andalusite powder (1 g) with lithium tetraborate (10 g) has been heated at 1100 °C for 1 h and cooled down before the chemical analysis. The crystalline phases of raw and sintered samples (from 1100 to 1600 °C) were identified by x-ray diffraction analysis (D8 Advance x-ray diffractometer, Bruker Company) equipped with a curved quartz monochromator operating with a Cu Kα radiation (V = 37.5 kV, λ = 1.5406 Å, I = 28 mA and acquisition time of 30 min). For raw data processing, DIFFRAC+ software was used whereas a method based on Rietveld refinement was developed to perform a quantitative phase analysis. X-ray diffraction patterns of sintered samples were fitted using TOPAS 2.1 software (Bruker AXS) in order to determine the amount of both crystalline and amorphous phases. The WinPlotr software, integrated into the FullProf program [20] was used to refine the crystalline structure of andalusite and mullite by the Rietveld method. The profile shape was described by a pseudo-Voigt function whereas a polynomial function modeled the background. The starting data required for Rietveld refinements are the unit cell parameters and the atomic positions, which were extracted from the previous works of Taylor et al [21] and Burnham et al [22]. Unit-cell parameters, background coefficients, scale factor, zero-point error, pseudo-Voigt correction for asymmetry parameters and atomic positions were deducted from the refined XRD data.

Thermal behavior of andalusite powder has been followed by Thermogravimetric Analysis (TGA, STA 449F3 graphite—Netzsch Company) using argon flow (20 ml min⁻¹) coupled with a Mass Spectrometer (Omnistar, Balzers Instrument). Calcined α-Al₂O₃ was used as a reference. The dimensional changes in pressed powder compact during thermal treatment have been followed using a vertical dilatometer (DIL 402 PC, Netzsch Company). The measurements were carried out from ambient to 1600 °C at a heating rate of 10 °C min⁻¹.

2.3.3. Bulk andalusite powdered compacts sintered at various temperatures
Infrared (FTIR) spectra of sintered samples were recorded in transmission mode using FT-IR Spectrometer Frontier (Perkin-Elmer Company) in the range of 2000–600 cm⁻¹.

The overall pore volume fraction and apparent density of the sintered disc-shaped samples were evaluated according to Archimedes’ principle.

The mechanical strength was assessed using Brazilian tests performed with a universal testing machine (UTM Ametek, Lloyd Instruments). Stress-displacement curves were obtained at a speed of 0.1 mm min⁻¹.

Indirect tensile stress (σ) was evaluated according to equation (1):

\[
\sigma = \frac{2F}{\pi D}
\]

where F (N) is the maximum load upon rupture, ‘h’ and ‘D’ are the height and the diameter of the disc-shaped samples (mm), respectively. For each sintering temperature, three samples were prepared to verify reproducibility.

3. Results and discussion

3.1. Characterization sectioned andalusite crystals
3.1.1. Morphology
Figure 5(a) shows andalusite crystals collected from the six different selected batches (referenced S1 to S6 and ranked by decreasing size fractions): the morphology is close to a rectangular parallelepiped with an almost square basal section whose (i) length ranges from about 0.3 to 3 cm and (ii) average width is up to 1.2 cm.
Andalusite crystals are clear nodules associated with metasomatic biotite-rich schists. Owing to their many crystals faces in single crystals and their idiomorphic shape, they can easily be separated. Visible textures by naked eye are caused by dynamic re-crystallization under severe natural conditions of ultrahigh integrated fluid-rock ratios. Coarsest crystals can yield refractory materials with a high apparent density and may confer an excellent mechanical strength under load while small grain sizes limit the use of andalusite to the manufacture of firebricks. Indeed, smaller grains with a mean size less than 0.5 mm are commonly used for monolithic applications. Figure 3(b) compares the crystal sizes of Moroccan andalusite with French and Iranian andalusites: the greatest average crystal size coming from Glomel (France) is approximately 3 mm whereas Iranian deposits exhibit much larger crystals (>6 cm).

3.1.2. Chemical composition
To investigate the relationship between the morphology and chemical composition of this Moroccan andalusite, six crystals with different sizes according to the batches referenced S1 to S6 (figure 3(a)) were analyzed by x-ray fluorescence spectrometry. The results reported in table 1 show the different detected oxides ranked by decreasing weight proportion. The analytical accuracy was approximately ±1.5%.

The coarsest crystals are the richest in alumina (54.97 wt%) whereas silica content (38.24 wt%) is inversely proportional to both Al2O3 proportion and crystals size. Fe2O3 is present in all the samples in low amounts (<2.9 wt%, average ~2.7), along with a non-negligible and variable quantity of K2O (<0.86 wt%). Small crystals exhibit a greater proportion of potassium oxide. Additionally, the results show slight differences in the weight percentage of MgO. As small crystals exhibit a greater surface-to-volume ratio compared to large crystals, these variations in chemical composition are probably due to a promoted exposure of their surface to impurities (Fe, Mg, Na, Ti) in their immediate environment coming from rock-hosting ore and also upon contact with soil. These results indicate that Moroccan andalusite chemical composition significantly depends on the size of considered crystals.

Figure 4 locates Moroccan andalusite in Al2O3-SiO2-Impurities ternary composition diagram in comparison with different commercial andalusites provided by Imerys Refractory Minerals Company. The differences in chemical composition are mainly related to the age of the mineral deposit. Recently, it has been

| S1 3–2.5 cm | S2 2.3–2 cm | S3 2–1.6 cm | S4 1.8–1.5 cm | S5 0.9–0.8 cm | S6 0.5–0.3 cm |
|-------------|-------------|-------------|--------------|--------------|--------------|
| Al2O3       | 54.97       | 53.74       | 53.16        | 53.04        | 52.13        | 51.22        |
| SiO2        | 38.24       | 38.77       | 38.86        | 38.93        | 39.16        | 39.07        |
| Fe2O3       | 2.31        | 2.63        | 2.74         | 2.81         | 2.94         | 2.86         |
| Na2O        | 0.17        | 0.26        | 0.41         | 0.52         | 0.85         | 1.10         |
| K2O         | 0.55        | 0.79        | 0.80         | 0.86         | 0.84         | 0.84         |
| TiO2        | 0.86        | 0.95        | 0.92         | 0.91         | 0.90         | 0.94         |
| MgO         | 0.35        | 0.50        | 0.45         | 0.43         | 0.52         | 0.61         |
| CaO         | 0.23        | 0.38        | 0.56         | 0.59         | 0.66         | 0.68         |
| P2O5        | 0.07        | 0.08        | 0.07         | 0.07         | 0.09         | 0.07         |
| MnO         | 0.03        | 0.03        | 0.02         | 0.03         | 0.02         | 0.04         |
suggested that this important 'time function' is related not only to the age of the minerals itself but also to the age of the individual crystals ('crystal age'), namely, the elapsed time between the initial crystal deposition and their removal (resorption process) from the host rock [24].

3.1.3. Microstructure
Optical microscopy and SEM have been carried out to observe the microstructure of a previously polished section of an andalusite crystal (figure 5).

The cross section shows an obscure off-white X cross with a blackish body color that is probably caused by carbonaceous substance inclusions (figure 5(a)) indicating that this andalusite is of the chiastolitic type (the most frequent mineral form) [7]. Furthermore, numerous microcracks and irregular rod-shaped inclusions can be observed (figure 5(b)).

3.1.4. Elemental chemical mapping
To evaluate the chemical distribution of elements and identify the nature of mineral inclusions within andalusite crystal microstructure, SEM-EDS elemental mapping was performed (figure 6).

From a general point of view, the results indicate a heterogeneous distribution of chemical elements. Extending over nearly the entire surface, the dark grey blocky phase observed on the original micrograph is rich in aluminum. As confirmed by the EDS color map, Al element (in red colour) was almost uniformly dispersed in the andalusite chiastolites. Simultaneously, most of the green round-like Si element is distributed in the Al zone with some coarse meshes of approximately 50 μm, which are not easily observed by SEM. In micaceous metamorphic rocks, Ríos et al [25] highlighted that Al-rich minerals such as andalusite form poikiloblasts rich in quartz inclusions.
EDS analysis also shows the existence of Fe (in yellow colour) in relatively small quantities, while the distribution of K and Mg elements distribution exhibits a complementary relationship, suggesting that Fe, K, and Mg may attest to the existence of the muscovite’s phase [19]. Ti (in orange colour) was also detected in the form of small lines. The results presented above are in line with those of other studies, as previously described by Wala et al [6] for South Africa’s andalusite. Concerning mineral inclusions, they have been probably incorporated inside andalusite through microstructural defects during crystal growth (as primary inclusions), and they have subsequently developed from the alteration of the host mineral (as secondary inclusions). However, the nature of the impurities and the size of chiastolite can vary widely from one deposit to another, depending on the conditions (such as temperature, pressure, and impurities present in the surrounding areas) governing the genesis of the andalusite minerals [19].

3.2. Characterization of andalusite powder
3.2.1. Particle-size distribution and density
The finely ground powder of the starting mixed andalusite crystals obtained after sieving at 50 μm was composed of 36 wt% S1, 22 wt% S2, 15 wt% S3, 7 wt% S4, 10 wt% S5, and 10 wt% S6 corresponding to the weight proportions collected for the batches with different sizes. Figure 7 shows an almost bimodal wide particle size distribution ranging from 1 to 65 μm and a median diameter (D50) of approximately 13.06 μm. Some particles with a maximum size of over 50 μm passed through the sieve because of their anisometric morphology. The powder density value of Moroccan andalusite was estimated using the helium pynometry method at 2.672 g cm⁻³.

3.2.2. Phase quantification by XRD
Mineralogical and structural analyses of the previous powder were performed using a Bruker D8 Advance x-ray diffractometer and Rietveld quantitative analysis. The XRD patterns recorded under ambient conditions (figure 8(a)) show the presence of (i) andalusite (PDF-00-042-1468) as the major phase, (ii) quartz inclusions, (PDF-00-046-1045), and (iii) muscovite (KAl₂(AlSi₃O₁₀)(OH,F)₂) (PDF-00-002-0467). The Rietveld quantitative analysis revealed the following estimated proportions: 90.36% andalusite (Rp = 4.72, Rwp = 5.95), 5.94% quartz (Rp = 6.34, Rwp = 7.06) and 3.70% muscovite (Rp = 5.25 and Rwp = 6.77) with Rp and Rwp as
Almost similar phases have been reported by other authors [6, 17]. Table 2 shows the refined crystallographic data of the Moroccan andalusite powder compared to data available in literature.

The refined structure was orthorhombic with a space group type of Pnmm, and lattice parameters of \(a(\text{Å}) = 7.7930(5), b(\text{Å}) = 7.8970(6), \) and \(c(\text{Å}) = 5.5540(6)\). The original structure provided by Taylor was shown to be Pnmm [21].

The MAn consists of aluminum with two coordination configurations, and approximately half of the aluminum atoms were bridged by six oxygen atoms (figure 8(b)). These octahedral groups form chains parallel to the \(c\)-axis and, share edges. Five oxygen atoms were octahedrally coordinated with the remaining aluminum atoms. These groups, which occur in pairs with a common edge, are bound to the silicon tetrahedra via oxygen, thereby forming a supporting framework for the chains of aluminum octahedra.

Table 2. Refined crystallographic data of Moroccan andalusite compared to literature values.

| Lattice parameters | Cell parameters | Space group | Crystal system |
|-------------------|----------------|-------------|----------------|
| \(a(\text{Å})\) | \(b(\text{Å})\) | \(c(\text{Å})\) | \(\alpha\) | \(\beta\) | \(\gamma\) | |
| 7.7930(5) | 7.8970(6) | 5.5540(6) | 90 | 90 | 90 | Pnmm | Orthorhombic |

profile R factor and weighted profile R factor, respectively. Almost similar phases have been reported by other authors [6, 17].

Figure 7. Particle-size distribution of the mixed ground and sieved Moroccan andalusite powder.

Figure 8. (a) XRD patterns obtained with the final Rietveld plot of the raw MAn powder (\(Q = \) quartz; \(An = \) andalusite; \(Mu = \) muscovite), (b) representation of structure after refined crystal structure of orthorhombic Moroccan andalusite; Al is within the light green tetrahedra, Si is within the blue tetrahedra, and O are represented in red.
3.2.3. Effect of the decomposition during thermal treatment

Thermal analyses were performed to study the effect of andalusite on the mullite transformation during heating. Figure 9, thermogravimetric analysis (TGA) shows a total weight loss of ∼0.9 wt% between 30 and 1600 °C.

Moreover, a remarkable loss of 0.3 wt% with the released gas at m/z = 44 (CO₂) detected by mass spectrometry (MS) may be assigned to the outgassing of the graphite contained in andalusite, which is responsible for the initial dark grey color. Wala et al[6] identified graphite in the mineral composition of andalusite from South Africa and France, thus supporting the above mass spectrometric results. The followed insignificant weight loss (1200 °C–1600 °C) with no gas released was ascribed to the structural reorganization process of andalusite, leading to the very gradual crystallization of mullite (equation (2)) [30].

\[
3\text{Al}_2\text{Si}_3\text{O}_9 \xrightarrow{1150 - 1500\degree C} (3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2) + \text{SiO}_2 \text{ (amorphous)}
\]

The changes in size of heated samples can supply additional and useful information with respect to TGA/MS analysis, especially during andalusite to mullite transformation. In figure 10, the dilatometric curve shows noticeable changes up to 1600 °C which can be divided in seven domains labelled D₁ to D₇.

From room temperature to 573 °C (D₁ domain), the material exhibits a progressive expansion of approximately 0.07% which can be attributed to the normal intrinsic dilatometric behavior. Around 573 °C, a slight expansion singularity highlights the α→β transition of quartz, which is the so-called quartz dilatometric anomaly [9]. Expansion continues to increase at a slower rate with a tiny change in the dimensions between 600 °C and 950 °C corresponding to D₂ domain.

Above 950 °C, a sharp shrinkage of approximately 0.12% occurred up to 1250 °C, corresponding to D₃ domain. This behavior can be explained by the existence of melting elements (impurities), particularly because of the collapse of the mica-muscovite (KAl₂Si₃AlO₁₀(OH)₂) network (figure 9(a)) [31, 32]. However, the curve stabilizes between 1300 and 1500 °C (D₄) owing to the mullitization process, where the Al/Si site reorganization reactions yield 3:2-mullite (3SiO₂·2Al₂O₃) and amorphous silica (SiO₂) according to equation (2) [30]. The significant shrinkage (D₅) occurring between 1500 °C and 1600 °C can be related to the sufficiently low viscosity
of a probably slight amount of amorphous phase (silica rich owing to the decomposition of andalusite and melting with initial impurities) [27, 28]. Coefficient of thermal expansion (CTE) value of andalusite powder compact is $13.35 \times 10^{-6}$ $\degree$C$^{-1}$ in the almost linear range 350 $\degree$C–500 $\degree$C, which differs from the average CTE value of andalusite crystals [9], probably because of the impurities. During the free cooling to room temperature, the dilatometric evolution is typical of a stable material: the recorded CTE value is equal to $7.01 \times 10^{-6}$ $\degree$C$^{-1}$ between 1450 and 1250 $\degree$C ($D_0$), which is in agreement with the average CTE value considering the $a$, $b$, and $c$ axes of mullite ($6.98 \times 10^{-6}$ $\degree$C$^{-1}$) [9, 33]. Finally, the change in the slope of the curve taking place at about 730 $\degree$C during cooling ($D_1$ domain) was probably due to a slight diffuse microcracking onset within the sintered specimen. The lack of a quartz beta-to-alpha transition indicates that quartz was no longer within the phases of the sample.

### 3.3. Characterization of compacted-powder discs sintered at different temperatures

#### 3.3.1. Visual inspection

Figure 11 shows the resulting surface of pressed disc-shaped andalusite specimens after sintering at various temperatures: increasing the temperature of the heat treatment changes gradually its color from dark grey to light red after sintering at 1100 $\degree$C and, subsequently, at 1200 $\degree$C.

In comparison, the initial darkening color can be attributed to the presence of carbonaceous substances as highlighted in the previous section. Therefore, this change in color during heating can be explained by both the outgassing of volatile carbon compounds and mainly by $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation. With the additional mechanistic insights described by Taran and Koch-Müller [9], the light red color could be highlighted by the $\text{Fe}^{3+}$ ions responsible for the hematite phase ($\text{Fe}_2\text{O}_3$).

However, further thermal treatments showed a decrease in the intensity of the red coloration until the color disappeared from 1300 $\degree$C to 1500 $\degree$C, temperature which corresponds to the formation a significant amount of mullite phase. This result suggests that the interaction between mullite and iron oxide decreases the red hematite phase when sufficient mullite is formed to dissolve all the present $\text{Fe}_2\text{O}_3$. Thus, the white color of the mullite phase becomes predominant [34]. In contrast, excessive sintering (i.e., 1600 $\degree$C) causes the formation of oxidation and the collapse of the sample structure, and therefore, a significant melt color change was observed. According to Eigenmann and Günthard [35], Fe-Ti interactions are probably involved in this color change, as has been concluded with a Brazilian andalusite.

#### 3.3.2. Evolution of crystalline phases after various thermal treatments

Infrared spectroscopy (FTIR) measurements have been performed in order to follow the evolution of the main phases in andalusite powder after different sintering at 1100, 1200, 1300, 1400, 1500, and 1600 $\degree$C for 2 h. Figure 12 clearly shows the disappearance of andalusite for the benefit of mullite: a progressive lowering of the bands related to andalusite ($1073, 1017, 936, 905$ and $776$ cm$^{-1}$) can be observed and correlated with the rising amplitude of the bands associated the 3:2-mullite ($1175, 1125, 830, 814$ and $725$ cm$^{-1}$) [17, 36].

In addition, the room-temperature XRD patterns of andalusite powder previously heat-treated for 2 h between 1100 and 1600 $\degree$C are shown in figure 13.

At the sintering temperature range of 1100 $\degree$C–1200 $\degree$C, the intensity of the andalusite and quartz ($\text{SiO}_2$) peaks decreases and the crystallization of mullite begins but it is still not clearly identified. Note that muscovite originally present in the raw powder is not detected which may be due to its partial melting. Indeed, Barlow et al [32] highlighted that muscovite may even be transformed into aluminosilicate at temperatures above approximately 757 $\degree$C and can be thoroughly replaced by kyanite based or potash feldspar-based melts. In addition, the early stages of muscovite breakdown over the temperature range 680 $\degree$C–757 $\degree$C have been evidenced by the development of melting process on an extremely localized scale along grain boundaries between quartz and muscovite [37]. Over 1300 $\degree$C, intensity of andalusite peaks is strongly attenuated, indicating that it is consumed during the formation of mullite and amorphous silica through a topotactical reaction while the peaks of mullite appeared and those of quartz vanished.
When the sintering temperature reached 1400 °C, the andalusite peaks entirely disappeared, giving rise to intense mullite peaks. These features indicate that Moroccan andalusite’s transformation into 3:2 mullite started at 1100 °C and ended at 1500 °C. Various studies have suggested that the actual temperature of the andalusite to mullite transformation depends on several kinetic parameters, such as the origin of the andalusite, sintering duration, and particle size distribution of the investigated powder. For example, Li et al\[38\] reported that when andalusite is pulverized into a micron-sized powder (<10 μm), the temperature necessary to completely decompose andalusite to mullite decreases to 1200 °C–1250 °C. Furthermore, impurities such as Fe_2O_3 and CaO tend to reduce the temperature transformation\[39\]. Li et al\[38\] found that TiO_2 and MgO encouraged mullite formation from andalusite by decreasing the temperature, thus forming liquid crystalline systems.

3.3.3. Quantitative analysis of crystalline and amorphous phases
To evaluate the amount of crystalline and amorphous phase originating from andalusite transformation after various thermal treatments, each phase was quantified using TOPAS 2.1 software (Internal Standard Method). The results are shown in figure 14.

First, even at 1100 °C, the formation of both mullite and amorphous phases starts to appear according to equation (3). The quantity of the remaining orthorhombic-andalusite was approximately equal to 85 wt%, ~5.2 wt% for mullite, and a small amount of the amorphous phase (~5 wt%) was observed. By increasing the sintering temperature to 1200 °C, both mullite and the amorphous phase gradually formed together. However, from 1200 °C to 1300 °C, andalusite started to decompose noticeably, and the rate of transformation into mullite
increased. No quartz is observed above 1200 °C. At 1400 °C, some untransformed andalusite (∼18.75 wt%) was still observed, whereas at 1500 °C, the andalusite was completely decomposed into mullite. At this point, the maximum quantity of mullite (83.4 wt%) was reached, accompanied by a remarkable increase in the amorphous phase content to 16.6 wt%. Upon further sintering at 1600 °C, the amorphous phase increases further up to 21.8 wt% concomitantly to reducing of mullite phase (78.2 wt%). This result is consistent with previous findings [39–41].

3.3.4. Structural refinement of the formed mullite by the Rietveld method

The crystallographic structure of the mullite phase occurring during the transformation of Sidi Bou Othman deposit (Morocco) andalusite at 1500 °C has been refined the Rietveld method with R-factor = 1.27. The results were compared with those of other studies available in the scientific literature. As summarized in table 3, the crystal structure of 3:2-mullite is orthorhombic with space groups of Pbam and lattice parameters of a (Å) = 7.552(1), b (Å) = 7.699(3), and c (Å) = 2.8891(3) (based on the XRD pattern shown in figure 15(a)), which are very close to the literature data.

Both mullite and andalusite consist of chains composed of edge-sharing AlO₆ octahedra extending parallel to the crystallographic c-axis (figure 15(b)). However, in the mullite phase, the link between the AlO₆ octahedral chains was formed by double Al-Si-tetrahedral chains with a statistical cation occupation model in the tetrahedra. Owing to the higher Al₂O₃ content in mullite, more available tetrahedral sites are occupied by Al³⁺ ions than by Si⁴⁺, and some of the oxygen atoms bridging the tetrahedra are removed for charge compensation. These findings were in agreement with the original structure determined by Taylor [21].

3.3.5. Microstructure

To provide further evidence supporting the XRD and Rietveld quantification results and to better understand the microstructural change involved in the andalusite to mullite transformation, the microstructure of all samples sintered between 1100 and 1600 °C has been observed by SEM (figure 16).

At 1100 °C, distinguishable andalusite grains similar to those of the raw state can be observed. However, the material sintered at 1300 °C shows the occurrence of a crystalline mullite network composed of small granular andalusite crystals. Between 1400 and 1500 °C, wider and interconnected mullite crystals were generated from andalusite grains. The linking mechanism can also be seen as a bridge between the formed mullite crystals.
At 1600 °C, significant changes in the microstructure characterized by the growth of mullite crystals and an increase in the amount of the amorphous phase are recorded (figure 17). The shape of the silica capillary network exhibits a typical dimension of a few tens of micrometers, strongly embedding mullite crystals. In contrast, the existence of a wide vitreous phase in the sample suggests that the contacts between the mullite grains increased, thereby leading to the formation of more crystal interconnections and reduced porosity during sintering, thus facilitating densification [38, 40].

3.3.6. Mechanical properties

The mechanical properties of the sintered specimens were assessed using indirect tensile strength testing (figure 18) at room temperature. When the sintering temperature increased from 1100 °C to 1600 °C, stress to rupture values increase from 5.6 to 13.4 MPa concomitantly with a decrease in apparent porosity from 32.4% to 13.7% (table 4). Indeed, the samples sintered at a higher temperature exhibit greater densification, which is why the mechanical strength immediately increased before fracture, as is frequently observed for dense and rigid materials [45, 46]. This result indicates that the mullitisation rate of andalusite observed with increasing sintering temperature has a significant influence on the mechanical properties of andalusite-based materials. During the thermal transformation of andalusite, the formed mullite (as a strong crystalline phase) and vitreous silica promoted two interconnected networks within the microstructure; the amorphous phase filled small pores and significantly strengthened the material body [42].

The findings of this study show that the microstructural properties and mechanical features of the studied andalusite-based sintered material can be proven by an optimal choice of sintering temperature.
4. Conclusion

A Moroccan andalusite belonging to the chiastolite group localized in the region of Sidi Bou Othman has been extensively investigated. Both andalusite crystals, ground powder, and disc-shaped specimens fired at different temperatures were analyzed to understand the effect of andalusite to mullite transformation on the structure, microstructure, thermal behavior, and mechanical properties. The main conclusions are as follows:

1. Andalusite single crystals: The chemical composition is closely dependent on the crystal grain size, which is related to the alumina content (42–45.16 wt% Al₂O₃) and to impurities such as Fe, Ti, K, and Na mostly

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Table 4. Effects of sintering temperature on the porosity and mechanical characteristics.

| Sintering temperature (°C) | Apparent porosity (%) | Indirect tensile strength (MPa) |
|---------------------------|-----------------------|-------------------------------|
| 1100                      | 32.4 ± 0.2            | 5.6 ± 0.6                     |
| 1200                      | 30.5 ± 0.1            | 7.5 ± 1.0                     |
| 1300                      | 28.1 ± 0.09           | 9.5 ± 1.6                     |
| 1400                      | 28.4 ± 0.5            | 10.2 ± 0.9                    |
| 1500                      | 26.2 ± 0.07           | 11.4 ± 1.3                    |
| 1600                      | 13.7 ± 0.2            | 13.4 ± 1.5                    |

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Figure 17. Magnified SEM image of mullite after sintering at 1600 °C.

Figure 18. Typical strength versus displacement curves of disc-shaped samples after a thermal treatment at various temperatures.
localized at the surface of grains. The secondary crystalline phases detected in the studied deposits are quartz and muscovite.

2. Andalusite ground powder during thermal treatment: Increasing the heat treatment temperature led to a linear thermal expansion coefficient value of \(13.35 \times 10^{-6} \text{ K}^{-1}\) at the beginning of heating. Moreover, outgassing of carbonate compounds occurred at approximately 800°C (m/z = 44 - CO₂), and discoloration of the samples due to Fe²⁺/Fe³⁺ oxidation has been observed. Furthermore, the crystal structure of the andalusite powder and the mullite phase refined by the Rietveld method exhibited an orthorhombic structure with the space groups Pnmm and Pbam and lattice parameters a (Å) = 7.793, b (Å) = 7.897, c (Å) = 5.554, and a (Å) = 7.552, b (Å) = 7.699, c (Å) = 2.889, respectively, which is consistent with the results provided in the literature.

3. Disc-shaped specimens: After various heat treatments ranging from 1100 to 1600°C, XRD, quantitative phase analysis, and microstructural observations have shown that the formation of in situ 3:2 mullite started at 1100°C to 1200°C and finished between 1400°C and 1500°C. At 1500°C, the maximum quantity of mullite (83.4 ± 1.5 wt%) concomitantly to 16.6 wt% silica-rich amorphous phase have been achieved. Furthermore, the formed mullite and vitreous silica reduced the porosity from 32.4 to 13.7% when the sintering temperature increases up to 1600°C, thereby leading to an improved mechanical strength. The mechanical strength has been increased from 5.6 (1100°C) to 13.4 MPa (1600°C), highlighting promising performance for high-temperature applications. These results provide new insights into the exploitation of Moroccan andalusite as a raw material for the development of highly pure mullite and pave the way for the development of high-quality aluminosilicate refractory materials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this study.

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References

[1] Peter Ihlen M 2000 Utilisation of sillimanite minerals, their geology, and potential occurrences in Norway—an overview Ngu-Bull. 436 113–28
[2] Lehtinen M 2015 Industrial minerals and rocks Min. Depos. of Finland 685–710 Chapter 9.5
[3] Hu X, Liu X, He Q and Wang H 2011 Thermal expansion of andalusite and sillimanite at ambient pressure: a powder x-ray diffraction study up to 1000°C Min. Mag. 75 363–74
[4] Nyoka M, Brazier D, Courtney T and Parry R A 2013 Merits of using andalusite-based refractories compared to bauxite-based refractories J. S. Afr. Inst. Min. Metal. 113 647–50
[5] Bohač M and Gregorová M 2009 The influence of blast-furnace slag hydration products on microcracking of concrete Mater. Charact. 60 729–34
[6] Schneider H and Komarneni S 2005 Mullite (Weinheim: Wiley) (https://doi.org/10.1002/3527607358)
[7] Wala T, Psitk B, Kubacki J, Stec K and Podwórny J 2014 Mullitization process of andalusite concentrates—role of natural inclusions Ceram. Inter. 40 5129–36
[8] Namiranian A and Kalantar M M 2011 Mullite synthesis and formation from kyanite concentrates in different conditions of heat treatment and particle size Iranian J. Mater. Sci. & Eng. 8 29–36
[9] Taran M N and Koch- Müller M 2013 FTIR spectroscopic study of natural andalusite showing electronic Fe–Ti charge-transfer processes: zoning and thermal evolutions of OH-vibration bands Phys. Chem. Min. 40 63–71
[10] Kakroudi M G, Huger M, Gault C and Chotard T 2009 Anisotropic behaviour of andalusite particles used as aggregates on refractory castables J. Eur. Ceram. 29 571–9
[11] Ren B, Li Y, Nath M, Wang Q and Xu Y 2018 Enhanced alkali vapor attack resistance of bauxite–SiC refractories for the working lining of cement rotary kilns via incorporation of andalusite Ceram. Int. 44 22113–20
[12] Ding D, Chen L, Liao G, Zheng L, Gao S and Ye G 1989 Preparation of andalusite–corundum–KAlSi2O6 material for the calcification of Li-ion battery cathode materials J. Alloys & Comp. 798 367–74
[13] Overbeek P W 1989 Andalusite in South Africa J. South African Inst. Min. & Met. 89 157–71
[14] Market analysis report, Andalusite Market Size, Share & Trends Analysis Report by Application (Refractories, Foundry, Kiln Furniture), By Region (North America, Europe, Asia Pacific, Central & South America, MEA), And Segment Forecasts, 2019–2025 (https://grandviewresearch.com/industry-analysis/global-andalusite-market) 2019 1–80
[15] Feytis A 2009 South African andalusite expansions Industrial Minerals, (London (UK)) (https://scholar.google.com/scholar_lookup?title=+South+Africa+andalusite+expansions+&author=Feytis+A.&publication_year=2009)
[16] Xiong X Y and Heever V D 2010 A refractory raw material andalusite: properties and application Proc. Conf. Metal. (COM 2010), Vancouver BC Canada 3–6
[17] Arib A, El Ouattab R, Remmal T and Moussa R 2004 Thermal behaviour and structural transformations of andalusite-rich aluminous nodules from Morocco Key Eng. Mater. 264 1815–8
[18] Sardy M, Arib A, El Abbassi K, Moussa R and Gomina M 2012 Elaboration and characterization of mullite refractory products from moroccan andalusite New J. Glass & Ceram. 2 121–5
[19] Clarke D B, Dorais M and Barbarin B 2005 Occurrence and origin of andalusite in peraluminous felsic igneous rocks J. Petrology 46 441–72
[20] Rodríguez-Carvajal J 1993 Recent advances in magnetic structure determination by neutron powder diffraction + FullProf Phys. B Cond. Matter. 192 55–69
[21] Taylor W H 1961 The structure of andalusite Zeitschr für Kristallographie—Crystalline Materials. 71 205–218
[22] Burnham C W and Buerger M J 1961 Refinement of the crystal structure of andalusite Z. Kristallogr. 115 269–90
[23] Imerys Refractory Minerals, Andalusite - Run of mine grade (https://imers-refractoryminerals.com/wpcontent/uploads/2014/09/Andalusite-Run-of-Mine.pdf) 2014 (Accessed 30 September 2017)
[24] Visona D, Carosi R, Montomoli C, Tiepolo M and Peruzzo L 2012 Miocene andalusite leucogranite in central–east himalaya (everest masang kang area): low-pressure melting during heating Liithos 144–145 194–208
[25] Rios C A and Castellanos O M 2016 Petrologic significance of Fe-rich staurolite in pelitic schists of the Silgará Formation, Santander Massif Earth Sci. Res. J. 20 1–7
[26] Anbalagan G and Sangeetha V 2015 Characterization of Indian Natural Mineral Andalusite Using XRD, Optical Absorption, Infrared, EPR and NMR Spectroscopic Techniques J. Phys. Res. 5 1–12
[27] Pannhorst W and Schneider H 1978 The high-temperature transformation of andalusite Bulletin of Mineralogy and Petrology 69 1–9
[28] Imerys Refractory Minerals, Andalusite - Run of mine grade (https://imers-refractoryminerals.com/wpcontent/uploads/2014/09/Andalusite-Run-of-Mine.pdf) 2014 (Accessed 30 September 2017)
[29] Visona D, Carosi R, Montomoli C, Tiepolo M and Peruzzo L 2012 Miocene andalusite leucogranite in central–east himalaya (everest masang kang area): low-pressure melting during heating Liithos 144–145 194–208
[30] Rios C A and Castellanos O M 2016 Petrologic significance of Fe-rich staurolite in pelitic schists of the Silgará Formation, Santander Massif Earth Sci. Res. J. 20 1–7
[31] Anbalagan G and Sangeetha V 2015 Characterization of Indian Natural Mineral Andalusite Using XRD, Optical Absorption, Infrared, EPR and NMR Spectroscopic Techniques J. Phys. Res. 5 1–12
[32] Pannhorst W and Schneider H 1978 The high-temperature transformation of andalusite (Al2SiO5) into 3/2-mullite (3Al2O3, 2SiO2) and vitreous silica (SiO2) Mineral. Mag. 42 195–8
[33] Winter J K and Ghose S 1979 Thermal expansion and high temperature crystal chemistry of the Al2SiO5 polymorphs Am. Min. 64 635–78
[34] Burt J B, Ross N L, Angel R J and Koch M 2006 Equations of state and structure of andalusite from 9.8 GPa and sillimanite to 8.5 GPa Am. Min. 91 319–26
[35] Mazzoni A D and Aglietti E F 1999 Study of the mechanism of andalusite-Al¹²-N2 reaction using the combination of DTA-TG-DTG techniques Ceramics 45 292–3
[36] Leece-NNana G L, Bonnet J-P and Blanchart P 2011 Investigation of the sintering mechanisms of kaolin–muscovite App. Clay Sci. 51 445–51
[37] Barlow S G and Manning D A C 1999 Influence of time and temperature on reactions and transformations of muscovite mica British Ceram. Trans. 98 122–6
[38] Rebouillat L and Rigaud M 2002 Andalusite-based high-alumina castables J. Am. Ceram. Soc. 85 373–8
[39] Meisel W, Schnellnath J, Griesbach P and Gutlich P 1990 The state of iron in andalusite Hyperfine Interact. 57 2261–8
[40] Eisengarn K and Gunhild H 1972 Valence states, redox reactions and biparticle formation of Fe and Ti doped sapphire Eigenmann K and Gunthard H 1972 Valence states, redox reactions and biparticle formation of Fe and Ti doped sapphire Chem. Phys. Letter 13 58–61
[41] Zhai K, Xue W, Wang H, Wu X and Zhai S 2020 Raman spectra of sillimanite, andalusite, and kyanite at various temperatures Phys. Chem. Min. 7 426–32
[42] Faust J and Knittle E 1994 The equation of state, amorphization, and high pressure phase diagram of muscovite IGR Solid Earth 99 19785–92
[43] Li B, He M and Wang H 2017 Phase transformation of andalusite-mullite and its roles in the microstructure and sinterability of refractory ceramic Metall. & Mater. Trans. A 48 3188–92
[44] Pudavarvdh V, Baghsahi S, Mirbadi B, Souri A R and Arabi H 2012 Effect of MgO and CaO on transformation of Andalusite to Mullite J. Mater. Eng. & Perform. 21 1637–44
[45] Fang J, Yan B and Deng T 2019 Fast transformation of andalusite into mullite by addition of yttria Boletin de la Sociedad Española de Cerámica y Vidrio 58 142–50
[46] Kemethmuller S, Roosen A, Goetz- Neunhoeffer F and Neubauer J 2006 Quantitative analysis of crystalline and amorphous phases in glass–ceramic composites like LTCC by the rietveld method J. Am. Ceram. Soc. 89 2632–7
[47] Piaty P, Tesser-Doyen N, Njopwouo D and Bonnet J-P 2009 Effect of densification and mullitization on the evolution of elastic properties of a clay-based material during firing J. Eur. Ceram. Soc. 29 1579–86
[48] Majidian H, Nikzad L, Esfami-Shahed H and Ebadzadeh T 2016 Phase evolution, microstructure, and mechanical properties of aluminamullite–zirconia composites prepared by Iranian andalusite Int. J. Appl. Ceram. Technol. 13 1024–32
[49] Hua C, Wub J, Xub X and Chen P 2018 Investigating the effect of andalusite on mechanical strength and thermal shock resistance of cordierite-spodumene composite ceramics Ceram Int. 44 3240–7
[50] Mouiya M et al Effect of sintering temperature on the microstructure and mechanical behavior of porous ceramics made from clay and banana peel powder Res. Mater. 4 2019100028
[51] Mouiya M, Abourrache A, Benhammou A, El Hafiane Y, Aboulaiyim Y, Nibou L, Oumam M, Hannache H and Smith A 2017 Porous ceramic from Moroccan natural phosphate and raw clay for microfiltration applications Desalin. Water Treat. 83 277–80