

# Manufacture of mullite substrates from andalusite for the development of thin film solar cells

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## Abstract

The purpose of this work is the manufacture of dense thin mullite substrates by tape casting of the natural silicate mineral andalusite. The targeted application for such substrates is the manufacture of thin film solar cells. Indeed, in addition to a good resistance at high temperature (up to 1200 °C), this application requires a good correspondence between the thermal expansion coefficient of the substrate and silicon film in order to lower the stresses in the film and in the substrate after cooling. The work was performed in three successive stages. First, the study of the transformation during sintering of andalusite + alumina mixtures. Second, the optimisation of the slurries and of the parameters for tape casting. Finally, green tapes prepared from various powder compositions were characterised before and after sintering. The addition of alumina to andalusite reduces the final amount of vitreous phase. This limits the risk of impurity diffusion in the silicon film. However, the addition of alumina also slows down the sintering process leading to more porosity in the substrates. A good compromise is obtained with an initial mixture of 80 wt.% andalusite with 20 wt.% alumina. In that case, the thermal expansion behaviour is very close to pure mullite and the mechanical properties of the substrates can be considered as sufficient for the targeted application. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Al<sub>2</sub>O<sub>3</sub>; Andalusite; Mullite; Sintering; Solar cells; Tape casting

## 1. Introduction

Due to its high refractoriness and its good mechanical properties, mullite is a material widely used in the manufacture of industrial ceramic parts. Natural mullite is too rare for industrial use but synthetic mullites can be obtained by transformation on heating of natural aluminosilicate minerals and also from chemical routes.<sup>1</sup> The use of natural minerals is of high interest on the economic point of view, even if the products obtained are much less pure than when using a chemical process.

Mullite is the only crystalline compound stable under atmospheric pressure, in the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> system (Fig. 1). Mullite is proposed to be a solid state solution between 70.5 and 74.0 wt.% alumina.<sup>2,3</sup> It has also been shown, that metastable mullite compositions are possible between 74.0 and 83.6 wt.% alumina.<sup>4–7</sup> The overall composition of mullite can be written as follows:<sup>9,10</sup>



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When  $x=0.25$  (71.8 wt.% alumina), the composition corresponds to 3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>; the mullite is called 3:2 mullite. This composition is commonly thought to form by reaction in the solid state.<sup>7</sup> More alumina rich compositions are obtained from melts.<sup>2–7</sup> When  $x=0.4$  (77.2 wt.% alumina) the composition corresponds to 2Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> and is called 2:1.

Two main types of natural raw materials can be used to produce mullite.

(1) Hydrous aluminosilicates. Mainly based on kaolinite (2SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O), they contain high amounts of silica so that their transformation yield to mullite is very poor (max. 64 wt.%). Moreover they often contain high amounts of impurities.

(2) Anhydrous aluminosilicates. Sillimanite, andalusite and kyanite are polymorph minerals having the same composition: Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>. Their transformation yield to mullite is high (88 wt.%). Unlike kyanite, the densities of andalusite and sillimanite are very close to that of mullite so their transformation does not lead to significant volume changes (Table 1). Moreover the temperature required to form mullite is much lower with andalusite than with sillimanite. Therefore, andalusite seems to be the best candidate to manufacture dense

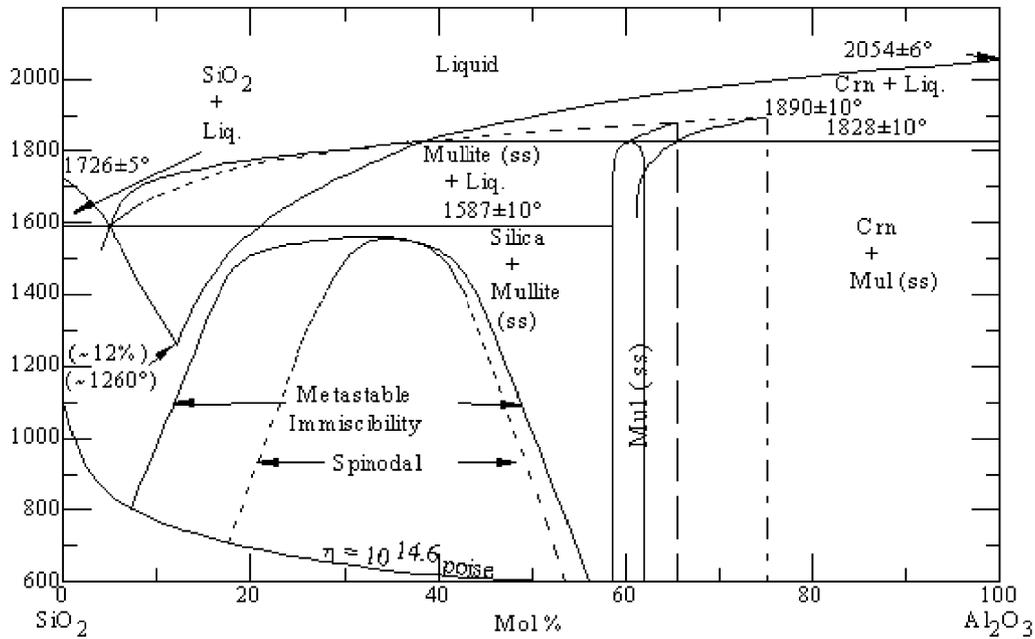
Fig. 1.  $\text{Al}_2\text{O}_3/\text{SiO}_2$  phase diagram.<sup>6</sup>

Table 1  
General information on the transformation of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  minerals into mullite

|                                  | Sillimanite  | Andalusite   | Kyanite   | Mullite      |
|----------------------------------|--------------|--------------|-----------|--------------|
| Density                          | 3.23–3.27    | 3.13–3.20    | 3.55–3.65 | 3.15–3.22    |
| Crystalline structure            | Orthorhombic | Orthorhombic | Triclinic | Orthorhombic |
| Temperature of mullite formation | 1550         | 1380–1400    | 1350–1380 | –            |
| Volume changes                   | +2%          | ≈0           | +15–18%   | –            |

mullite parts with good properties. From the industrial point of view, andalusite is also an interesting raw material as this mineral is available at low cost from several extraction sites.

The target of the present work is the manufacture of thin ceramic substrates (thickness <1 mm) that can be used for microelectronic applications and especially for the manufacture of thin film solar cells. In this specific case, the interest in using mullite instead of alumina, as it is often the case in microelectronic, is the thermal expansion behaviour of mullite. Indeed, the behaviour of mullite is very close to that of polycrystalline silicon ( $\alpha_{20-900\text{ °C}} = 5.0 \times 10^{-6}$  and  $4.0 \times 10^{-6} \text{ K}^{-1}$  respectively against  $8.4 \times 10^{-6} \text{ K}^{-1}$  for alumina). Matching dilatometric coefficients is a great advantage when a silicon film must be deposited on the ceramic substrate at high temperature (e.g. by CVD or LPE) while lower the residual stresses after cooling.<sup>8</sup>

The shaping process best adapted for manufacturing such thin ceramic parts is tape casting. This process is widely used in microelectronic industry and allows the manufacture of parts with high surface and low thickness, down to 50  $\mu\text{m}$ .

## 2. Experimental procedure

The experimental work has been performed in three successive stages:

- First, investigation of the transformation of andalusite + alumina mixtures on heating and of the sintering behaviour of these mixtures.
- Second, optimisation of the slurries and of the tape casting conditions of the best composition determined in stage one.
- Finally, preparation and characterisation of green and sintered ceramic tapes.

### 2.1. Characterisation of the transformation of the andalusite + alumina mixtures into mullite

Mixtures of andalusite with alumina were prepared by mixing the powders in a mixing mill for 2 h (Table 2). A fine andalusite powder (Kerphalite KF5, DAMREC, France), with an average grain size  $d_{50}$  equal to 3.6  $\mu\text{m}$ , was chosen to favour subsequent mullite formation. A very fine alumina powder (P172SB, Aluminium

Table 2  
Initial powder composition of the samples

| Sample reference      | 100/0 | 80/20 | 70/30 | 60/40 |
|-----------------------|-------|-------|-------|-------|
| Andalusite KF5 (wt.%) | 100   | 80    | 70    | 60    |
| Alumina P172SB (wt.%) | 0     | 20    | 30    | 40    |

Pechiney, France), with a  $d_{50}$  of 0.6  $\mu\text{m}$ , was also chosen to increase the reactivity with the silica produced by transformation of andalusite into mullite. The main characteristics of powders KF5 and P172SB are given in Table 3.

The phase transformations during heating were followed by X-ray analysis. Compacts of andalusite + alumina mixtures were prepared by uniaxial pressing in a stainless steel die under 100 MPa. These compacts were heat-treated in air during 2 h at various temperatures between 1200 and 1700 °C. After cooling, an X-ray analysis was performed on each sample with a diffractometer Siemens D500 using copper  $K_{\alpha 1,2}$  radiation. The amounts of mullite and residual alumina were determined from the X-ray diffraction patterns. The calculations were based on the relative intensities of selected Bragg reflections (Table 4) and by comparison to the relative intensities obtained on a standard containing the same crystalline phases.

The sintering behaviour of the mixtures andalusite + alumina was investigated by dilatometry (Adamel DI 24) from room temperature up to 1700 °C with a heating rate of 5 °C/min. Powder compacts were also used for this study.

## 2.2. Optimisation of the tape casting

The type and relative fractions of the additives used in the preparation of the slurries were selected from

Table 3  
Main characteristics for the andalusite and alumina powders

| Powder                                  | KF5  | P172SB |
|---|------|--------|
| Specific area ( $\text{m}^2/\text{g}$ ) | 4.3  | 10.3   |
| Grain size $d_{50}$ ( $\mu\text{m}$ )   | 3.6  | 0.62   |
| $\text{Al}_2\text{O}_3$ (wt.%)          | 61.9 | 99.7   |
| $\text{SiO}_2$ (wt.%)                   | 36.8 | 0.05   |
| Other compounds (wt.%)                  | 1.3  | 0.25   |

Table 4  
Bragg reflections used for the determination of the amounts of each crystalline phase

| Crystalline phase | $D$ ( $\text{\AA}$ ) | $2\theta^\circ$ | $h k l$ |
|-------------------|----------------------|-----------------|---------|
| Alumina           | 2.08                 | 43.4            | 1 1 3   |
| Mullite           | 2.69                 | 33.2            | 2 2 0   |
| Andalusite        | 2.77                 | 32.2            | 2 2 0   |

literature data. Only the type of solvents, the amount of dispersing agent and the total amount of additives were investigated.

Organic azeotropic systems as butanone-2 (MEK)/ethanol (66/34 wt.%) or trichloroethylene/ethanol (72/28 wt.%) are often used as dispersing liquid phase in tape casting.<sup>11</sup> A preliminary study had shown that the MEK/ethanol system leads to a better dispersion of the andalusite powder (less dispersing agent required) and to a better stability of the slurry. Moreover, it allowed an increase in the fraction of powder in the slurry for a targeted viscosity. This lowering in amount of liquid makes easier the step of evaporation after tape casting.

The types and relative fractions of additives were chosen according to literature data. The dispersing agent was the polyester/polyamide co-polymer Hypermer KD1 (ICI Surfactant, USA). Polyvinylbutyral PVB (Butvar B-98, Monsanto, France) was chosen as the binder. Two plasticisers in the volume ratio 1:1 were introduced in the slurries (polyethylene glycol PEG<sub>400</sub>,  $M = 400$  g/mol,  $d = 1.13$ , Prolabo, France and dibutyl phthalate DBP,  $M = 278$  g/mol,  $d = 1.04$ , Aldrich, France). The volume ratio plasticisers/binder was fixed at 1.75.

The successive steps for the preparation of the slurries are shown in (Fig. 2). At a first stage, the andalusite and alumina powders are mixed and de-agglomerated in the solvents in the presence of the dispersing agent by ball milling for 5 h. Then, the binder and the plasticisers are added to the slurry and mixed in a ball mill for 20 h for good homogenisation. After sieving, the gas trapped in the slurry is removed under partial vacuum in order to avoid bubbles in the final tape. The slurry is then ready for tape casting.

The optimisation of the amount of dispersing agent was performed by viscosity measurement on the mixture of solvents + dispersing agent + powders using a Rotovisco VT500 viscometer (Haake) at  $21 \pm 2$  °C and with a shear rate of  $350 \text{ s}^{-1}$ . The rheologic behaviour of the slurries after addition of the binder and plasticisers was

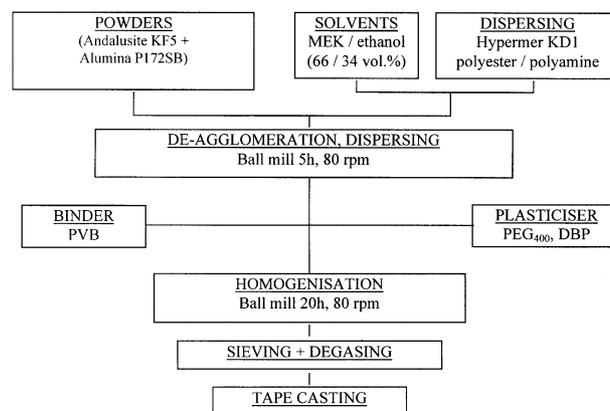


Fig. 2. Preparation of the slurries for tape casting.

investigated with the same equipment and by varying the shear rate between 0 and 250 s<sup>-1</sup> for 6 min.

### 2.3. Characterisation of the green and sintered substrates

The porosity of the substrates after organic additives burning out and after sintering was measured by mercury porosimetry with a Micromeritics Autopore III 9420.

The additive burning out conditions were determined from TGA on the green tapes. These conditions were: 120 °C/h up to 150 °C, 7.5 °C/h up to 300 °C, 15 °C/h up to 500 °C, holding of 2 h at 500 °C then cooling to room temperature at 300 °C/h.

The sintering conditions were: 300 °C/h up to 1700 °C, holding of 2 hours and cooling to room temperature at 300 °C. The strength of the sintered tapes were measured by four point bending tests (upper span = 8 mm, lower span = 22 mm) using a drop by drop loading of the sample with water.

The thermal expansion coefficient of the sintered tapes was measured with a dilatometer Adamel DI 24. The thermal expansion curves measured on the tapes were compared to a substrate made by sintering of a pure mullite powder (KM 101 Kyoritsu, Japan).

## 3. Experimental results and discussion

### 3.1. Transformation of the andalusite powder on heating

The transformation of andalusite into mullite produces amorphous silica according to the reaction:



The vitreous phase can act as a preferential route for impurity diffusion. This can be a problem for the present application, as a very pure silicon film has to be deposited at the surface of the ceramic substrate. Therefore, additions of alumina to the initial andalusite powder were performed in order to investigate the possible transformation of the residual amorphous silica into mullite by direct reaction:



The mullite produced by reaction (1) is called primary mullite while mullite produced by reaction (2) is called secondary mullite. The compositions investigated are given in Table 2.

The X-ray patterns collected with the pure andalusite compacts (sample 100/0) show that the intensity of the andalusite peaks starts decreasing after heat-treatment at 1300 °C (Fig. 3). Simultaneously, the first peaks of

mullite are observed. The transformation seems to be completed after heat-treatment at 1450 °C as no more andalusite peaks are observed. As for pure andalusite, the X-ray patterns collected on compacts 80/20 show the transformation of andalusite into mullite occurred between 1300 and 1450 °C (Fig. 4). The addition of alumina does not seem to have any effect on the kinetic of transformation of andalusite into mullite. Indeed, the curves showing the fraction of andalusite transformed with temperature for the samples 100/0, 80/20 and 60/40 are perfectly superimposed (Fig. 5).

The reaction (2) starts above 1300–1350 °C, as soon as amorphous silica is produced from reaction (1). Fig. 6 shows the fraction of alumina transformed with temperature. For sample 80/20, a temperature of 1600 °C is required to transform all the alumina. For sample 60/40, about 1/3 of the initial alumina content is still observed after heat treatment at 1600 °C.

The dilatometric curve of pure andalusite shows two stages (Fig. 7). The sintering of the powder starts over 1100 °C but the transformation: andalusite to mullite + silica slows down this process between 1300 and 1400 °C. This is due to a slight increase in volume between andalusite and mullite. For temperatures higher than 1450 °C, the shrinkage rate increases rapidly. This step corresponds to the sintering of the mullite in the presence of a high amount of vitreous silica.

With the addition of alumina, the shrinkage starts at a lower temperature (approximately 1050 °C for mixture 60/40 instead of more than 1100 °C for mixtures 80/20 and 100/0). This corresponds to the early sintering of the highly reactive alumina powder. As previously the transformation andalusite into mullite + silica slows down the shrinkage between 1300 and 1400 °C. Over 1450 °C, the reaction between the alumina powder and the vitreous silica to form secondary mullite drastically decreases the amount of vitreous phase. This is not favourable to the sintering of the mullite already formed. Therefore, the shrinkage rates decrease significantly with the addition of alumina.

### 3.2. Tape casting of the andalusite + alumina mixtures

The first point investigated was the determination of the optimal content of dispersing agent. This was done by viscosity measurements on slurries containing 50 g solvent/100 g powder. The optimal content of dispersing agent was determined separately for the alumina and for the andalusite. A minimum in viscosity is obtained for a fraction 0.35 g dispersing agent/100 g andalusite powder and 1.2 g dispersing agent/100 g alumina powder (Fig. 8). The amount of dispersing agent requires for a good dispersion depends directly on the specific surface of the powder. This explains the significant difference between the alumina powder (specific surface: 10.3 m<sup>2</sup>/g) and the andalusite powder (4.3 m<sup>2</sup>/g). Sedimentation

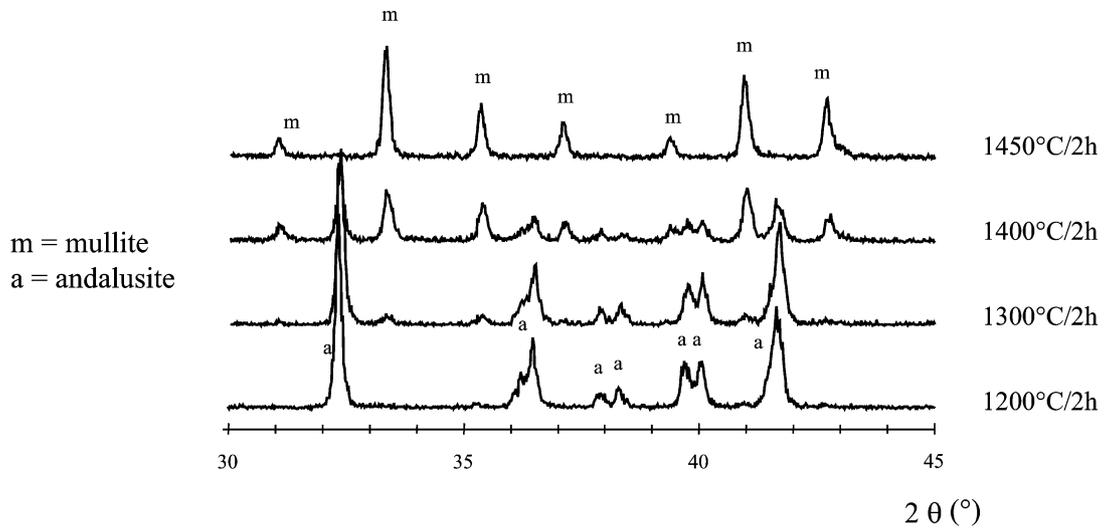


Fig. 3. X-ray diffraction patterns obtained after heat-treatments on pure andalusite.

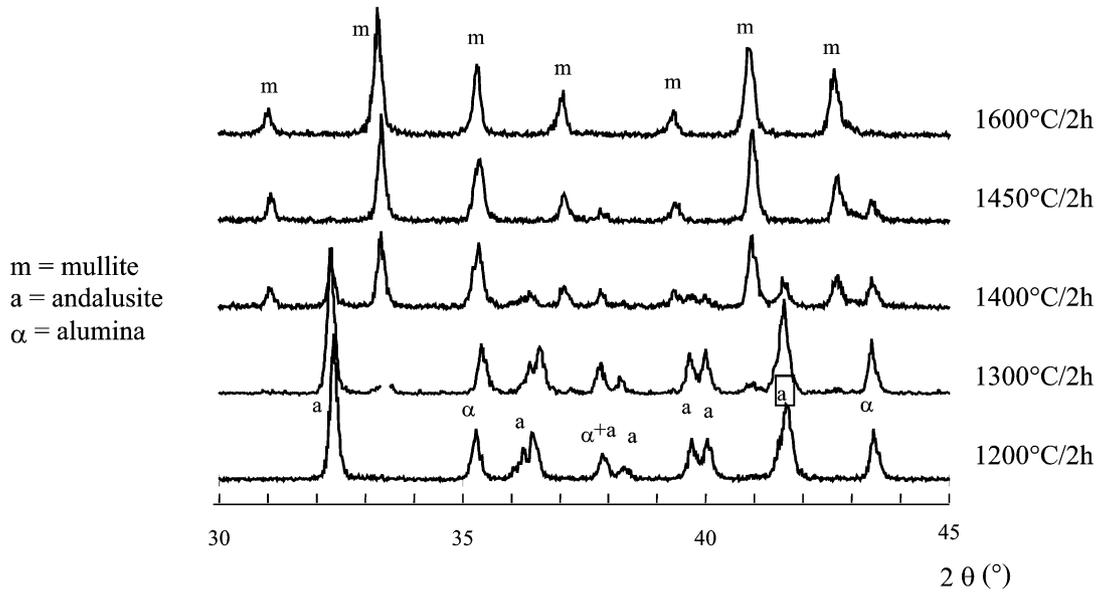


Fig. 4. X-ray diffraction patterns obtained after heat-treatments on sample 80/20.

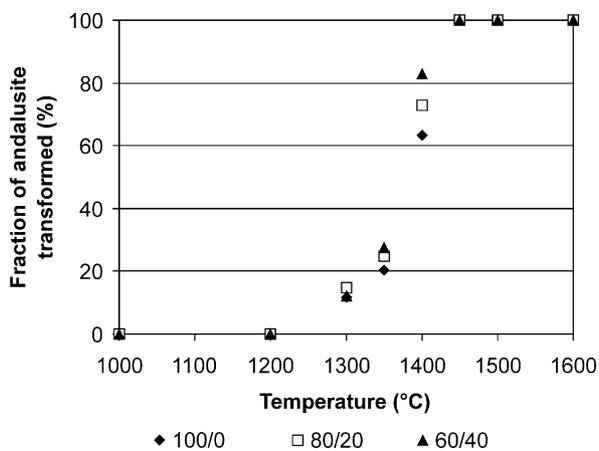


Fig. 5. Fraction of andalusite transformed versus temperature.

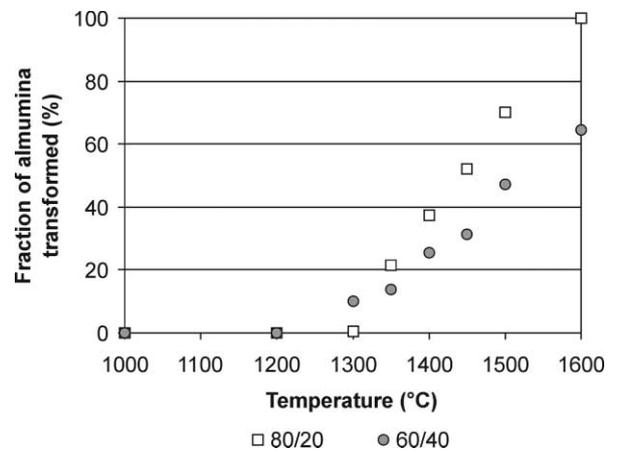


Fig. 6. Fraction of alumina transformed versus temperature.

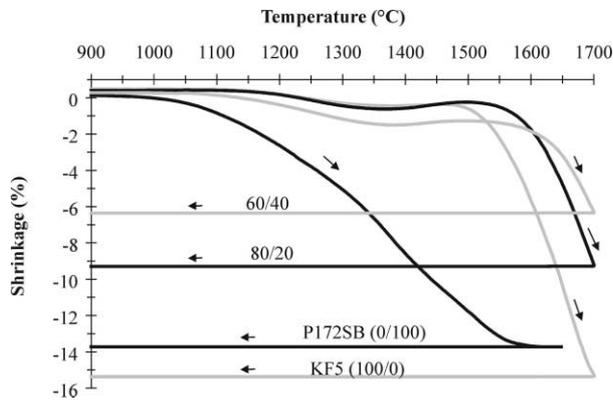


Fig. 7. Dilatometric curves during sintering.

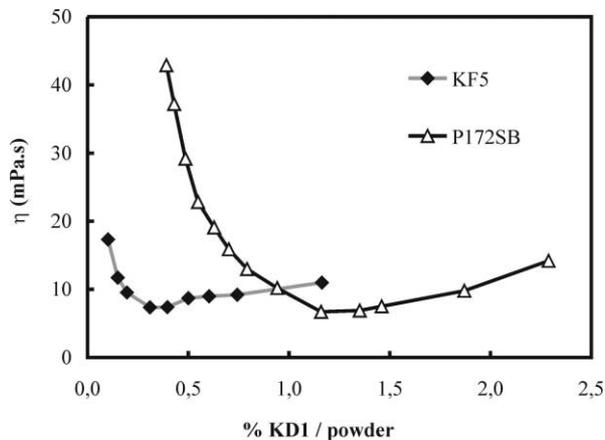


Fig. 8. Influence of the amount of dispersing agent on the viscosity.

tests have shown the high stability of the suspensions for these amounts.

The rheological behaviour of the slurries containing the binder + plasticisers was also studied separately for andalusite and alumina and with a mixture 20 wt.% alumina + 80 wt.% andalusite. In all cases, the amount of binder + plasticisers was fixed to 13 g/100 g powder. As previously, the amount of solvent was 50 g/100 g powder. The curves for viscosity versus shear rate show a pseudo-plastic behaviour for all slurries (Fig. 9). This behaviour is very suitable for tape casting. It is also noteworthy that the mixture has a lower viscosity than the separate powder suspensions. The mixture can be considered as a bi-modal powder with a ratio of coarse grains/fine grain equal to 7. In such a situation, the small grains act as a lubricant between the bigger grains.

Tapes containing 0, 20, 30 and 40 wt.% alumina were prepared. In order to obtain good mechanical properties of the tapes after solvent evaporation, the total amount of binder + plasticisers was increased from 13 g/100 g powder up to 22 g/100 g powder for all compositions. Tape casting was performed with a shear rate of 20 s<sup>-1</sup>. The displacement rate and the height of the blade were adjusted according the thickness targeted for the green tape.

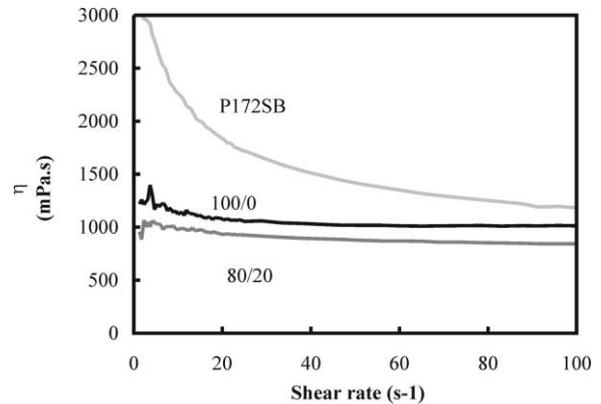


Fig. 9. Rheological behaviour of the andalusite and alumina powders and of the mixture 80/20.

### 3.3. Characterisation of the ceramic tapes

After sintering, SEM observations show a decrease in the amount of glassy phase with addition of alumina (Fig. 10). Pure andalusite leads to a high residual amount of glassy phase (Fig. 10a). This amount significantly decreases with composition 80/20 (Fig. 10b). With composition 70/30 and 60/40, almost no more glassy phase is observed but alumina grains are still present in the 60/40 preparation (Fig. 10c and d).

The amount of porosity in the green tapes (after additives are burnt out) decreases continuously with increasing alumina powder (Table 5). The alumina grains are much smaller than the andalusite grains ( $d_{50} = 0.6 \mu\text{m}$  instead of  $3.6 \mu\text{m}$  respectively). Therefore, the alumina can easily fill the pores between the andalusite grains. This also leads to a decrease of the pore size in the green tapes with the addition of alumina (Fig. 11). This decrease of the pore size is also observed after sintering (Fig. 12).

As is usually observed during sintering, it is mainly the small pores that disappear during the process while the size of the larger pores increases slightly (Fig. 13). Therefore, it can be considered that the increase in alumina leads to a competition between two phenomena influencing the sinterability of the mixture. On the one hand the increase in alumina should increase the sinterability by decreasing the average pore size in the green tape. On the other hand, the increase in alumina lowers the amount of vitreous phase at high temperature and then slows down the sintering of the mullite (see Section 1). In the case of samples 80/20 and 70/30, the second phenomenon dominates and sinterability decreases. After sintering, the open porosity measured by mercury porosimetry is 0 with pure andalusite but reaches 8% with 20 wt.% alumina and 13% with 30 wt.% alumina (Table 6). The total amount of porosity, calculated from the ratio apparent density/absolute density, follows the same variation. These results are also confirmed by the SEM observations (Fig. 10). In the case of sample 60/40

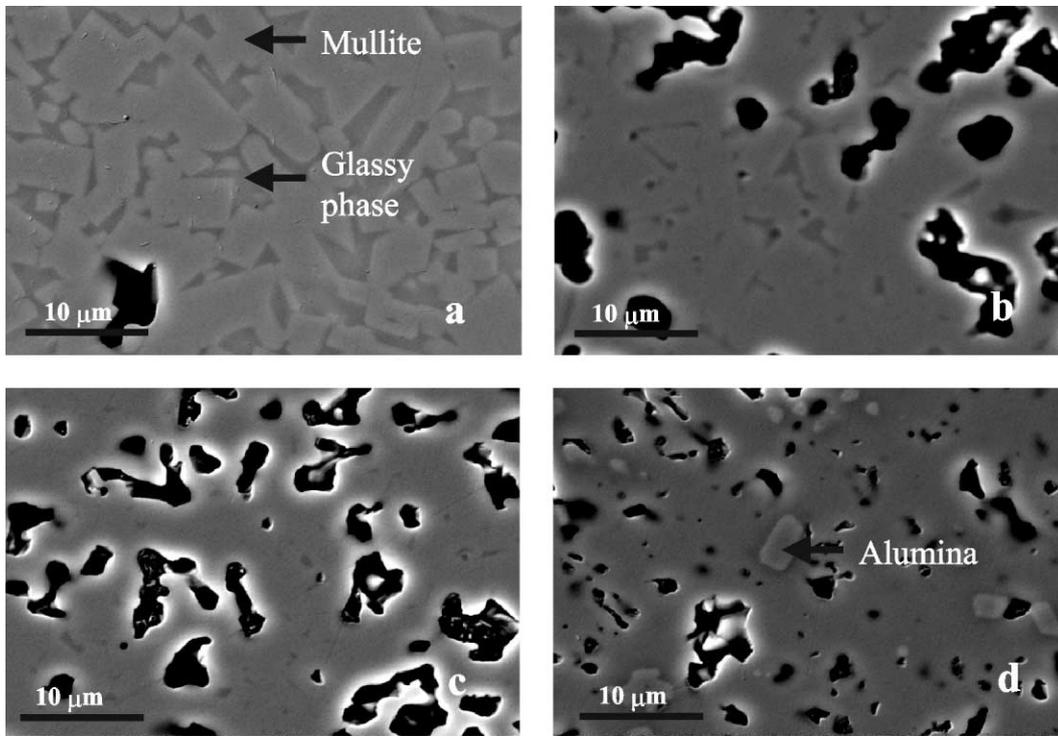


Fig. 10. SEM observation of the final samples (a: 100/0, b: 80/20, c: 70/30 and d: 60/40).

Table 5  
Porosity of the green tapes after additives burning out

| Green tapes | Open porosity (%) | Average pore diameter (μm) | Pore ranges (μm) |
|-------------|-------------------|----------------------------|------------------|
| 100/00      | 47                | 0.71                       | 1.3–0.06         |
| 80/20       | 45                | 0.52                       | 1.0–0.03         |
| 70/30       | 43                | 0.35                       | 0.8–0.03         |
| 60/40       | 40                | 0.17                       | 0.5–0.02         |

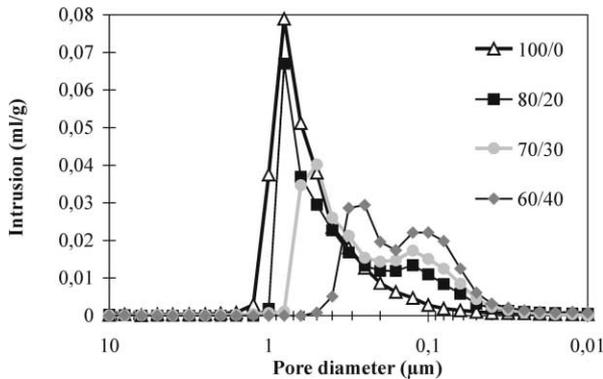


Fig. 11. Pore size distribution in the green tapes after additives were burnt out.

the high alumina content leads to very small pores in the green tape. This is highly favourable to the first phenomenon and the sinterability increases. The open porosity after sintering decreases to 8%.

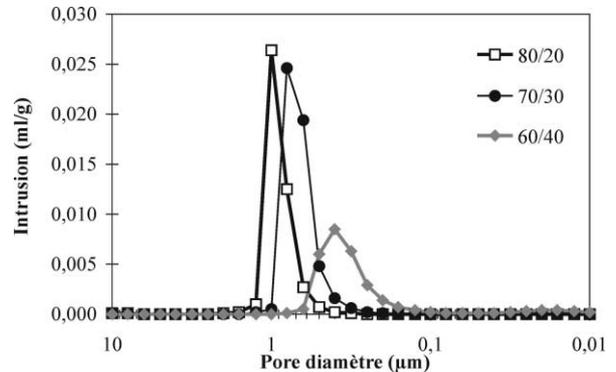


Fig. 12. Pore size distribution in the sintered tapes.

The strength of the samples follows the porosity (Table 6). However, for the same amount of porosity, the strength of the substrates obtained from pure mullite KM101 is higher than that of substrates obtained from andalusite. This can be explained by the larger pore size for substrates made from andalusite; these pores act as defects during testing. Dispersion is about the same for all compositions. For the targeted application these results can be considered as sufficient.

The thermal expansion curves measured on the tapes were compared to a substrate made by sintering of the pure mullite powder KM101 and to polycrystalline silicon (Fig. 14). The curve measured for sample 100/0 is lower than that of pure mullite. This is easily explained by the high quantity of vitreous phase remaining in the sintered material. The samples 80/20 and 70/30 contain

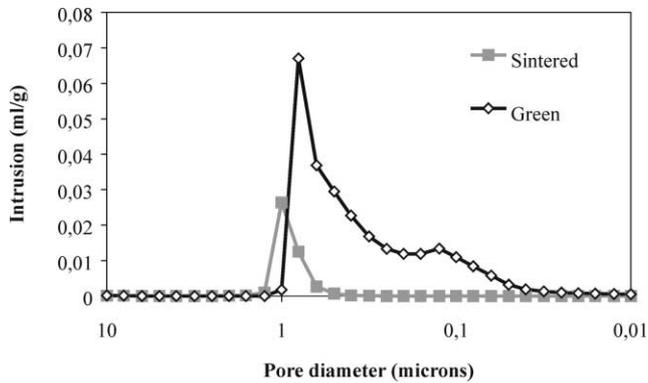


Fig. 13. Comparison of the pore size distribution in the green and sintered tapes for composition 80/20.

Table 6  
Porosity and strength of the sintered tapes

| Samples       | Open porosity (%) | Total porosity (%) | $\sigma_R$ (MPa) | $\Delta\sigma_R$ (%) |
|---------------|-------------------|--------------------|------------------|----------------------|
| Mullite KM101 | 0                 | 2                  | 172.2            | 10.3                 |
| 100/00        | 0                 | 2.5                | 142.6            | 9.5                  |
| 80/20         | 8                 | 16                 | 118.3            | 9.9                  |
| 70/30         | 12                | 21                 | 109.9            | 10.3                 |
| 60/40         | 8                 | 12                 | 138.0            | 12.7                 |

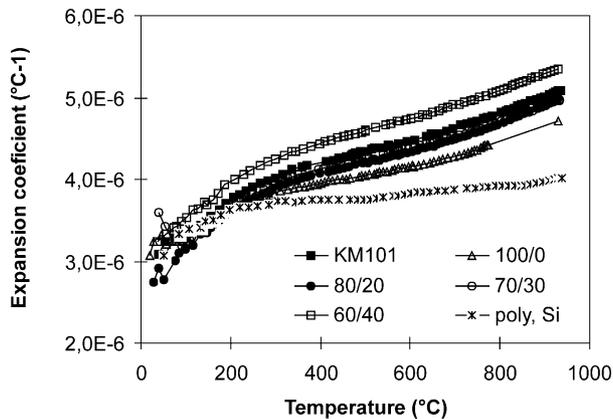


Fig. 14. Thermal expansion curves.

very little vitreous phase and their curves are very close to that of pure mullite. The residual alumina explains the high values obtained with sample 60/40. All curves are only slightly higher than that of polycrystalline silicon. This situation is highly favourable to thin film silicon deposition at high temperature. Indeed this leads to low compression stresses in the thin film after cooling, which lowers the risk of crack formation and propagation.

#### 4. Conclusion

The goal of this work was to obtain dense thin substrates by tape casting of andalusite with alumina. The

targeted application is the manufacture of ceramic substrates suitable for thin film solar cells.

It was shown that the sintering of pure andalusite leads to a high amount of residual vitreous phase but produces dense substrates by sintering for 2 h at 1700 °C.

The addition of alumina can reduce the residual amount of vitreous phase. Indeed, over 1400 °C, the alumina reacts with the vitreous silica resulting in the transformation of andalusite into mullite between 1300 and 1450 °C. However, the decrease in vitreous phase slows down the sintering process of the mullite already formed. Consequently, the porosity of the substrates prepared with 20 or 30 wt.% alumina is higher than with pure andalusite.

The thermal expansion curves of the substrates prepared with 20 and 30 wt.% alumina are very close to substrates made from a pure mullite powder. This is explained by the low amount of glassy phase. Anyway, for all compositions the curves are close to that of polycrystalline silicon. This is very favourable to the targeted application.

Substrates exhibiting a limited porosity, sufficient strength for the targeted application and a low residual amount of glassy phase can be obtained from a mixture of 80 wt.% andalusite and 20 wt.% alumina.

However, a high temperature (1700 °C) is required to produce these substrates. This is a major problem to produce substrates at low cost. It would, therefore, be of high interest to lower the sintering temperature, at least down 1600 °C. Several papers have shown the improvement of the sinterability of mullite by additions of sintering aids such as MgO. Another possibility is the improvement of the sinterability of the andalusite by decreasing of the grain size of the initial powder. These possibilities and their effects on the properties of the substrates will be further investigated.

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