JOURNAL OF MATERIALS SCIENCE 18 (1983) 1005–1014

Thermal and mechanical properties of mullitic substrates for low-cost solar cells obtained by dry-pressing

G. CELOTTI
Istituto Lamel-CNR, Bologna, Italy
L. MORETTINI
Istituto di Chimica Fisica, Universita di Modenà, Italy
G. ORTELLI
Istituto Statale d'Arte per la Ceramica, Faenza, Italy

A study has been made of the possibility of producing ceramic substrates for low-cost solar cells by means of the simple technology of moulding by dry-pressing. Special attention was taken to avoid adding costly materials (organic and inorganic) to the basic commercial kaolin. It emerged that the only treatment necessary was the precalcination of approximately half the powder at temperatures of 1200 to 1350° C. The various characterization techniques showed that, in spite of the simplicity of the technologies utilized, after a final firing at 1600° C, one can obtain finished products with the same thermal expansion coefficient as silicon (from ambient temperature to 800° C) and with mechanical characteristics that make the products perfectly suitable for resistance to the thermal shock, resulting from contact with molten silicon (the lower resistance to bending compared to products made with sophisticated production techniques being perfectly well compensated for by the greater elasticity, which is due to a considerably lower Young's modulus value). Even if this methodology has been applied on a laboratory scale, it is quite easy to automate it for industrial scale production.

1. Introduction

Exploitation of the photovoltaic effect for using the sun's energy on earth has by now become a technological and industrial reality. The particular applications it is proposed for, require large surface areas of materials that can transform solar energy into electric energy with an adequate conversion efficiency. The possibility of obtaining large quantities of low-cost solar cells involves the perfection of production techniques that are different from the ones in common use, that are still based mainly on the use of monocrystalline silicon.

At present, a noteworthy step forward seems to lie in the prospects offered by the so-called "semicrystalline" silicon, that is, very large-grained, polycrystalline silicon (grains from a few millimetres to several centimetres in diameter), normally obtained by casting techniques. As a longer-term projection into the future, even better possibilities may well be offered by polycrystalline silicon (grains with average sizes ranging from 100 μm to a few millimetres), both crystallized in self-supporting ribbons and desposited on suitable low-cost substrates.

Amorphous silicon also deserves brief mention: this is still being studied at a laboratory level and is characterized by quite singular physical and technological preparation properties.

Various researchers [1–7] have recently examined the possibility of using mullitic ceramic materials as bases for silicon solar cells. Most commercial mixes of mullite are obtained by blending kaolin clays with alumina. After firing the result is

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a material composed of mullite crystals ($3Al_2O_3 \cdot 2SiO_2$) bound by a vitreous phase with a high content of silica (SiO_2). Since commercial mullite has the following thermal expansion coefficient: $5.3 \times 10^{-6}\,^\circ C^{-1}$ (from ambient temperature to 800° C) and is mechanically stable at 1450° C, it comes very close to meeting requirements for the manufacture of substrates and containers in contact with molten silicon.

1.2. The different moulding methodologies

Mullite substrates may prove to be an interesting material for solar energy photovoltaic conversion and particularly for continuous production processes, which one relies on for obtaining low-cost solar cells, using the resources offered by the "scale-factor" of mass production.

One such process (called SOC, silicon on ceramic), discontinuous, developed by Honeywell (with the co-operation of Coors Porcelain Co. as regards the substrates), consists in immersing the mullite substrate in molten silicon: one side of the substrate is faced with carbon (graphite), which during the removal phase, favours the formation of a thin (100 to 200 μm), uniform layer of fairly large-grained polycrystalline silicon in appropriate cooling conditions. The silicon layer forms only on the side faced with carbon; the other side is not "wetted" at all.

Systems of holes or slots are made in the substrate in such a way that the silicon film easily bridges them. This is done so that electric contacts can be applied from the back to the side of the silicon layer adhering to the base.

A similar process, but this time continuous, uses the so-called "inverted meniscus" technique (SCIM, silicon coating by inverted meniscus) [8, 9]. With this technique, a fired substrate, 50 to 100 cm long and about 1 mm thick, with one side "graphitized", is brought into contact with a meniscus of molten silicon which suitably adheres to it from the bottom: the molten silicon is held in a suitably shaped and replenished quartz crucible and the mullitic sheet is run over it at the appropriate angle, until it is completely covered. The conversion efficiency of the solar cell prototypes made with dip-coating techniques hovers around 10 to 11%, which is close to that of solar cells conventionally obtained (13 to 16%) and 7 to 8% for more complex SCIM, yet to be optimized.

When making ceramic-base photovoltaic devices, great importance obviously lies in the actual ceramic substrate, on account of the effect it has on the ultimate energy conversion efficiency.

The substrates produced by Coors Porcelain Co. are made with the roll-compaction technique, starting with mixes containing organic additives and ending up with thin ceramic sheets, large and flexible (when raw). The substrates are made from these sheets, the slots being punched in simultaneously. Firing then takes place, with the substrates being placed on flat, faced-plates of mullite-bond alumina: firing temperature exceeds 1600° C.

A worthy alternative to the roll-compaction technique seems to be casting on belt with "doctor blade" shaping, similar to the casting method used in the manufacture of alumina substrates for electronics. Equally suitable for the manufacture of thin ceramic sheets, flexible, large and easy to punch when raw, this technique is the object of active research.

The drawing, die-injection and impregnation of appropriate shapes in volatile material when hot may also provide interest; however, all these moulding technologies involve passing through ceramic mixes that have been made more or less fluid or plastic by means of great quantities of solvents or organic additives. There are three basic objections to using such materials: (a) the rather high cost; (b) toxicity, implying the existence of "safe" plants for handling and evacuating fumes during the drying stage; (c) the difficulty of controlling and evaluating the dimensional shrinking of the substrate during firing.

For all these reasons, therefore, an attempt has been made to produce substates of the same type by means of the simple, conventional technique of dry-pressing powders; among other things, with suitable continuous-cycle machinery (basically presses and dies), this methodology is also suitable for automation and serialization. Obviously, working in the laboratory with limited technical means, the processes were modified to enable small-scale production without any demanding speed-of-output requirements: the main objective was, in fact, to ascertain the feasibility of a ceramic product of this type and to characterize it fairly completely.

2. Experimental details

2.1. Sample preparation

The basic raw materials chosen were obviously kaolin clays: their basic constituent part (with the

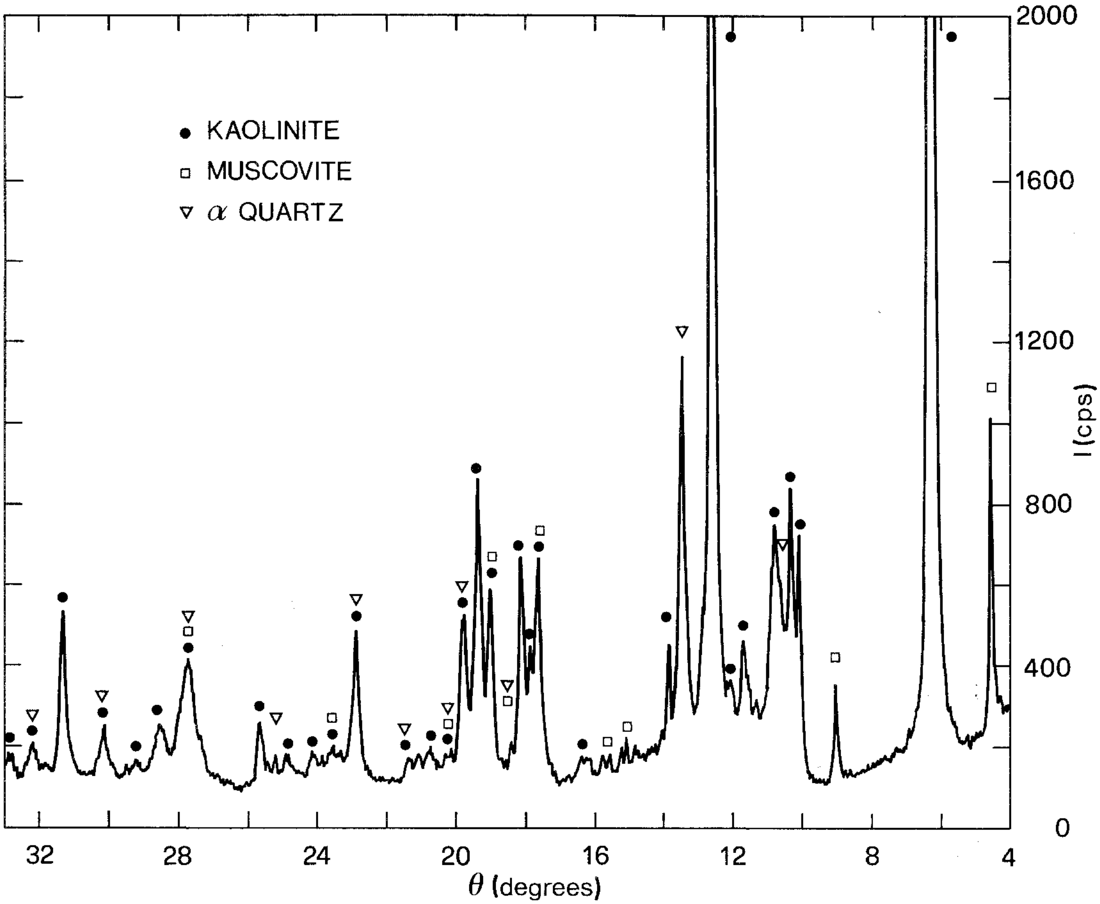

Figure 1 X-ray powder diffractogram of commercial Kamig P-50 kaolin, chosen as raw material for our substrates.

formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), when annealed at temperatures between 1400 and 1700° C first loses its chemically bound water and then, according to the following reaction:

$$3(Al_2O_3 \cdot 2SiO_2) \xrightarrow{T} Al_2O_3 \cdot 2SiO_2 + 4SiO_2 ,$$

is transformed into a mixture of needle-shaped mullite crystals immersed in a vitreous matrix composed essentially of silica. The proportions between Al_2O_3 and SiO_2 in the kaolinite are already very close to those ideal for obtaining a thermal expansion coefficient in the finished product between 3.5 and 4.3×10^{-6} ° C^{-1}, that is foreseeably able to equal that of silicon (which between ambient temperature and 700 to 800° C ranges from 3.9 and 4.0×10^{-6} ° C^{-1}) in the region preceding the softening of the vitreous phase, which can quite easily offset any thermal stress while the molten material cools.

The main phases present as impurities in commercial kaolin clays are illites and micas (muscovites): all involve the presence of potassium cations, but the former may also contain sodium, calcium, magnesium, iron, manganese and titanium, which makes them decidedly less attractive for our purposes.

Before selecting the basic raw material, we examined three good-quality commercial kaolinites, both from the diffractometric point of view with X-rays, and with the electron microprobe: they were Zettlitz, Osmose and Kamig P-50. The presence of muscovite and α-quartz was detected in all three with a lower quantity in the third. Special attention was paid when checking the absence (or negligible traces) of those metallic cations that are more harmful to the electric properties of silicon, titanium in particular [10–12]. As microanalysis confirmed a low content of alkaline impurities in this third clay again, Kamig P-50 was finally chosen as the raw material for our investigation: in Fig. 1 the relative X-ray powder diffractogram is reported. Since kaolinite clays are normally very fine and powdery, the all too frequent inconvenience of flaking during dry-pressing

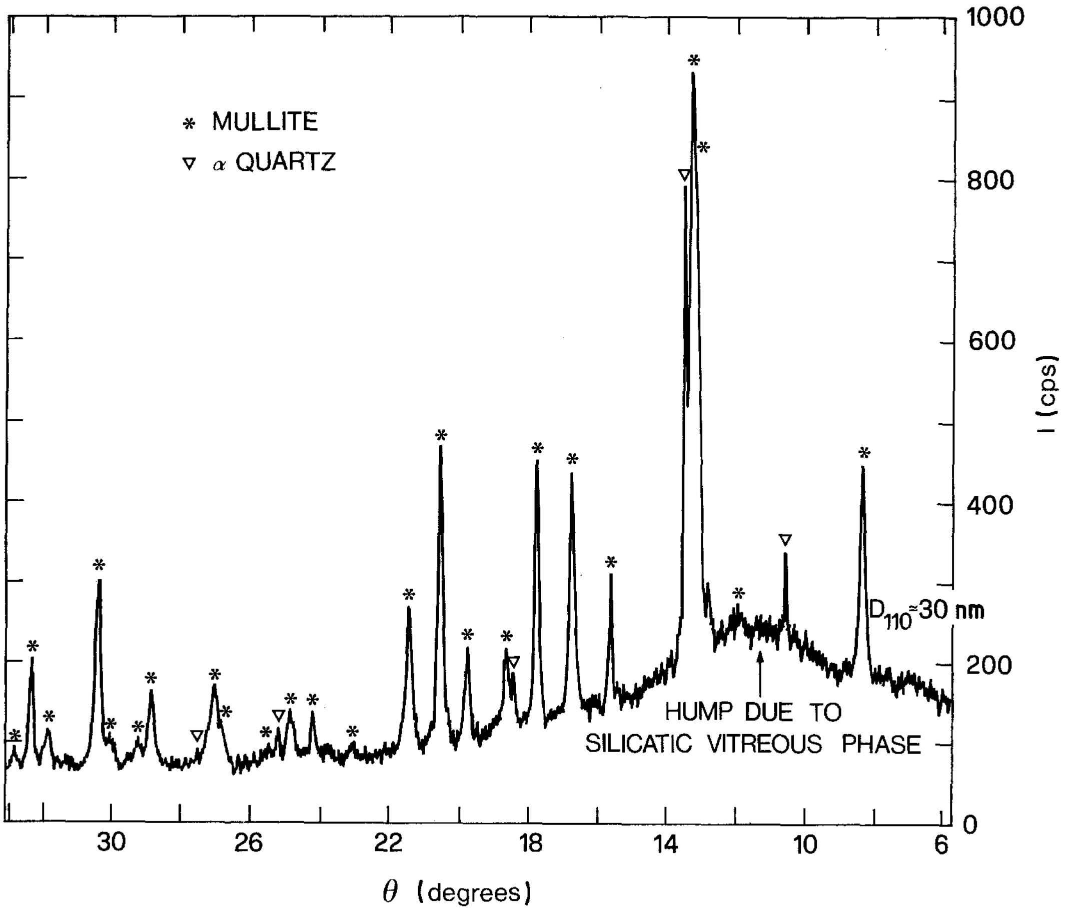

Figure 2 X-ray powder diffractogram of our substrate after thermal pre-treatment at 1200° C (Cu$K\alpha$ radiation); note the small dimensions of crystallites (obtained by half-width of the peak through Scherrer formula), typical of low-temperature formed mullite.

forming operations was avoided by granulating the product beforehand, using an aqueous solution with 0.5 to 1.0% of carboxy-methyl-cellulose (CMC).

This solution was sprayed in the form of finely subdivided drops on the original powder, which was then passed through sieves with 16 to 36 meshes per cm^2, so as to leave adequately solid granules with maximum diameters of 1.5 to 2.5 mm. After homogenization of the humidity in the granulated mass, pressing took place, in the usual two stages, in a laboratory hydraulic press with a powder of some 300 kg cm^{-2}. After the thin rectangular plates (measuring 90 mm x 50 mm x 1 mm, approximately) had been formed, they had to be endowed with a certain mechanical resistance which would enable them to be worked without the risk of breakage before the final high-temperature firing took place. In actual fact, the plates can be subjected to no further processing after this stage. The problem was solved by preliminary firing at a temperature of 1200° C, which turned out to be the best heat level: in Fig. 2 the X-ray powder spectrum of the substrates after this thermal pre-treatment is shown.

At this point, a series of cross-slots (necessary for applying electric contacts from the back to the finished solar cell) was made in the plates, as were the holes that would be used for suspending them in the molten silicon: for these purposes, a special sliding faceplate frame was used, together with a diamond wheel (20 mm in diameter and 0.8 mm thick) mounted on a small electric drill.

After shaping, the plates were subjected to final firing in a laboratory intermittent furnace (resistances in Super-kantal) at 1600° C. The plates were placed in refractory bases made of 80% Al_2O_3 and covered with Al_2O_3 powder to avoid sticking.

A few hours at 1600° C showed more uniform

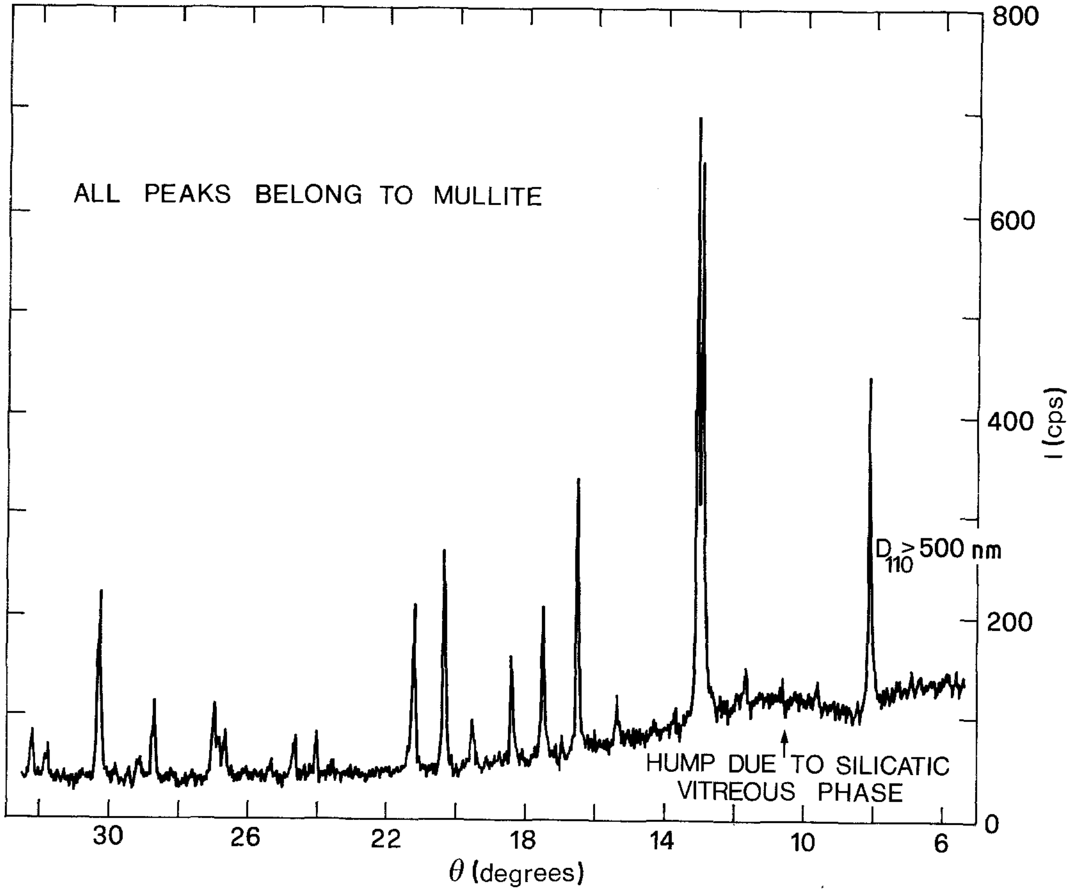

Figure 3 X-ray powder diffractogram of our substrates after final annealing at 1600°C for two hours (Cu$K\alpha$ radiation); note that now crystallite dimensions of mullite are well beyond the maximum value attainable by conventional Scherrer method.

results compared to samples that had been maintained to that temperature only for a very short time: in Fig. 3 the characteristic X-ray powder diffractometer record for substrates after final annealing is reported. Fig. 4 shows the typical look of these finished products. In this way, various mixes were prepared, with the following variables being systematically evaluated:

(a) firing temperature of the "chamotte' (precalcined Kamig P-50 kaolin).

(b) particle size of the "chamotte",

(c) type of additive to the material when raw,

(d) proportion of additive to the material when raw,

(e) pre-firing temperature of the formed sheet,

(f) final firing temperature,

(g) duration of exposure in final temperature.

An important piece of knowledge acquired was, that if the "chamotte" is annealed at temperatures greater than 1300° C, there occurs an almost complete sintering of the kaolin grains: during final firing (at 1600° C), this results in microfractures between the "chamotte" granule and the clay matrix, which still has to finish shrinking.

This phenomenon decreases the density and mechanical resistance of the finished sheet. Calcined at lower temperatures, the "chamotte' still remains porous and, during final annealing, can shrink along with the matrix, thereby avoiding the formation of microfractures.

On the other hand, the addition of an optimal quantity of "chamotte" is required both to avoid deformations in firing produced by the excessive shrinking of the raw kaolin alone, and to encourage a more complete and uniform crystallization of the mullite within the vitreous phase.

3. Sample characterization

3.1. Thermal expansion coefficient

In the temperature range 20 to 800° C, the thermal

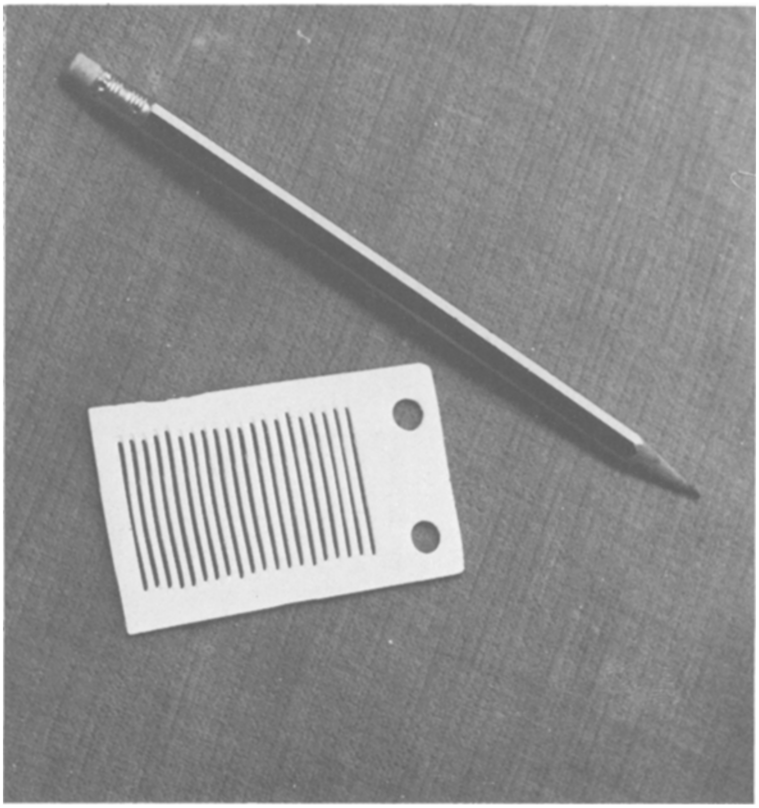

Figure 4 Typical look of an our finished mullitic substrate.

expansion coefficient of the different mixes was measured with an electronic recording dilatometer ADAMEL mod. DHT-60, calibration being done by using a sample of Al_2O_3 (more than 99% pure) with a density of about 98%.

Only a few trials were required to reproduce fairly faithfully the trend of α (silicon) in the same temperature range.

3.2. Bend tensile strength

Bend tensile strength was established on specially shaped specimens, the edges of which were treated so as to eliminate as far as possible the microfractures ever present in them. The samples, usually measuring 100 mm x 50 mm x 3 mm, were subjected to bending on three points by a Gebruder Netzsch instrument. The σ_F value is obtained from the relation:

$$\sigma_F = 3PL/2h^2b \qquad (1)$$

where P is the weight applied to the upper knife, which causes the break, L is the distance between the two lower supporting knives, h is the thickness of the sample and b is the width. Load application speed was about 0.1 mm min^{-1}.

Naturally, given the high dispersion of the results obtained with this technique, at least 5 measurements were made on each kind of specimen, and the mean and standard deviation were thus obtained.

3.3. Elastic modulus (Young's modulus)

Elastic modulus measurements were made on 40 mm x 5 mm x 1 mm specimens; after careful cleaning with acetone, one base of each sample was made conductive by means of depositing on it (by vacuum evaporation) a thin layer of approximately 1 μm of 99.99% pure aluminum. Measurements of vibrometric elastic modulus were taken in air at ambient temperature by means of Bordoni-type electrostatic-excitation instrument [13].

This method involves the identification of the resonance frequency of the specimen being examined, ν_r, from which it is possible to compute the speed of sound in the medium:

$$c_s = \nu_r l^2/1.027h \qquad (2)$$

(with l being the length of the specimen and h its thickness) and, hence, by knowing the density of the medium itself, the Young's modulus $E = \rho \cdot c_s^2$.

In our case, the frequencies fell within a range of 3.5 to 5.0 kHz and the accuracy of the method of determining resonance frequency is about 0.1%. Calculation of E was made by using the expressions above, derived by thin, non-restrained rods. In our case, measurement error on E turns out to be from 2 to 4%, above all on account of uncertainties in the evaluation of the sizes of the specimen and its density.

3.4. Density

Density of the specimens was measured by determining the value of the ratio of weight to volume for regular-shaped specimens and by hydrostatic method for the others. The values obtained (the result of the average of at least three different measurements) are obviously all lower than that of pure mullite ($3.16\,\mathrm{g\,cm^{-3}}$). This is due to the presence of fair quantities of silicatic vitreous phase, the density of which is on average equivalent to that of molten silica ($2.20\,\mathrm{g\,cm^{-3}}$), and a certain degree of closed porosity, responsible for the fact that the full "theoretical" density is never attained, this latter density, for kaolin-only mixes without additives, being around $2.82\,\mathrm{g\,cm^{-3}}$ after high-temperature firing.

3.5. Shrinking

Linear shrinking of our mixes after annealing at 1600° C, evaluated with size measurements to 1/100 mm, fell in every case within the narrow range of 8 to 11% and this is decidedly low compared to forming methodologies involving the use of mixes containing large quantities of organic additives and solvents.

3.6. Crystallographic phases present

X-ray diffractograms reveal that the only crystalline phase present after annealing at 1600° C is mullite (see Fig. 3); the effects of the silicatic vitreous phase (associated with a large band with a maximum Bragg's distance of around 0.38 to 0.40 nm) are clearly evident, as are sometimes the weak effects of Al_2O_3, when it turns out that the additives have not reacted fully.

4. Results and discussion

Identification of the physical-mechanical characteristics of a ceramic material destined for the use we have defined is of fundamental importance. The focal point of the problem is that the substrate should have a thermal expansion coefficient almost identical to that of silicon (at least, between ambient temperature and 700 to 800° C) so as to minimize tensions between base and cover film in recrystallization phase.

Other fundamental requirements are good resistance to thermal shock, which ensure substrate integrity during heating, immersion in molten silicon and subsequent cooling, and a very small solubility in the molten bath to avoid its contamination.

As for resistance to thermal shock, it is commonly accepted that breaking takes place during cooling, when surface tensions due to the temperature difference between the specimen's surface and its inside reach a certain critical value σ_c.

There are various expressions for interpreting the phenomenon, related to the geometry of the specimen under examination and to test conditions. In our case, an appropriate but sufficiently significant one, which expresses resistance to thermal shock, can be provided by [14]:

$$\Delta T = C\sigma_F(1-\nu)/\alpha E \qquad (3)$$

where ΔT is the difference between surface temperature and inside temperature necessary to cause breaking, C is a factor depending on the geometry of the specimen, ν is the Poisson' modulus, α is the thermal expansion coefficient, σ_F is the bend tensile strength and E is the elastic or Young's modulus.

Since in many ceramic materials ν is very similar (around 0.25), it can be seen that, geometry being equal, critical ΔT increases in proportion to the ratio $\sigma_F/\alpha E$. A relative comparison of the resistance to thermal shock of different materials may be made on the basis of the above ratio. Such a comparison, carried out with consideration to the cost of the various materials, has revealed the advantageous conditions offered by mullitic porcelains, which show $\sigma_F/\alpha E \geqslant 180°\,C$, to be compared with the ones between 35 to 85° C of the principal pure crystalline ceramic oxides.

Obviously, when deciding, it should not be forgotten that although it is possible to obtain much higher values for this ratio with certain materials, one discriminating requirement, leaving aside economic considerations for the moment, is that α should not diverge too much from that of silicon.

Table I shows the values relative to certain mixes described in it regarding their density, polycrystalline elastic modulus, resistance to bending, thermal expansion coeffficient (from 20 to

TABLE I Thermal and mechanical properties of ceramic mullitic substrates obtained from kaolin by dry-pressing

Mixes	Density, ρ ($g\,cm^{-3}$)	Polycrystalline elastic modulus, E ($GN\,m^{-2}$)	Bend tensile strength, σ_F ($MN\,m^{-2}$)	Thermal expansion coefficient, α ($ppm\,°C^{-1}$)	Factor of thermal shock resistance $\sigma_F/\alpha E$ (°C)
Kaolin (alone) when raw	2.33	75	35–40	4.18	120
Kaolin with 30% fine chamotte (1300° C)	2.38	85	45	4.03	131
Kaolin with 30% coarse chamotte (1300° C)	2.42	85	45	3.91	135
Kaolin with 40% chamotte (1300° C)	2.52	80	60–65	3.90	200
Kaolin with 50% chamotte (1300° C)	2.55	80	60–65	3.88	201
Kaolin with 60% chamotte (1300° C)	2.57	80	60–65	3.86	202
Kaolin with 50% chamotte (1100° C)	2.40	90	55	3.70	165
Kaolin with 50% chamotte (1200° C)	2.60	85	65–70	3.82	208
Kaolin with 50% chamotte (1250° C)	2.50	85	50–55	3.85	160
Kaolin with 50% chamotte (1350° C)	2.30	80	55–60	3.85	187
Kaolin with 50% chamotte (1500° C)	2.15	80	40–45	3.80	140
Kaolin with 20% $Al_2O_3 \cdot nH_2O$	1.65	70	30	4.05	106
Kaolin with 30% chamotte (1300° C) and 20% $Al_2O_3 \cdot nH_2O$	1.85	70	40	4.00	143
Kaolin with 40% chamotte (1200° C) and 10% anhydrous Al_2O_3	2.25	90	60	3.75	178

800° C) and the $\sigma_F/\alpha E$ ratio, which, as we have seen, is a figure of merit as regards resistance to thermal shock for several mixes in the same table. The first thing to notice is that the proportions of "chamotte" added and its firing temperature do not have any notable effect on the characteristics of the final product, at least as long as the percentage does not diverge too much from 50% and the temperature does not exceed 1400° C. The addition of "chamotte" to mixes, in comparison with raw kaolin alone, increases the density, leaving thermal expansion and mechanical properties virtually unaltered: the main advantages emerge during pressing operations and in a decrease of total shrinkage, with a consequent reduction of firing deformation.

The effects of addition of Al_2O_3, both hydrate and anhydrous, are decidely negative. Alumina hydrate ($Al_2O_3 \cdot nH_2O$, with $n \simeq 2$ to 3) in the mix considerably lowers the density on account of the outflow of water of constitution, clearly increases the thermal expansion value, in that some α-Al_2O_3 remains in the fired body, with a high expansion coefficient, without all of it becoming mullite, decreases the elasticity of the sheets (and, therefore, also their resistance to thermal shock) and, lastly, also lowers their mechanical resistance.

All these characteristics deteriorate in proportion to the increase of the $Al_2O_3 \cdot nH_2O$ content of the mix. Therefore, the addition of anhydrous α-Al_2O_3 is to be avoided, in that not only does a considerable unreacted quantity remain, but it also seems to inhibit, and not activate, the crystallization of the mullite, by leaving too much silicatic vitreous phase in the finished sheet, compared with the best products.

In Fig. 5 the thermal expansion coefficient α for silicon is reported as a function of temperature.

Fig. 6 shows linear thermal expansion trends (in %) as a function of temperature, compared with silicon: it can be seen how, in every case, not only were very similar values from ambient temperature to 800° C obtained without excessive dif-

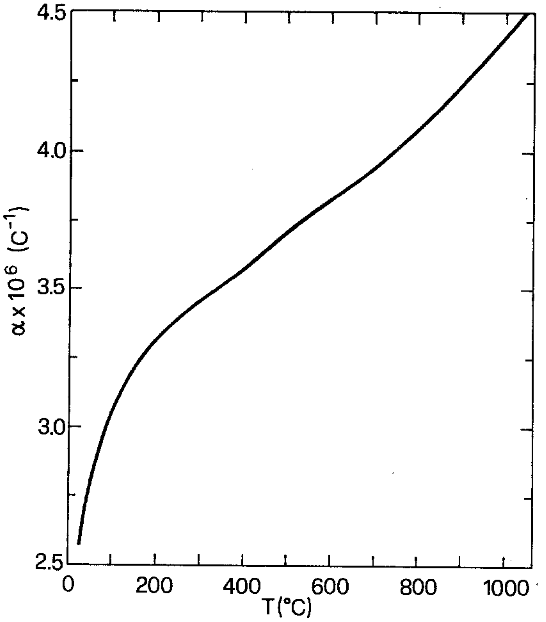

Figure 5 Thermal expansion coefficient for solid silicon as a function of temperature.

ficulties, but also the same variation as a function of temperature. This ensures that, during the whole cooling cycle, the layer of silicon and the substrate shrink together, without creating thermal stress problems that would cause the two to separate.

As for mechanical properties, it can be seen that this simplified technique leads to σ_F values that are 30 to 50% lower than that obtained by roll-compaction: this is, however, fully offset by the E values that are over 50% lower (less rigidity and hence more elasticity) than the products obtained by the above mentioned technique.

The result of this is that it is easy to obtain ratios of $\sigma_F/\alpha E \geqslant 180°$ C and, therefore, finished products that can brilliantly resist the thermal shock caused by immersion in and subsequent removal from the molten silicon bath.

5. Conclusions

It is well worth pointing out that the good thermal and mechanical properties of the mullitic substrates produced were obtained:

(a) from low-cost commercial raw materials, without any treatment (apart from precalcination of about half the mass at $T < 1400°$ C) or the addition of other components consisting of different crystallographic phases,

(b) using a simple and easy-to-automate moulding technique,

(c) renouncing any eventual sophistication in the various technological processes involved.

In conclusion, therefore, verification has been made of the feasibility of making, on a laboratory scale, mullitic ceramic substrates for solar cells by means of dry-pressing.

The most suitable characteristics of the mixes have also been identified and defined in order to obtain not only a thermal expansion coefficient practically identical to that of silicon from ambient temperature to 800° C, but also an acceptable density (with a prevailingly closed porosity), a good mechanical resistance and an elasticity sufficient to offer genuine guarantees of favourable behaviour in the face of thermal shock.

Furthermore, the relevant, economic viability factors allow one to envisage interesting development possibilities for these moulding methods on an industrial scale.

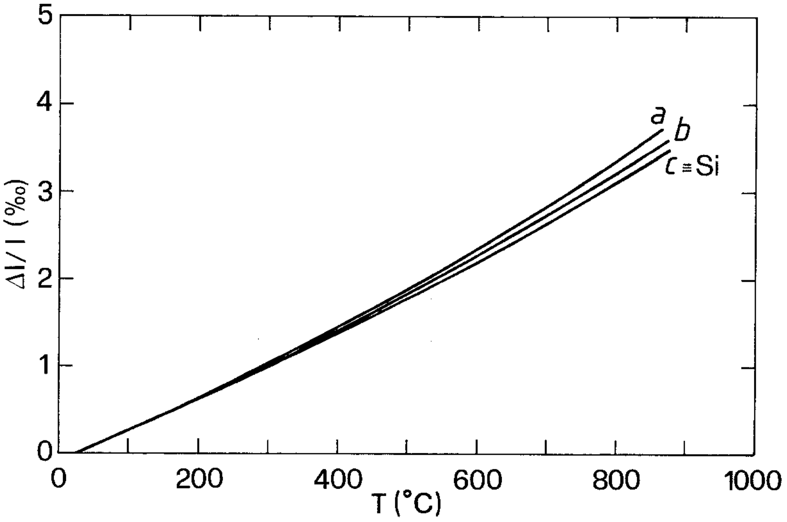

Figure 6 Dilatometric curves (linear relative expansion against temperature) of various substrates: (a) only thermally untreated kaolin; (b) with 30% fine-granulated chamotte annealed at 1300° C; (c) with 50% chamotte annealed at 1300° C (perfectly coincident with silicon behaviour).

Acknowledgements

Many thanks are due to Professor G. Vecchi for having made available the equipment of his Institute and for thus having made this research programme possible; to Mr G. Bassi for his authoritative and unflagging technical assistance; to Messrs Merendi, Nediani and Samori for their willing cooperation during all the experimental stages of this present work.

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Received 9 June
and accepted 16 July 1982