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Thermal stabilization of aluminium titanate and properties of aluminium titanate solid solutions

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Aluminium titanate has a near zero thermal expansion coefficient ($\alpha = 0.8 \times 10^{-6}\,°C^{-1}$) in the range 20 to 1000 °C, nevertheless it decomposes below 1200 °C.

The thermal stabilization of Al_2TiO_5 without altering its thermal expansion has been considered by partial substitution in the structure compound of Al^{3+} ions by Fe^{3+} ions.

The solid solutions prepared by solid state reaction are in agreement with the general formula

$$Al(1 - x)_2Fe_{2x}TiO_5 \, (0 < x < 0.2)$$

The iron ions present in the crystal structure of Al_2TiO_5 act on its lattice parameters and bring about a catalytic effect in the formation of materials.

Solid solutions show a strong thermal stability and a thermal expansion coefficient specially for the solid solution ($x = 0.1$) which is not far from the Al_2TiO_5 value even after annealing for 300 h at 1000 °C.

The mechanical properties of such materials corresponding to that solid solution present strength values lower than Al_2TiO_5 ones. After annealing, however, these are improved later due to a microcrystallization.

1. Introduction
Aluminium titanate (Al_2TiO_5) is included in the class of ceramics having a near zero thermal expansion coefficient and a high thermal shock resistance. The material is nevertheless unstable below 1200 °C and it decomposes giving rise to Al_2O_3 α and titanium oxide (rutile) by an eutectoid reaction.

The aim of this paper is to carry out the thermal stabilization of aluminium titanate without notable alteration of its thermal expansion coefficient.

2. Thermal instability of aluminium titanate
Thermal instability of Al_2TiO_5 compound must be considered from both the structural and dimensional viewpoints. The crystal structure of aluminium titanate is of the pseudobrookite type [1]. Pseudobrookite is the homologous Fe_2TiO_5 compound thermally stable in the TiO_2–Fe_2O_3 system. It is the prototype of a series of compounds with general formula A_2BO_5 (where A is a trivalent ion and B a tetravalent one) which crystallize with this same structure.

In Al_2TiO_5 structure, each Al^{3+} or Ti^{4+} cation is surrounded by six oxygen ions forming distorted oxygen octaedra. These TiO_6 or AlO_6 octaedra form (001) oriented chains weakly bonded by edge-shared in the AB plane. The small ionic radius of aluminium (Al^{3+} 0.050 nm), is in a structural site of higher dimension and then the thermal stability of the structure should be affected.

On the contrary, in Fe_2TiO_5, the Fe^{3+} ion radius (Fe^{3+} 0.064 nm) is very similar to that of titanium (Ti^{4+} 0.068 nm) involving a higher thermal stability. Preliminary experiments and previous papers reporting the effect of small amounts on thermal behaviour of aluminium titanate [2–6], lead us to study the thermal stabilization of this material by partial substitution of Al^{3+} ions by some larger Fe^{3+} ones.

3. Preparation
Aluminium titanate and solid solutions with general formula $Al(1 - x)_2Fe_{2x}TiO_5 (0 < x < 0.2)$ were synthesized over 1200 °C in solid state reaction by mixing the appropriate amounts of Al_2O_3, TiO_2 and Fe_2O_3. The powder can be then uniaxially cold-pressed in air ($P = 370$ MPa) or hot-pressed under vacuum ($P = 30$ MPa).

4. Formation and crystallization mechanism
Partial substitution of Al^{3+} ions by Fe^{3+} ions in

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Al_2TiO_5 structure leads after total reaction to formation of solid solutions. RX spectra are similar to the Al_2TiO_5 one but with some angular shift.

During sintering reaction, an evolution of some high lines of the RX spectra is observed as a function of the temperature. A several steps process is involved.

In a first step ($T \leqslant 1100\,°C$) a Fe_2TiO_5 type solid solution is formed. This solid solution observed with all the x values studied is due to the lower temperature formation for the Fe_2TiO_5 compound. With increasing temperature ($T \leqslant 1350\,°C$), in addition to this Fe_2TiO_5 type solid solution, an Al_2TiO_5 one is observed for $x < 0.2$. The coexistence of these two solid solutions is based on the behaviour of some high lines of the RX spectra. For $x = 0.2$ (the highest Fe_2O_3 content studied), the Fe_2TiO_5 type solution is only observed. It is likely that for this iron amount (16.5 wt %), the two solid solutions have the same composition and then lead the dividing of lines previously observed to vanish on the RX spectra of these materials.

Finally at high temperature ($> 1400\,°C$) the two solid solutions react together and the RX spectra only show the existence of the Al_2TiO_5 type solid solution. In Fig. 1, the evolution relative to (0 2 3) line (of RX spectra) as a function of temperature is presented in the case of $x = 0.15$ (12.5 wt % Fe_2O_3) solid solution. This fact was observed with materials synthesized by solid state reaction whatever the pressure mode. In addition, the substitution of Al^{3+} ions by Fe^{3+} ions involves a catalytic effect on the kinetic of the reaction. Al_2TiO_5 formation thus needs heat treatments higher than 1350 °C; in the presence of additional Fe_2O_3, the temperature reaction is lowered and the rate of formation is increased.

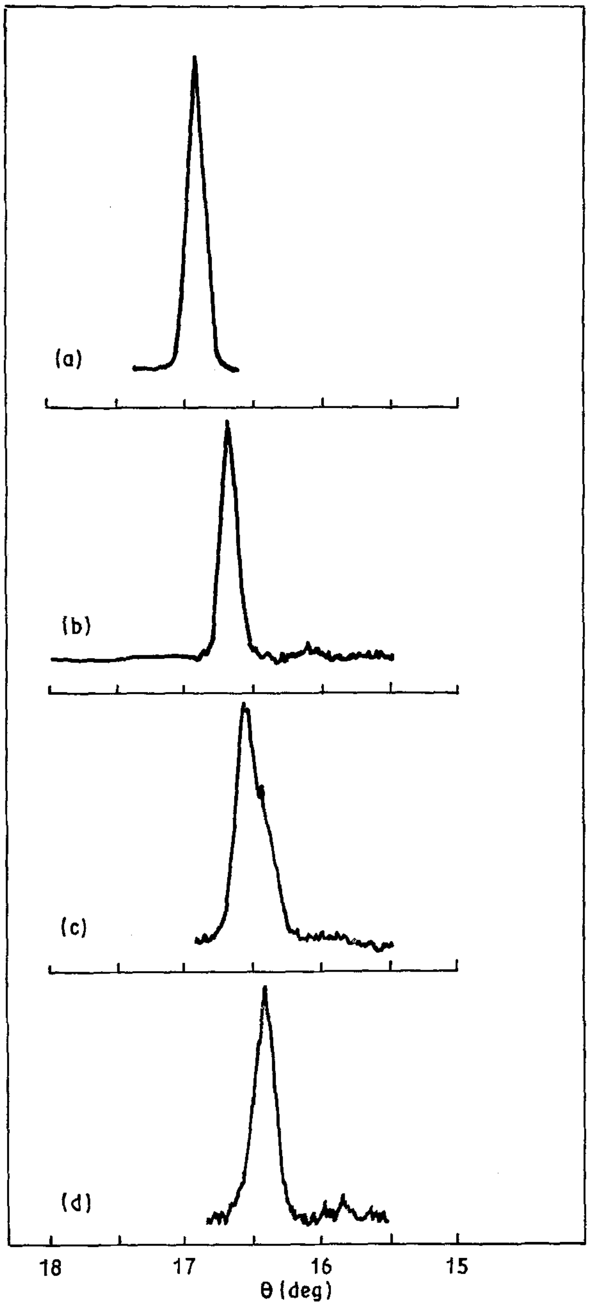

Figure 1 The X-ray, CuK_α spectra: (0 2 3) line evolution as a function of temperature for solid solution $Al(1-x)_2Fe_{2x}\ TiO_5$ ($x = 0.15$ i.e. 12.5 wt % Fe_2O_3) (a) 1480 °C, (b) 1300 °C, (c) 1200 °C, (d) 1100 °C.

5. Effects of the substitution on the solid solutions parameters

5.1. Lattice parameters

Fe^{3+} ions included in the Al_2TiO_5 structure involve a lattice expansion and then an increase in the lattice parameters. The higher the Fe_2O_3 amount the higher the lattice modification. Fig. 2 shows parameters and volume variation of Al_2TiO_5 lattice as a function of Fe_2O_3 content. The larger evolutions concern the a and c parameters.

5.2. Thermal stability

Aluminium titanate is stable from 1200 °C to melting (1800 °C). Below 1200 °C, it decomposes by an eutectoid reaction into TiO_2 rutile and alumina α.

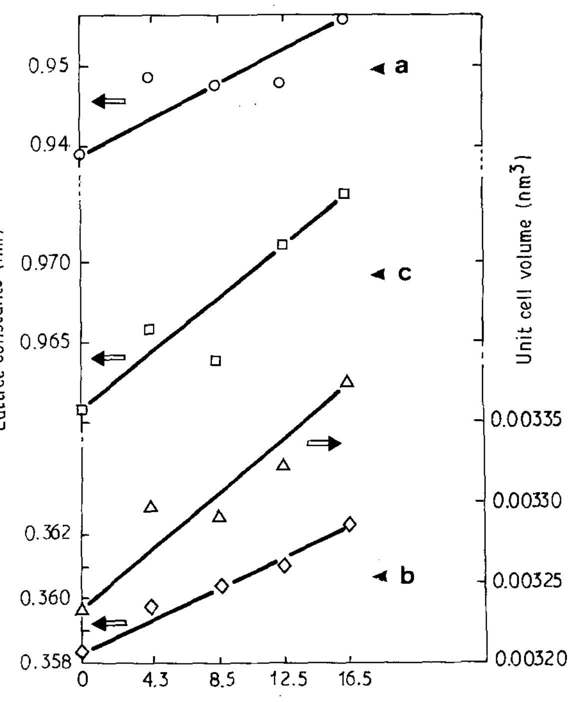

Figure 2 Effect of Fe_2O_3 amount substitution on lattice parameters of aluminium titanate.

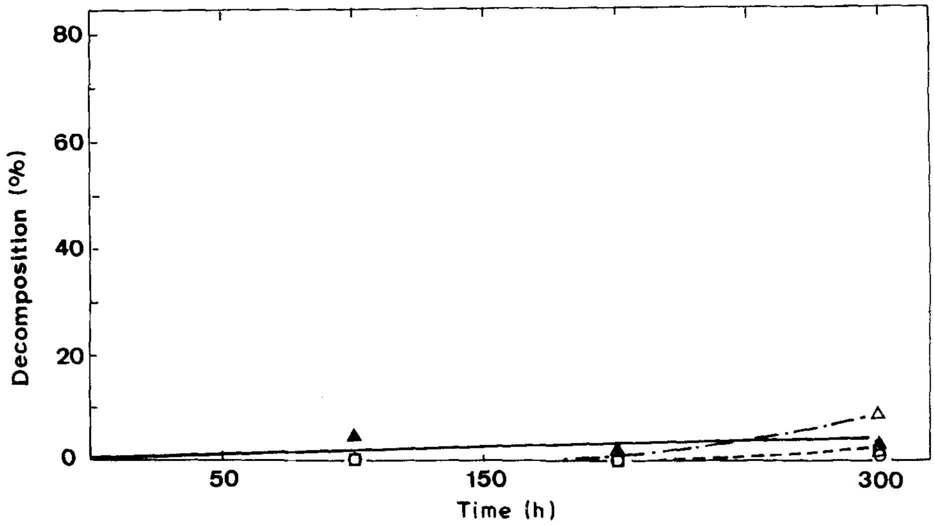

Figure 3 Thermal stability of solid solutions as a function of Fe_2O_3 content after annealing at 1000 °C. (▲ 16.5 wt % Fe_2O_3, □ 8.5 wt % Fe_2O_3, ○ 12.5 wt % Fe_2O_3, △ 4.3 wt % Fe_2O_3).

In a previous paper [7] it was shown that an isothermal treatment of tens of hours at 1000 °C involves a total decomposition of the material, with large alterations in its properties.

The thermal stability of solid solutions prepared with various Fe_2O_3 contents was studied using X-ray quantitative powder diffraction analysis. After isothermal annealing at 1000 °C for up to 300 h, the degree of decomposition of annealed samples was determined from specific relative intensity $I(Al_2TiO_5)/I(Al_2TiO_5) + I(TiO_2)$. These values were obtained measuring the peak area of (0 2 3) line of Al_2TiO_5 and (1 0 1) one for TiO_2. The thermal behaviour of these annealed solid solutions (Fig. 3) exhibits a strong stability with rate of decomposition not exceeding 9% after this long heat treatment.

Comparative decompositions of aluminium titanate and rich Fe_2O_3 solid solutions have been measured after annealing for 300 h at 1000 °C. A distinct thermal stability for these materials clearly appears on Fig. 4.

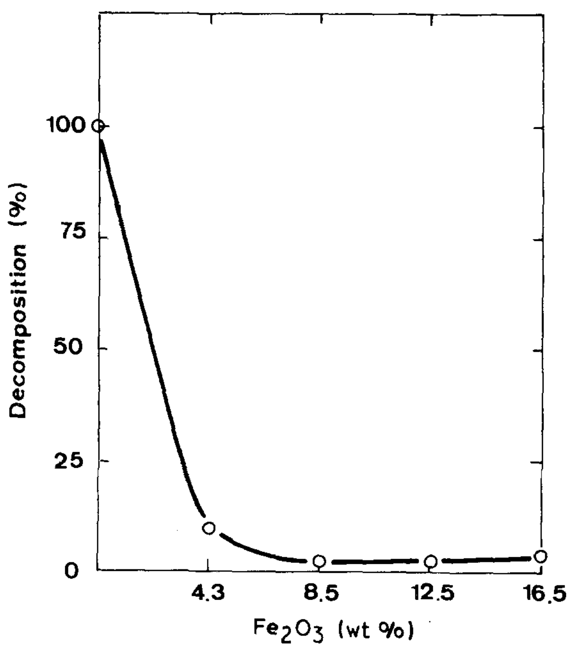

Figure 4 Disparity in thermal stability of Al_2TiO_5 and rich Fe_2O_3 solid solutions after annealing 300 h at 1000 °C.

5.3. Microstructure of Al_2TiO_5 and $Al(1-x)_2Fe_{2x}TiO_5$ solid solutions

Al_2TiO_5 samples synthesized by solid state reaction under cold or hot pressing conditions and after heat treatment (1500 °C, 15 h) exhibit a nearly homogeneous microstructure with $\simeq 1$ µm grains and some cracks on the boundaries of grains when studied by scanning electron microscopy (Fig. 5a).

After annealing at 1000 °C the samples show grains with a swollen area that implies that a decomposition of the material has occurred (Fig. 5b). This fact is confirmed by X-ray analysis.

The scanning electron microscopy examination of solid solutions samples with 8.5 wt % Fe_2O_3 ($x = 0.1$) show a grain size of 1 µm for cold-pressed materials (Fig. 6). Whereas a main grain size of 4 to 5 µm is observed for those from hot-pressed materials. In this case a high content of cracks is noticed.

A 200 h annealing at 1000 °C has no effect upon grain size whatever pressing mode is used, moreover no sign of surface alteration is observed meaning that there is none (or weak) decomposition of these materials. This is in good accordance with results obtained in the thermal stability section.

5.4. Thermal expansion

In the range 20 to 1000 °C, the thermal expansion of Al_2TiO_5 is low (0.8×10^{-6} °C^{-1}) [8] relative to the iron titanate value (3.3×10^{-6} °C^{-1}).

The Fe^{3+} ion in Al_2TiO_5 structure compound will thus lead to an increase of its thermal expansion coefficient. Then to be effective, Fe^{3+} substitution agent will have to answer two requirements: first to stabilize thermally the material below 1200 °C and moreover to hold its thermal expansion coefficient near the Al_2TiO_5 level.

Fig. 7 exhibits expansion curves for Al_2TiO_5, Fe_2TiO_5 compounds and $Al(1-x)_2Fe_{2x}TiO_5$ solid

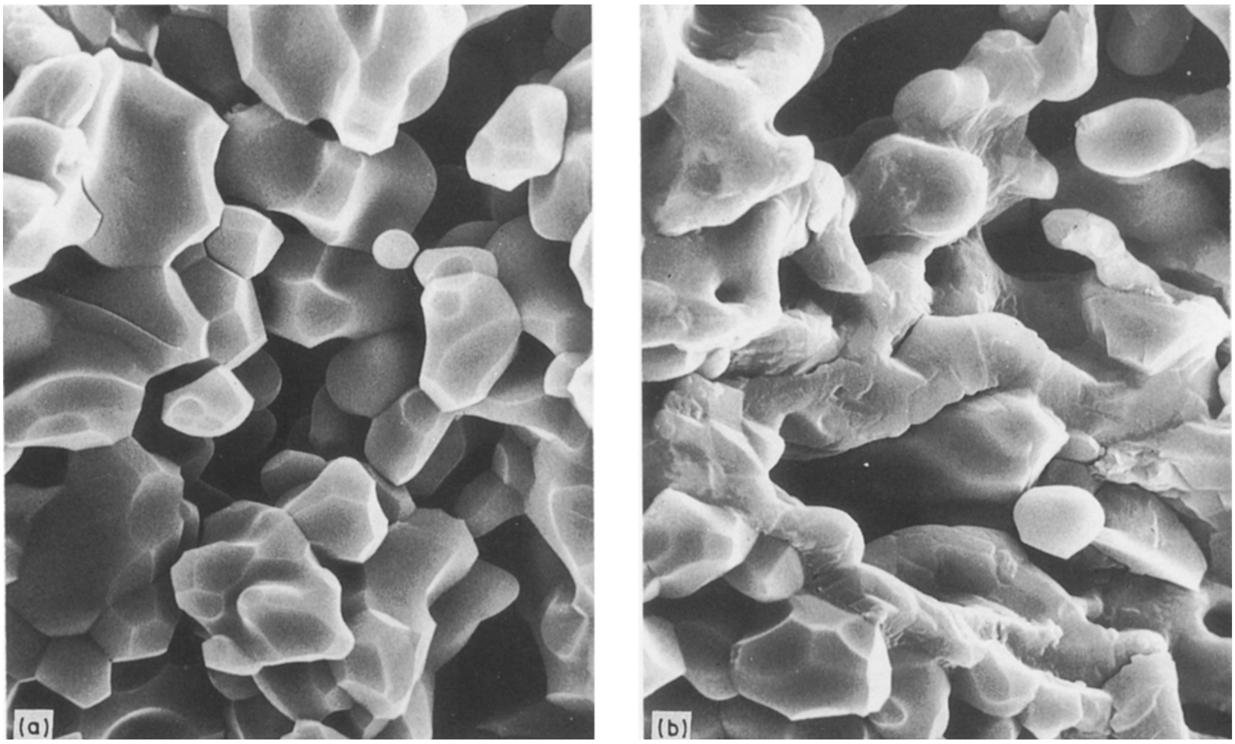

Figure 5 Scanning electron micrograph of Al_2TiO_5 (a) fired at 1500 °C for 15 h (G × 4800) (b) annealed at 1000 °C for 200 h (G × 4800).

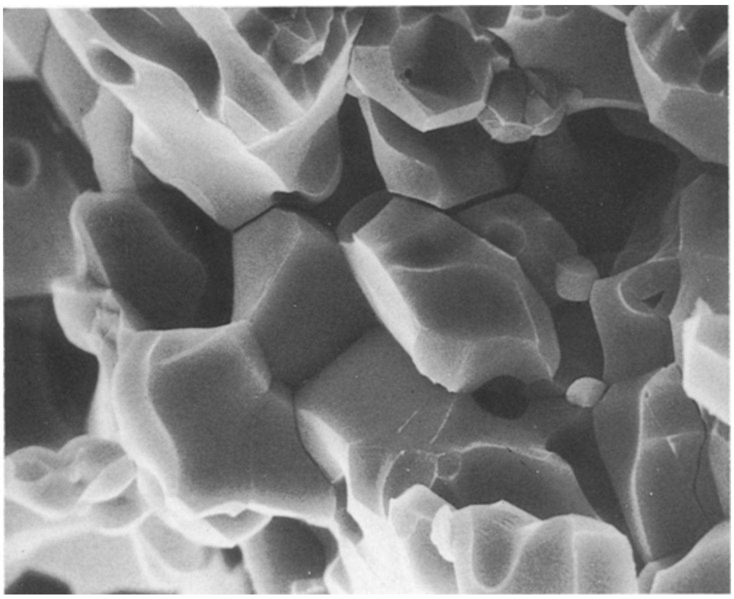

Figure 6 Scanning electron micrograph of solid solution $Al(1-x)_2\ Fe_{2x}TiO_5$ ($x = 0.1$ i.e. 8.5 wt % Fe_2O_3) (G × 4800) cold pressed and fired at 1500 °C (15 h).

solution ($x = 0.1$ i.e. 8.5 wt % Fe_2O_3). It can be seen on the heating portion of the curves, that Fe_2O_3 amount included in the structure does not change the thermal expansion value. This behaviour is also observed with the other solid solutions studied ($0 < x < 0.2$).

Moreover, as previously presented, these solid solutions have a great thermal stability even after annealing for 300 h at 1000 °C; then it was of interest to test their dilatometric behaviour after a so long a treatment.

Fig. 8 shows the thermal expansion curves of these solid solutions after this long annealing time. An increase in the thermal expansion coefficient of these materials can be seen; the lower the Fe_2O_3 amount, the higher the coefficient. The solid solution with the smallest Fe_2O_3 content ($x = 0.05$ i.e. 4.3 wt % Fe_2O_3) thus exhibits the strongest expansion ($\alpha = 3.4 \times 10^{-6}\,°C^{-1}$) in the range 20 to 1000 °C. For other solid solutions, the increase of thermal expansion is more limited ($\alpha = 1.2$ and $0.9 \times 10^{-6}\,°C^{-1}$ for $x = 0.1$ and 0.2, respectively). This evolution of the thermal expansion coefficient of solid solutions must be connected with their thermal behaviour. Solid solution ($x = 0.05$) is thus the least thermically stable (although its decomposition rate is weak = 9%) of the studied solid solutions and also presents the greatest increase in the thermal expansion coefficient.

It appears that the solid solution with $x = 0.1$ (8.5 wt % Fe_2O_3) shows a great thermal stability and

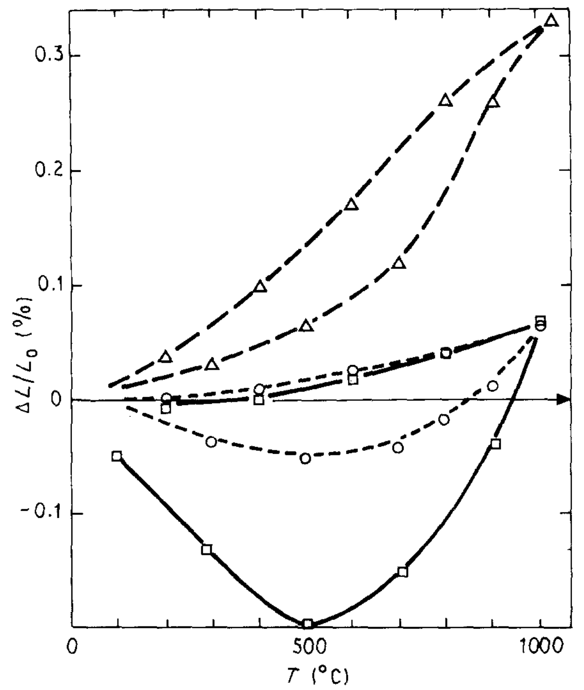

Figure 7 Thermal expansion curves of Al_2TiO_5 (○), Fe_2TiO_5 (△), sol-solution $Al(1-x)_2Fe_{2x}TiO_5$ ($x = 0.1$ i.e. 8.5 wt % Fe_2O_3 (□).

an expansion coefficient near to that of Al_2TiO_5 even after annealing for 300 h at 1000 °C.

5.5. Mechanical properties

The mechanical properties of hot-pressed samples (1350 °C) which were then heat treated (15 h at 1500 °C) and correspond to a solid solution Al $(1-x)_2Fe_{2x}TiO_5$ where $x = 0.1$ were studied. Mechanical strength and Young's modulus are obtained using the three-point flexural test at room temperature. Experimental values are shown in Table I.

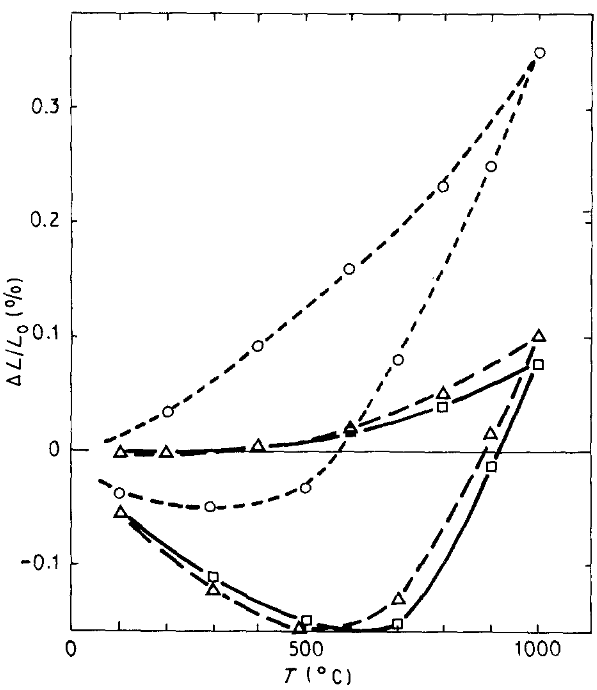

Figure 8 Thermal expansion of solid solutions $Al(1-x)_2$ Fe_{2x} TiO_5 after 300 h annealing at 1000 °C (a) $x = 0.05$ i.e. 4.3 wt % Fe_2O_3 (○), (b) $x = 0.1$ i.e. 8.5 wt % Fe_2O_3 (△), (c) $x = 0.2$ i.e. 16.5 wt % Fe_2O_3 (□).

TABLE I

	Strength (MPa)	Young's modulus (GPa)
Al_2TiO_5	10	4
$Al(1-x)_2Fe_{2x}TiO_5$ Initial state	5.5	5
Annealed 300 h at 1000 °C	7	5

For these ceramics synthesized under our experimental conditions, we can see a decrease in the mechanical strength value relative to the Al_2TiO_5 one, whereas the Young's modulus is stable. This is certainly due to higher grain size ($\simeq 5$ µm).

It is likely that by optimizing experimental conditions, materials having this solid solution composition should present mechanical characteristics at least equal to those of Al_2TiO_5.

After 300 h annealing at 1000 °C, the mechanical strength of materials is increased. MEB examination of annealed samples shows fine crystallization which improves mechanical properties.

6. Conclusions

The partial substitution of Al^{3+} ions in Al_2TiO_5 structure by Fe^{3+} ions leads to the formation of solid solutions with a general formula $Al(1-x)_2Fe_{2x}TiO_5$.

The study of these solid solutions (with $0 < x < 0.2$, prepared by solid state reaction), shows that the presence of iron ions, brings about a catalytic effect in the material formation.

Crystallization of these solid solutions as a function of the heat treatment temperature exhibits process in several steps.

Solid solutions are characterized by

(i) change in the lattice parameters compared to the Al_2TiO_5 ones
(ii) great thermal stability (even after 300 h annealing at 1000 °C)
(iii) the scanning electron microscopy examination of samples, shows a microstructure with grains size smaller for the cold-pressed specimens than for the hot-pressed ones; after 200 h annealing at 1000 °C, there is no alteration of the surface area
(iv) the thermal expansion coefficient of these materials is similar to that of Al_2TiO_5, and is independent of the iron content. A long annealing (300 h) at 1000 °C increases the thermal expansion. The lower the iron content is the greater the coefficient.

A solid solution with $x = 0.1$ (8.5 wt % Fe_2O_3) presents a strong thermal stability and a thermal expansion coefficient near the Al_2TiO_5 value even after such long annealing.

Mechanical properties of such materials corresponding to this solid solution exhibit lower strength than Al_2TiO_5. After annealing, properties are, however, improved owing to a microcrystallization in the samples.

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