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# Effect of micro-cracking on the thermal conductivity and thermal expansion of tialite ($Al_2TiO_5$) ceramics

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**Abstract**

*The pure and magnesium silicate ($Mg^{2+}/Si^{4+}$) doped tialite ceramics were prepared from the homogenized mixture of alumina and titania by uniaxial pressing and pressure-less sintering at 1550 °C in air. Thermal conductivity and thermal expansion of the doped and undoped tialite ceramics were measured from 30 to 700 °C. The identical trend in the behaviour of these thermal properties most probably is influenced by the population, size and shape of microcracks present throughout the grain and grain boundaries as complemented by the microstructural observations. The observed decrease in thermal properties of the doped in comparison to the pure tialite can be attributed to the substitutional $Mg^{2+}$ and $Si^{4+}$ at $Al^{3+}$ site in $Al_2TiO_5$ which promotes the phonon scattering and causes modifications in micro-crack density and the morphology of the cracks.*

***Keywords****: tialite ceramics, solid state synthesis, thermal conductivity, thermal expansion*

## I. Introduction

Tialite ($Al_2TiO_5$) is explored as a candidate material for new generation of diesel exhaust particulate filters because of its high thermal shock resistance resulting from inherent thermal expansion in combination with high refractoriness and low thermal conductivity [1,2]. In addition, it is also used extensively as crucibles and as raiser tubes in non-ferrous foundries [3,4]. Tialite has a pseudo brookite structure with orthorhombic unit cell with each $Al^{3+}$ or $Ti^{4+}$ cation surrounded by six oxygen ions forming distorted oxygen octahedra. These $AlO_6$ or $TiO_6$ octahedra form (001) oriented chains weakly bonded by shared edges [5,6]. Such a structure is responsible for the thermal expansion anisotropy. A typical expansion of the single crystal for crystallographic axes $\alpha_a$, $\alpha_b$ and $\alpha_c$ are $11.8\times10^{-6}$/°C, $19.4\times10^{-6}$/°C and $-2.6\times10^{-6}$/°C (25–1000 °C) respectively [7]. Based on the crystallographic expansion the bulk thermal expansion value is estimated to be $9.4\times10^{-6}$/°C. However, the experimentally observed bulk thermal expansion is around $1\times10^{-6}$/°C, which can be attributed to the stresses at grain boundaries due to anisotropic expansion [8,9]. Hence, the objective of the current work is to correlate the effect of these microcracks with thermal properties, which plays a key role in controlling the thermal expansion and thermal conductivity of tialite ceramics as a function of temperature.

## II. Experimental procedure

In the present study tialite based formulations are prepared from commercially available powders. Alumina powder ($\alpha+\gamma$-$Al_2O_3$, Baikowski, France), titania ($TiO_2$, Qualigens, India) and talc ($Mg_3Si_4O_{10}(OH)_2$, India) were used for the processing of the specimens. The powders were characterized by X-ray diffraction (XRD, Bruker's D8 advanced) for phase analysis, particle size analyser for particle size distribution (Nano-S, Malvern) and scanning electron microscope (S-4300SE/N, Hitachi) for morphology. The formulations of the pure (AT) and $Mg^{2+}/Si^{4+}$ doped tialite (TAT-5) were prepared by mixing stoichiometric amounts of alumina and titania powders and addition of 5 wt.% of magnesium silicate (talc) in the TAT-5 sample [10].

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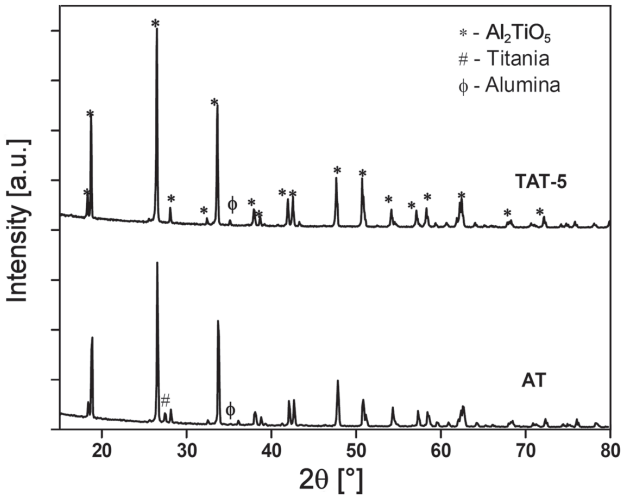


**Figure 1. XRD patterns of AT and TAT-5 samples sintered at 1550 °C**

These formulations were granulated with 2 wt.% of polyvinyl alcohol as a binder and compacted into green samples of dimensions 63 × 63 × 8 mm using a uniaxial hydraulic press with the pressure of 55 MPa. The green specimens were dried at 110 °C and green density of the compacted samples (estimated by the rule of mixtures) was found to be greater than 50% of the theoretical density. The samples were further subjected to binder removal at 500 °C at a heating rate of 2 °C/min followed by heating to the peak temperature of 1550 °C at a heating rate of 2 °C/min under pressure-less conditions for a soaking time of 1 h.

All characterizations were carried out on the samples prepared from the same batch as described above. The phase composition of the samples was characterized by XRD and microstructure was analysed by SEM at room temperature. In order to study the thermal expansion behaviour, the samples were cut into 25 mm length and 6 × 5 mm cross section and subjected to dilatometry (NETZSCH 402 C Dilatometer) at a heating rate of 5 °C/min. The samples were also cut into plates having dimension 10 × 10 mm and thickness of 3 mm for thermal conductivity determination using Netzsch LFA 429 analyser. The samples were heated from 30–700 °C at a heating rate of 10 °C/min and thermal diffusivity values were recorded.

## III. Results and discussion

The phase content, particle size and morphology of the alumina, titania and talc are given in Table 1 and the XRD patterns recorded for the tialite AT and TAT-5 samples sintered at 1550 °C are shown in Fig. 1. Phase composition of the tialite samples is calculated using the peak height intensity ratios from the XRD patterns [11–13]. It was shown that magnesium silicate addition in the pure AT sample has increased the phase content of $Al_2TiO_5$ phase from 92 to 96% (Fig. 1).

The variations of thermal expansion ($dL/L_0$) and thermal conductivity with temperature of the AT and TAT-5 samples are shown in Fig. 2a and Fig. 2b, respectively. It is evident from Fig. 2, that the thermal expansion and thermal conductivity of both samples have shown a decreasing trend till the temperature reaches 350 to 400 °C. Beyond 400 °C, a prominent slope change is evident in thermal conductivity, whereas, in the case of thermal expansion behaviour the slope change is observed beyond 500 °C.

The observed decrease in thermal conductivity from room temperature to 400 °C can be attributed to the low temperature phonon scattering in the AT and TAT-5 samples [9]. Relatively low thermal conductivity of the TAT-5 sample in comparison to the AT sample can be attributed to the presence of substitutional $Mg^{2+}$ and $Si^{4+}$ at $Al^{3+}$ site in $Al_2TiO_5$ generated during sintering, as a result of the high temperature decomposition of magnesium silicate. The substitution of $Al^{3+}$ with $Mg^{2+}$ and $Si^{4+}$ results in emergence of multivalent titanium ($Ti^{3+}$/$Ti^{4+}$) and oxygen vacancies which increases hopping of electrons in the sample TAT-5 and, thus, promoting the phonon scattering [9,10].

In addition, the observed inherent microcracks in the aluminium titanate ceramics (Fig. 3) are also expected to play important role in controlling the thermal behaviour. The population of the microcracks and morphology (size and shape) of the microcracks are dependent on the micromechanical stresses generated at the grain boundaries due to the anisotropic expansion along the crystallographic axis [8]. The low thermal expansion values observed for the TAT-5 sample can be attributed to the increased crack density along with narrow crack opening width unlike in the case of the AT sample with a comparatively larger crack opening width as marked in the micrographs shown in Fig. 3. Even though micrographs at different magnifications are obtained in each of the two samples only one representative microstructure in each case is included in the manuscript for the sake of clarity. Though distributed pores may arrest the crack propagation in the case of the AT sample, low stress tolerance of the matrix leads to macro flaws. In the earlier studies authors

**Table 1 Phase content, particle size and morphology of the alumina, titania and talc powders**

| Samples | Phases present | Particle size | Morphology |
|---|---|---|---|
| alumina | α-$Al_2O_3$ with 15–20% of γ-$Al_2O_3$ | 150–200 nm | irregular |
| titania | anatase | 200–300 nm | irregular |
| talc | magnesium silicate | 16 μm | plate-like |

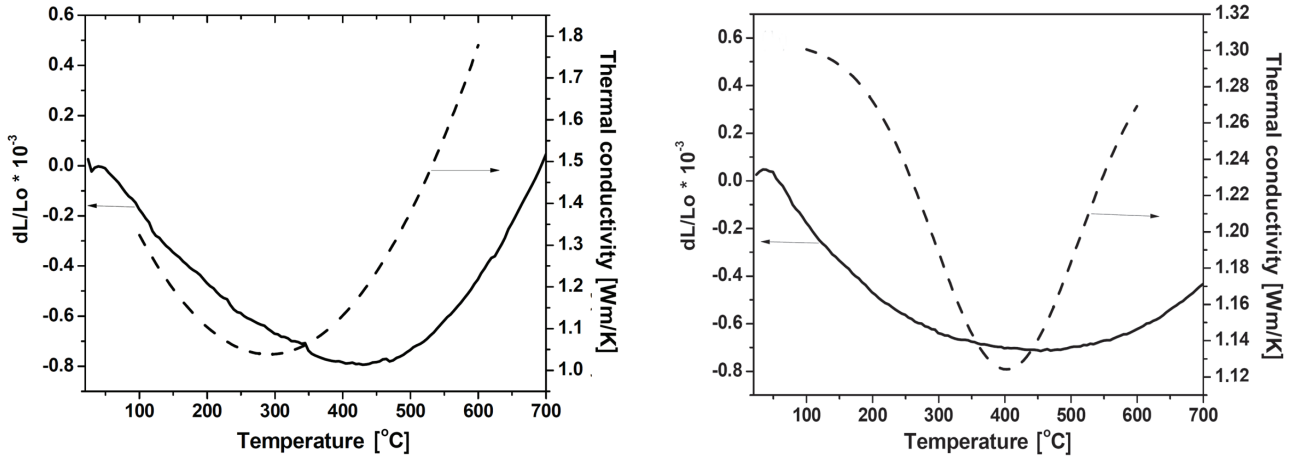


**Figure 2. Thermal expansion and thermal conductivity versus temperature for samples: a) AT and b) TAT-5**

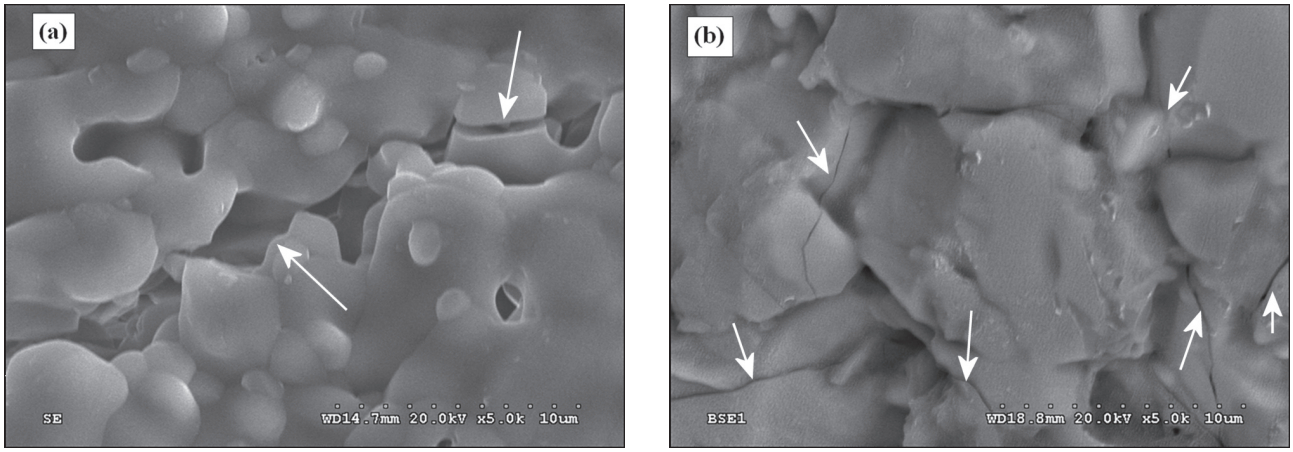


**Figure 3. Microstructure of sintered samples: a) AT and b) TAT-5**

have also reported the significant increase in crack volume in case of the TAT-5 samples through dilatometric hysteresis curves recorded during heating and cooling experiments [10].

It is believed that thermal behaviour of the prepared tialite samples above 400 °C is influenced by microstructural changes. Though phonon scattering is also operative in this temperature range and responsible for the decrease in thermal conductivity, the observed increase in thermal conductivity beyond 400 °C can be correlated with healing of the inherent microcracks, which becomes more prominent [10]. It can be understood that, as the temperature increases, inter and intragranular cracks get healed and provide paths for effective heat transfer through conduction. This explanation can be supported by the thermal expansion behaviour. The healing of the inherent microcracks, which are open at room temperature (Fig. 3), starts as the temperature increases and compensates for the expansion till it reaches ~500 °C. Above 500 °C, the healing of the microcracks is almost complete and it expands as a monolith resulting in a plateau followed by a slope change indicating initiation of bulk expansion.

## IV. Conclusions

The study suggests a possible role of density and morphology of microcracks on the thermal expansion and thermal conductivity behaviour of tialite. The study also reveals a significant decrease in the coefficient of thermal expansion value of $–0.62\times10^{-6}$/°C (30–600 °C) and a marginal decreases in thermal conductivity of 1.28 W/mK (at 600 °C) for the doped tialite (TAT-5) in comparison to the thermal expansion of $–0.44\times10^{-6}$/°C (30–600 °C) and thermal conductivity of 1.8 W/mK (600 °C) for the pure tialite ceramic (AT). The observed decrease in thermal properties of the TAT-5 sample in comparison to the AT samples due to magnesium silicate addition can be attributed to the existence of substitutional $Mg^{2+}$ and $Si^{4+}$ at $Al^{3+}$ site in $Al_2TiO_5$ which promotes the phonon scattering and causes modifications in micro-crack density and the morphology of the cracks.

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