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Preparation and properties of Y_2O_3 containing zirconia–mullite composites derived from sillimanite beach sand

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Abstract

Mullite–zirconia composites with 2–6 mol% yttrium oxide have been prepared from Indian coastal sillimanite beach sand, zirconia and alumina. All raw materials have been attrition milled and then isostatically pressed followed by sintering in the range of 1500–1600 °C with a 2-h soaking period. Then the sintered materials have been characterised in terms of bulk density, linear shrinkage, hot modulus of rupture, X-ray diffraction, infra red spectroscopy and microstructural features. The effect of yttrium oxide with change of sintering temperature for different properties have been discussed. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: Zirconia–mullite composites; Preparation; Properties

1. Introduction

Mullite is an alumino-silicate widely used in traditional refractory applications and one of the most studied crystalline phases in the SiO_2–Al_2O_3 system [1–3]. Its good chemical inertness, low thermal conductivity, high creep resistance, low thermal expansion co-efficient make it most suitable for high temperature technological use [4,5].

The relatively poor mechanical properties and difficulty in sintering has prevented its wide spread application. One of the method of improving both sintering and mechanical properties of mullite is by zirconia addition. In solid solution zirconia increases the sintering rate of mullite [6] and as a second phase, acts as a grain growth inhibitor [6] and transformation toughening agent [7].

In this study, we have worked with the system Al_2O_3–SiO_2–ZrO_2 (Fig. 1) as determined by Budnikov and Litvakovski, Doklady Akad. Nauk S.S.S.R. 106, 268 (1956) [8].

The gradual depletion of naturally occuring raw materials has compelled us to search for alternate materials for synthetic raw materials preparation. India is one of the countries with a long coast line (more than 7600 km) with large deposits of beach sand. Beach sand minerals contain some rare earths. After the extraction of these rare earths huge amounts of sand that are left over are nothing but a mechanical mixture of ilmenite, rutile, zircon, sillimanite, garnet and quartz. In the field of glass and ceramics, sillimanite, zircon and garnet are important. The various minerals are separated by wet gravity separation followed by dry separation technique, which includes magnetic and electrostatic processes [9]. Utilization of these minerals not only cleans the environment but also saves our valuable naturally occurring mineral reserves. In India, different beach sand minerals are obtained from Indian Rare Earths Limited (IREL), a Government of India undertaking organization.

In the present study, Indian coastal sillimanite beach sand, alumina and zirconia powders are selected as principal raw materials. The objective of the present work is to study the effect of Y_2O_3 on the physical, thermo-mechanical properties and micro structural characteristics of zirconia-mullite composites utilising sillimanite beach sand from the Indian coast.

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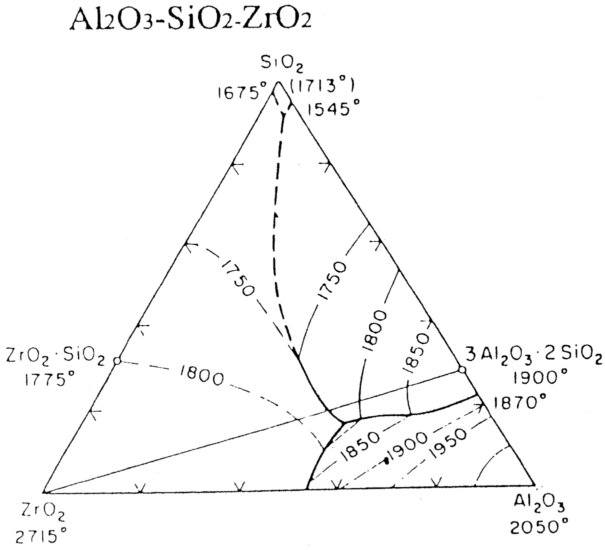

Fig. 1. System Al_2O_3–SiO_2–ZrO_2.

2. Experimental

The starting materials, sillimanite beach sand from Indian Coast, zirconia powders, Y_2O_3 (all supplied by IREL, Mumbai, India) and alumina (supplied by Indian Aluminum Company Limited, India) are ground together in an attritor mill for 9 h with zirconia balls in isopropyl alcohol medium. The batch compositions and sample codes of different batches are listed in Table 1. Chemical analyses and X R D of the raw materials are given in Table 2. The slurry from attritor mill is dried at 110±5 °C and the dried mass is granulated by sieving and uniaxially pressed into bars (65×6×6 mm) and discs (diameter 25 mm) at ~110 MPa followed by cold isostatic pressing at 260 MPa using a 5% PVA solution as binder. The isopressed samples are dried and sintered at temperature ranging between 1500 and 1600 °C with a 2-h soaking period. Yttria (2, 4, and 6 mol%) is added to the mixture with respect to zirconia content.

The apparent porosity of the sintered composite is measured by water displacement method. Linear shrinkage of the fired body is measured with the help of digital slide calipers.

Table 1
Batch composition and sample codes for different batches

Additive (Y_2O_3)		Sillimanite (wt.%)	Zirconia (wt.%)	Alumina (wt.%)	Sample code
(mol%)	(wt.%)				
0	0	45.33	40.0	14.67	A9
2	3.63	43.56	39.04	13.86	Y2
4	7.10	42.48	37.70	12.72	Y4
6	10.5	41.12	36.12	12.26	Y6

The high temperature modulus of rupture strength (HMOR) is measured by an instrument developed at the Central Glass and Ceramic Research Institute, Calcutta, India. The test is carried out under three point loading on a span of 45 mm. During testing the rate of temperature rise is maintained at 5 °C/min and the samples are allowed to experience a soaking of 30 min at testing temperature (1250 °C). The load is then applied at a rate of 4.90 MPa. Room temperature hardness and fracture toughness (K_{ic}) is measured by the Vickers's indentation method following the equation of Antis et al. [10] using Wolpert Hardness Tester, Germany. Modulus of elasticity (Young's modulus) of sintered samples are measured by sonic method [11]. This is a non-destructive testing method. this modulus of elasticity (MOE) value is utilized for the estimation of fracture toughness.

Different phases of the sintered bodies are identified by X-ray diffraction study through the diffractometer. Here, tetragonal zirconia in association with monoclinic zirconia and mullite are expected phases to be developed after sintering. The t-ZrO_2 fraction content is determined on the sintered surfaces from the ratio of XRD (Philips PW 1010) integrated peak intensity of t-ZrO_2 (111) to m-ZrO_2 (111) and m-ZrO_2 (111) following Garvie and Nicholson's equation [12].

IR spectrogram of the sillimanite sand and sintered samples are taken by Hitachi Spectrophotometer (270-90).

Micro structural analyses is performed on the mirror polished surface after thermal etching. A LEO SEM with EDAX facility is used for energy dispersive X-ray analyses.

3. Results and discussion

Chemical analyses of the raw materials have been done. sillimanite sand contains Fe_2O_3, TiO_2 and alkalis as impurities. Zirconia also contains 0.28% iron oxide.

Table 2
Chemical analyses and XRD of raw materials

Constituents	Sillimanite (wt.%)	Zirconia (wt.%)	Alumina (wt.%)
SiO_2	36.01	1.11	0.64
Al_2O_3	56.99	1.41	97.63
TiO_2	1.32	Trace	Trace
CaO	0.46	Trace	Trace
MgO	0.15	Trace	0.51
Fe_2O_3	0.57	0.28	0.19
ZrO_2	3.50	96.42	–
K_2O	0.19	0.12	0.13
Na_2O	0.07	0.05	0.4
XRD			
Main phase	Sillimanite	Monoclinic	α-Al_2O_3

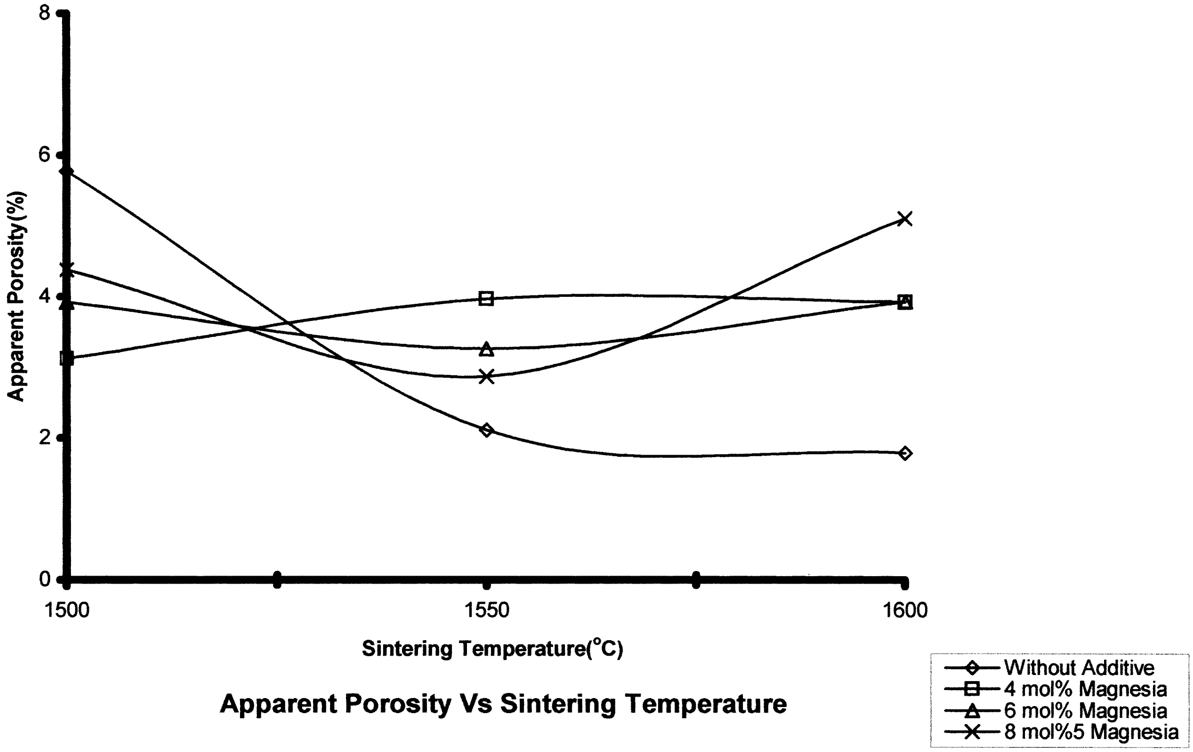

Fig. 2. Apparent porosity of sintered composites as a function of sintering temperature.

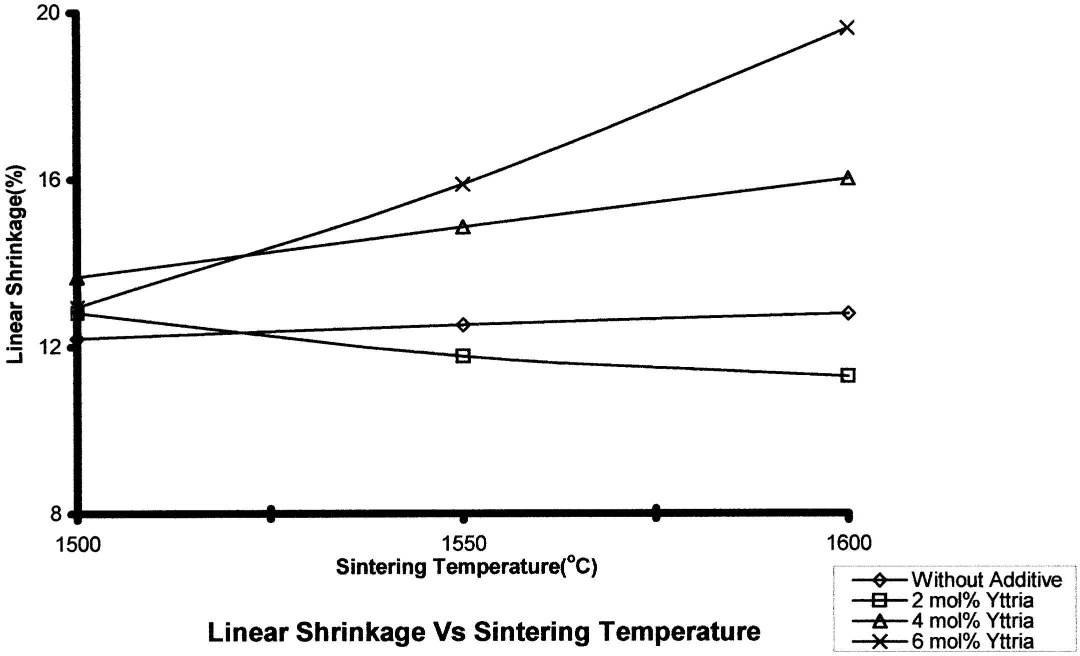

Fig. 3. Linear shrinkage of sintered composites as a function of sintering temperature.

Table 3
Vicker's hardness and fracture toughness of Y4 composite sintered at different temperatures

Sintering temperature (°C)	Hardness (GPa)	Fracture toughness (MPa $m^{1/2}$)
1500	11.52	3.93
1550	8.74	3.71
1600	4.30	3.69

Table 4
Young's modulus of different composites sintered at different temperatures

Sintering temperature (°C)	Young's modulus (GPa)		
	Y2	Y4	Y6
1500	169	210	158
1550	237	168	160
1600	308	293	198

X-ray diffraction study of zirconia reveals both tetragonal and monoclinic phases are present. In the case of Al_2O_3, α-Al_2O_3 is the sole phase.

3.1. Physical properties

In this type of reaction sintering process, the chemical reaction of the starting materials and the elimination of the porosity in the powder compact are both achieved in a single heat treatment step [13]. Fig. 2 shows the change in apparent porosity of the samples containing yttrium oxide against temperature. As the sintering temperature increases, yttrium oxide helps in grain growth of the samples. Exaggerated grain growth is responsible for higher porosity as the temperature increases. But the samples without additive show a downtrend in porosity with rise in temperature. Composite with 2 mol% yttrium oxide shows a downfall in linear shrinkage with increasing temperature. But with higher amount of yttrium oxide content, composites are showing increasing trend in shrinkage with increase in sintering temperature. The presence of this additive stabilizes the zirconia in the composite, which in turn increases the shrinkage of the composite. Fig. 3 shows the change in linear shrinkage with sintering temperature.

3.2. Mechanical properties

Composites with yttrium oxide show an increase in hot MOR value with increase in sintering temperature except Y2 samples. The variation of high temperature strength can be correlated to the increase of fracture

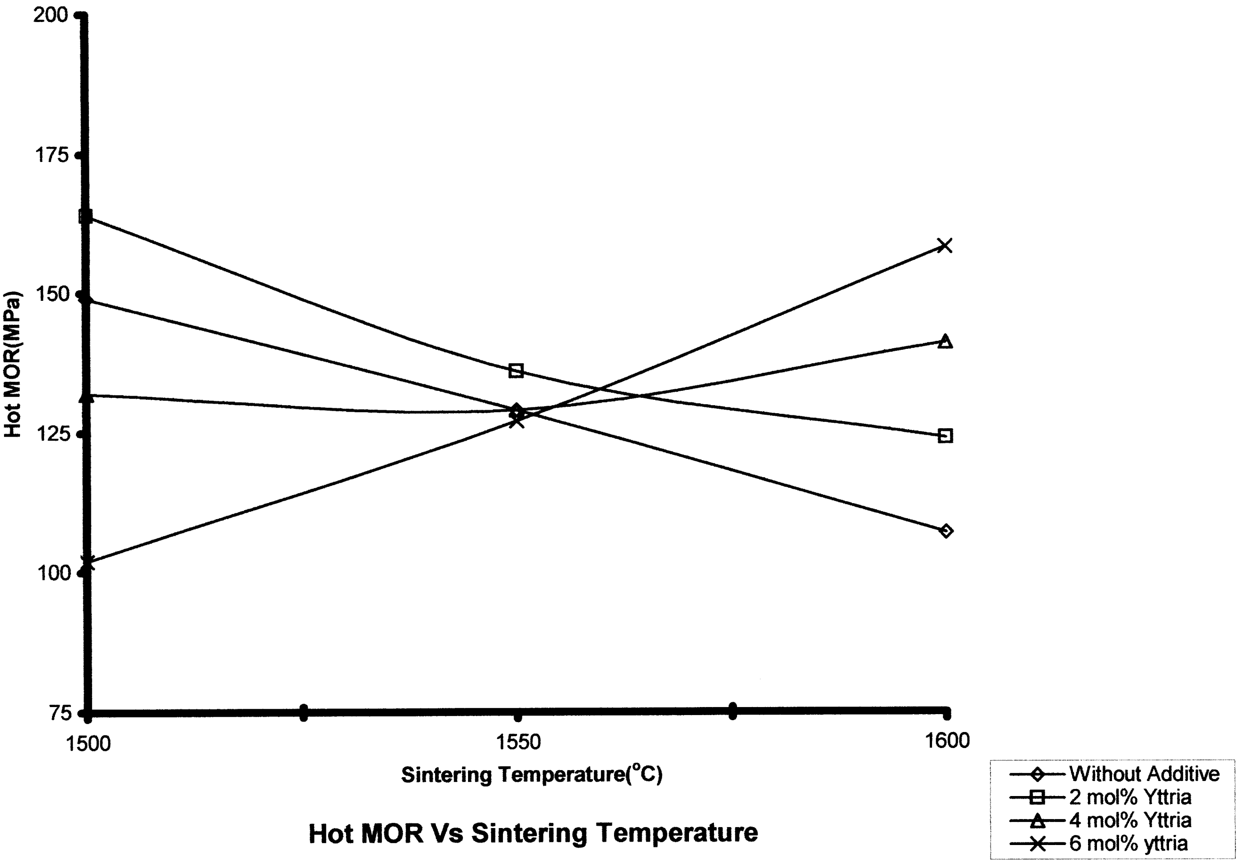

Fig. 4. Hot MOR of sintered composites as a function of sintering temperature.

energy due to a reduction of crack tip stress intensity in the plastic zone ahead of the crack by energy dissipation through relaxation occurring in the grain boundary phase [14]. The higher strength in case of Y6 and Y4 with rise in sintering temperature is observed. Viscosity plays a main role at high temperature. Viscous phase can relax the stress concentration ahead of the crack tip which inhibit the grain boundary sliding and as a result no plasticity is observed and no degradation of mechanical strength. This increases the strength at higher temperature. Fig. 4 shows the change in Hot MOR value with sintering temperature. Table 3 shows the result of Vickers's hardness (GPa) and fracture toughness (MPa $m^{1/2}$) of Y4 composite sintered at dif-

Table 5
Relative tetragonal zirconia (Z_t) content (%) of different composites sintered at different temperatures

Sintering temperature (°C)	Z_t content (%)		
	Y2	Y4	Y6
1500	54.79	58.26	84.90
1550	34.34	80.15	83.33
1600	22.58	49.51	50.88

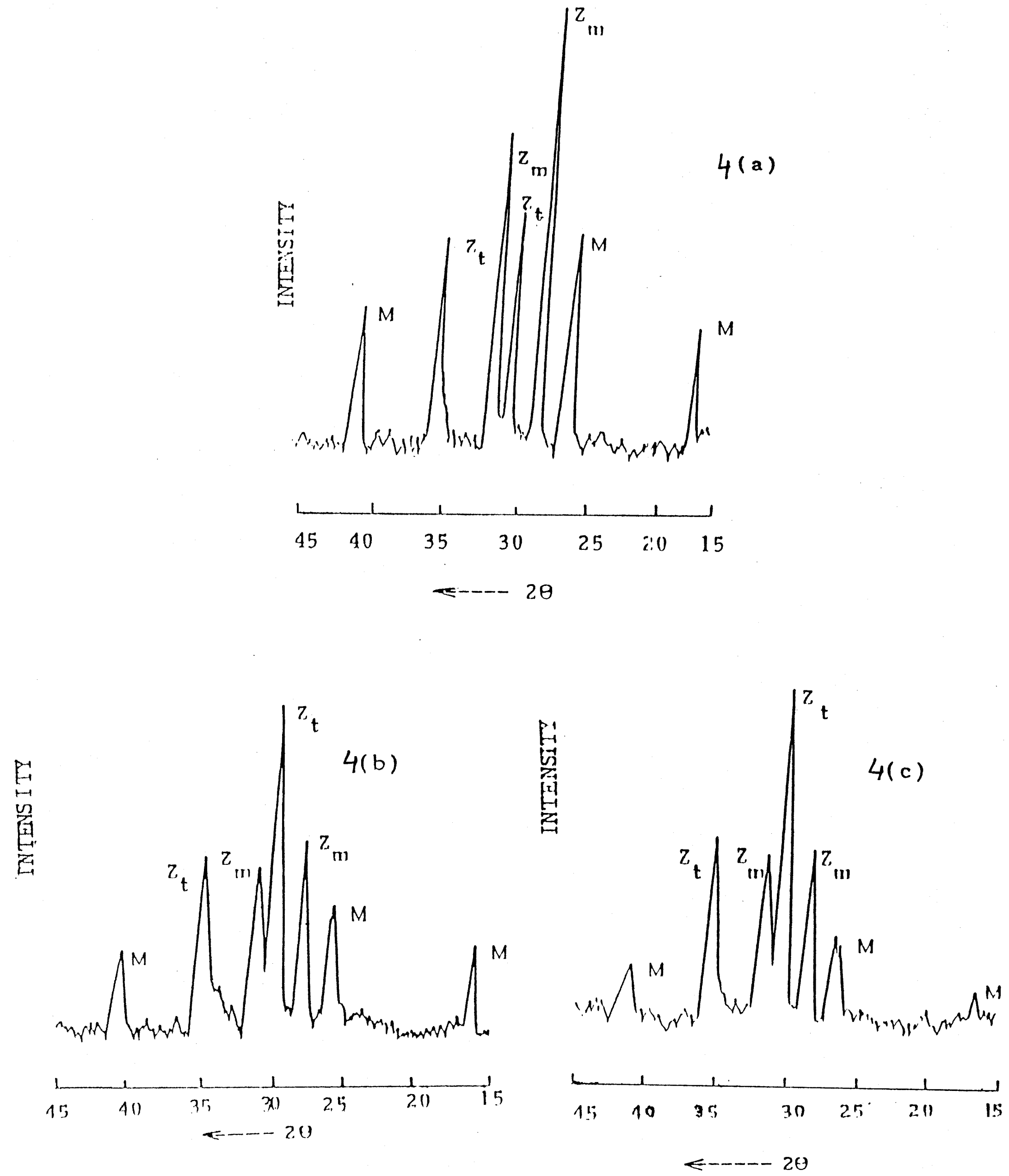

Fig. 5. X-ray diffraction patterns of zirconia–mullite composites (sintered at 1600 °C for 2 h) showing the main peaks of zirconia and mullite: (a) Y2 composite; (b) Y4 composite; (c) Y6 composite. Z_m monoclinic zirconia; Z_t tetragonal zirconia; M, mullite.

ferent temperatures. Y4 having highest hardness and toughness value at 1500 °C. Table 4 shows the result of Young's modulus value with change in sintering temperature. composites with yttrium oxide show an overall increasing trend in modulus of elasticity as the sintering temperature increases.

Fig. 5(a–c) shows the X-R-D of Y2, Y4, Y6 composites fired at 1600 °C for 2 h. Table 5 shows the relative tetragonal zirconia content (%) with change in sintering temperature.

IR spectrogram of Y4 composite fired at 1600 °C for 2 h has been given in Fig. 6(b).

3.3. Micro structural analyses

Fig. 7(a,b) shows the scanning electron microstructure of thermally etched polished surface of zirconia mullite composites sintered at 1550 °C. The microstructure contains elongated and equiaxed mullite grains (black) along with zirconia grains (white). Most of zirconia grains are intergranular and few are intragranular. Fig. 8(a,b) shows the EDX diagrams of mullite and zirconia phases of Y6 composite sintered at 1600 °C. Here, yttrium oxide goes into solid solution with zirconia and in smaller amount with mullite.

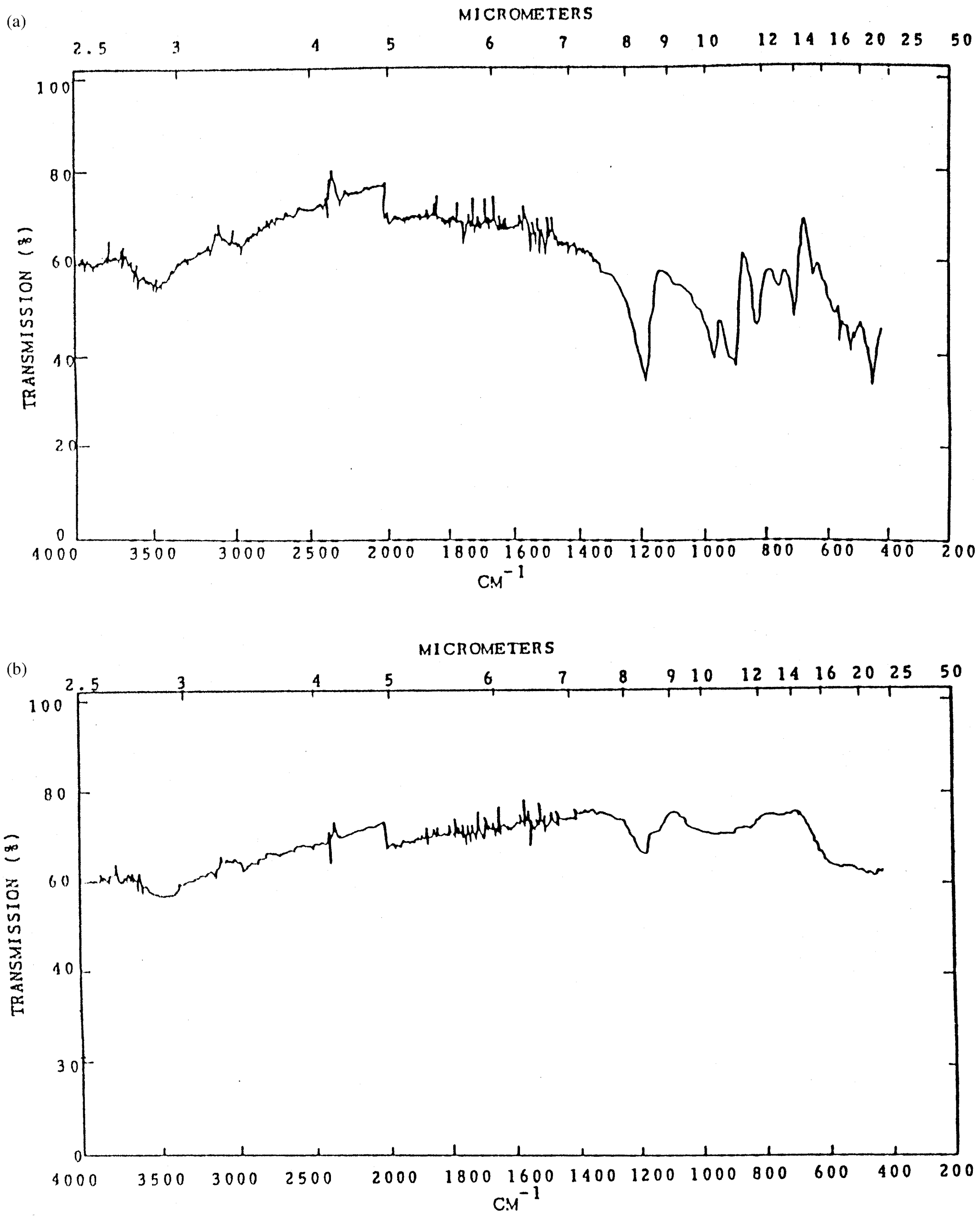

Fig. 6. Infra red spectroscopy of sillimanite sand and zirconia–mullite (Y4) composite (sintered at 1600 °C for 2 h): (a) sillimanite, (b) Y4.

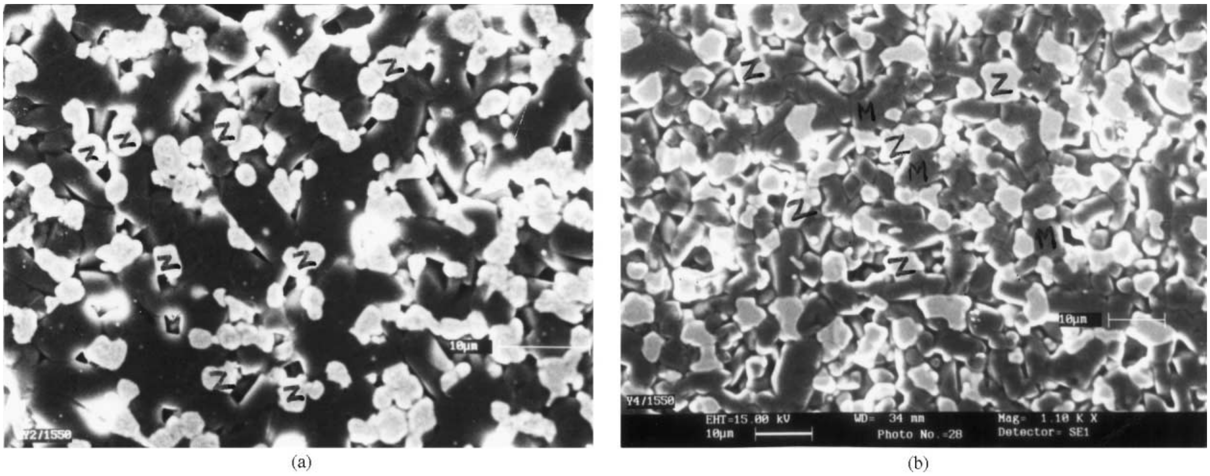

Fig. 7. Scanning electron microstructures of zirconia–mullite composites (sintered at 1550 °C for 2 h) showing the mullite (black) and zirconia (white) grains: (a) Y2; (b) Y4.

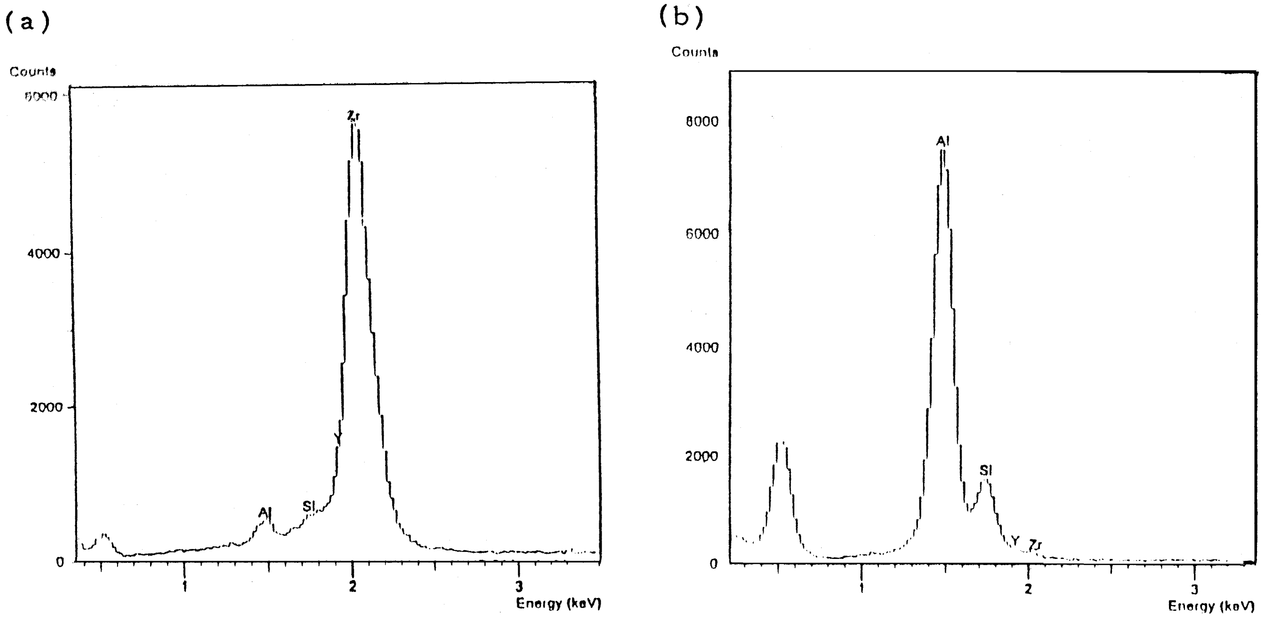

Fig. 8. EDX analysis of zirconia and mullite phases of zirconia–mullite composite (Y6 sintered at 1600 °C for 2 h): (a) zirconia; (b) mullite.

4. Conclusion

Mullite zirconia composites from Indian coastal sillimanite beach sand, zirconia and alumina can be prepared in the temperature range of 1500–1600 °C with yttrium oxide as an additive. The addition of yttrium oxide overall improves the physical, thermo-mechanical properties of the composites. The microstructure of zirconia-mullite composites are characterized by cross-linked structure of elongated mullite grains along with sub rounded to rounded zirconia grains. Zirconium has higher atomic number compared to aluminum and silicon, the zirconia particles clearly differ from their surrounding mullite matrix under SEM by sharing a brighter image. There are two types of zirconia particles present in the microstructures. One is intergranular and other one is intragranular.

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