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Effect of magnesia additions on the properties of zirconia–mullite composites derived from sillimanite beach sand

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Abstract

Zirconia–mullite composites with 4–8 mol% magnesium oxide have been prepared from Indian coastal sillimanite beach sand, zirconia and alumina. The X-ray diffraction study reveals all raw materials are crystalline in nature. In zirconia, monoclinic is the major phase detected. Alumina is having α-Al_2O_3 as main constituent. X-R-D of magnesia shows periclase is major phase. Milling of the mixtures of all raw materials has been carried out in an attritor mill for 9 h. After drying and pressing the samples were sintered between 1500 °C and 1600 °C with 2 h of soaking. The physical properties of the sintered materials namely bulk density and linear shrinkage have been evaluated. The infra-red spectrums of sillimanite sand and sintered samples have been described. The thermo-mechanical and mechanical properties namely hot modulus of rupture, hardness and fracture toughness of sintered materials have also been evaluated. Microstructural characterization of the sintered samples through scanning electron microscope have shown mullite and zirconia are the two main phases.

Keywords: A. Sintering; B. Composites; C. Mechanical properties; D. Mullite; D. ZrO_2; E. Refractories

1. Introduction

Mullite (MAl_2O_3–$NSiO_2$ with M/N ratio changes from 3:2 to 2:1) is a widely used and important compound in industrial ceramic products [1,2]. Although it is difficult to produce fully dense single phase bodies [3]. To achieve optimum mechanical properties different processing techniques have been attempted namely hot pressing, hot isostatic pressing and sol-gel processing [4,5]. It has been shown that significant toughening can be obtained by addition of zirconia particles to a mullite matrix [5]. Toughening of mullite composites by zirconia additions is dependent on different mechanisms: stress induced transformations, microcracking, crack bowing and crack deflection [6], and all mechanisms depend on variables such as matrix stiffness, zirconia particle size, chemical composition, temperature and strength.

In mullite–zirconia composites the effect of different additives on the physical, thermo-mechanical properties and also on formation has been extensively studied. For CaO contents of more than 4 wt.% alumina appears as a second phase and for CaO $<$ 4% mullite appears as the second phase [7]. TiO_2 forms solid solution with zirconia and mullite and its solid solubility in both is about 4 wt.% [8]. Addition of CeO_2 enhances the formation of mullite and also increases the fraction of tetragonal zirconia. CeO_2 also forms a solid solution with zirconia [9].

The aim of this work was to study the influence of magnesia on the microstructural, thermo-mechanical properties of zirconia–mullite composites. In the present study Indian coastal sillimanite beach sand, alumina and zirconia powder were used as the main raw materials.

2. Experimental

Here, sillimanite beach sand from Indian Coast, Zirconia powders and MgO (all supplied by Indian Rare Earth Ltd. Bombay, India) and Alumina (supplied by Indian Aluminium Company Limited, India) were ground together in an attritor mill for 9 h with zirconia balls in isopropyl alcohol medium. Chemical analyses of the raw materials are summarized in Table 1. The sample

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Table 1
Batch composition and sample codes for different batches

Sample code	Additive		Sillimanite	Zirconia	Alumina
	(mol%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
A9	0	0	45.3	40.0	14.7
M4	4	2.12	43.9	40.0	14.0
M6	6	3.21	43.5	39.3	14.0
M8	8	4.33	42.3	39.3	14.0

Table 2
Chemical analyses of raw materials

Constituents	Sillimanite (wt.%)	Zirconia (wt.%)	Alumina (wt.%)
SiO_2	36.0	1.1	0.6
Al_2O_3	57.0	1.4	97.6
TiO_2	1.3	Trace	Trace
CaO	0.5	Trace	Trace
MgO	0.2	Trace	0.5
Fe_2O_3	0.6	0.3	0.2
ZrO_2	3.5	96.4	–
K_2O	0.2	0.1	0.1
Na_2O	0.07	0.05	0.4

Table 3
X-ray diffraction analysis of raw materials

Raw materials	Phases
Sillimanite	sillimanite
Zirconia	Monoclinic
Alumina	α-Al_2O_3

codes and batch compositions of the four composites are given in Table 2. The slurry from the attritor mill was dried at 110±5 °C and subsequently granulated by sieving and uniaxially pressed into bars (60×60×6 mm) and discs (dia 25 mm) at 110 MPa followed by cold isostatic pressing at 260 MPa using 5% PVA solutions as binder. Isopressed samples were dried and sintered between 1500 °C and 1600 °C with 2 h soaking. 4, 6, 8 mol% MgO [Magnesium oxide, (light, extra pure) containing water soluble matter 2.0%, loss on ignition at 1000 °C 8.0%, manufactured by LOBA Chemie Pvt.

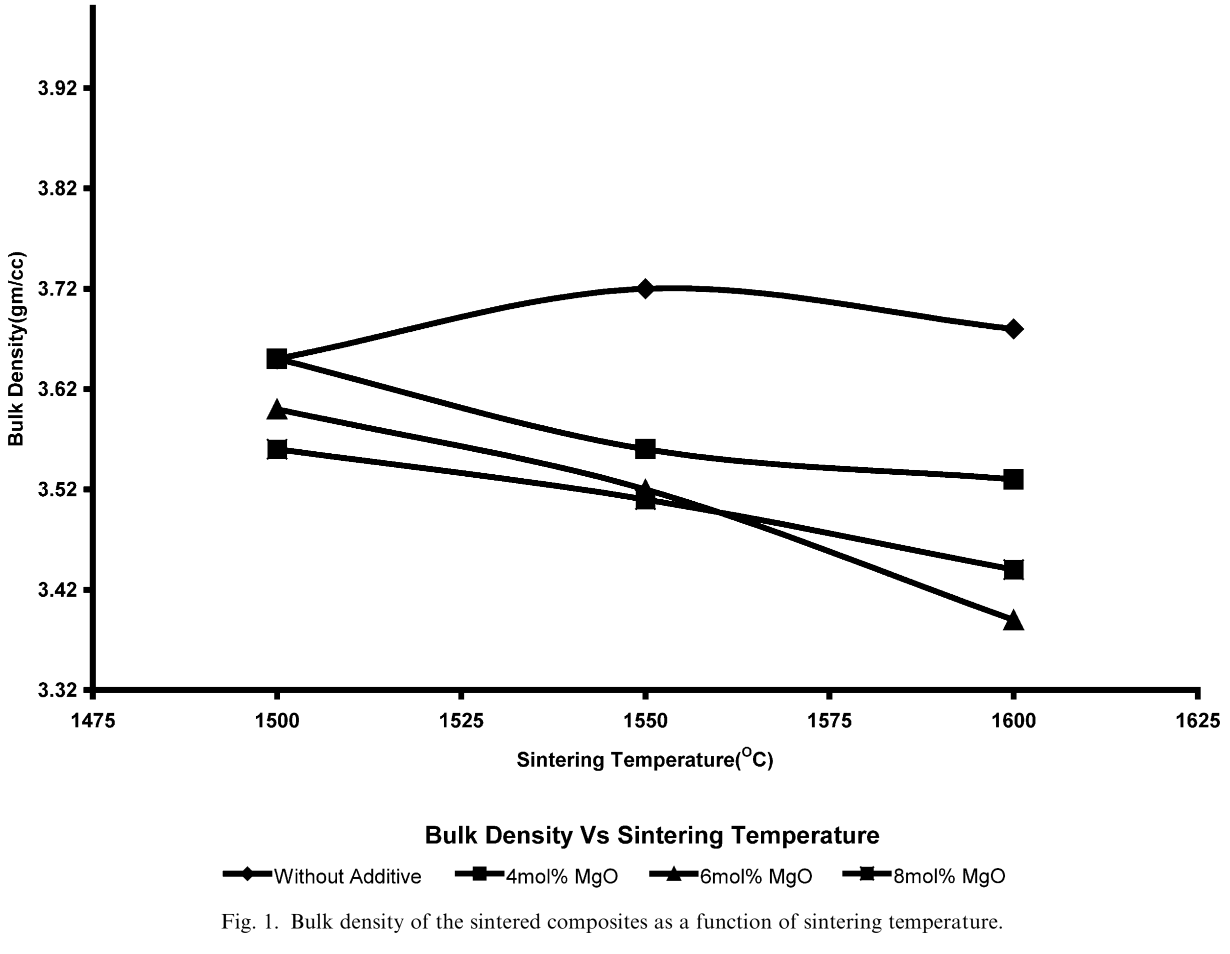

Fig. 1. Bulk density of the sintered composites as a function of sintering temperature.

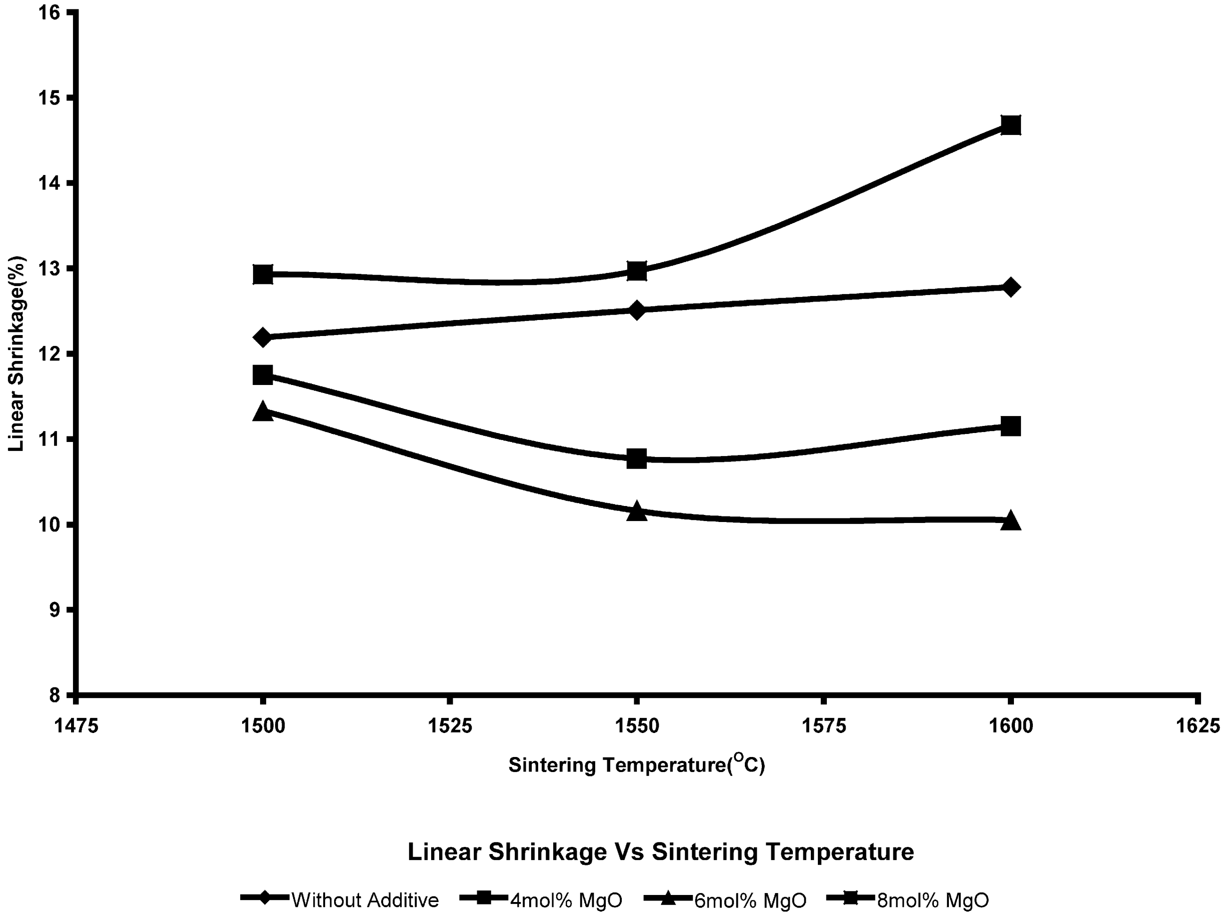

Fig. 2. Linear shrinkage of sintered composites as a function of sintering temperature.

Ltd, Bombay, India] was added to the mixture with respect to zirconia content.

The bulk density of the fired composites was measured by water displacement method. Linear shrinkage of the fired body was measured with the help of a digital slide calipers.

The high temperature modulus of rupture strength was measured by an instrument developed at CGCRI, Calcutta, India. The test was done under three point loading on a span of 45 mm. During testing the rate of temperature rise was maintained at 5 °C/min and samples were allowed a soaking period of 30 min at test temperature. The load then applied at a rate of 50 kg/min. Room temperature fracture toughness measured (K_{ic}) by Vicker's Indentation method following Antis et al. [10] using Wolpert Hardness Tester, Germany. Modulus of elasticity (Young's modulus) of sintered samples measured by sonic method [11]. This modulus of elasticity (MOE) value utilised for the estimation of fracture toughness. This is a non-destructive testing method.

Phases of the sintered bodies identified by X-ray diffraction using a diffractometer [manufactured by Philips PW (1790) using Ni filtered CuK_αX-radiation with a scanning speed of 2°(2θ) per minute]. The t-ZrO_2 fraction content determined on the sintered surfaces from the ratio of XRD integrated peak intensity of t-ZrO_2 (111) to m-ZrO_2 (111) and m-ZrO_2 ($11\bar{1}$) following Garvie and Nicholson's equation [12].

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

Microstructural analyses was done on mirror polished surface after thermal etching. A LEO SEM with EDAX facility is used for energy dispersive X-ray analyses.

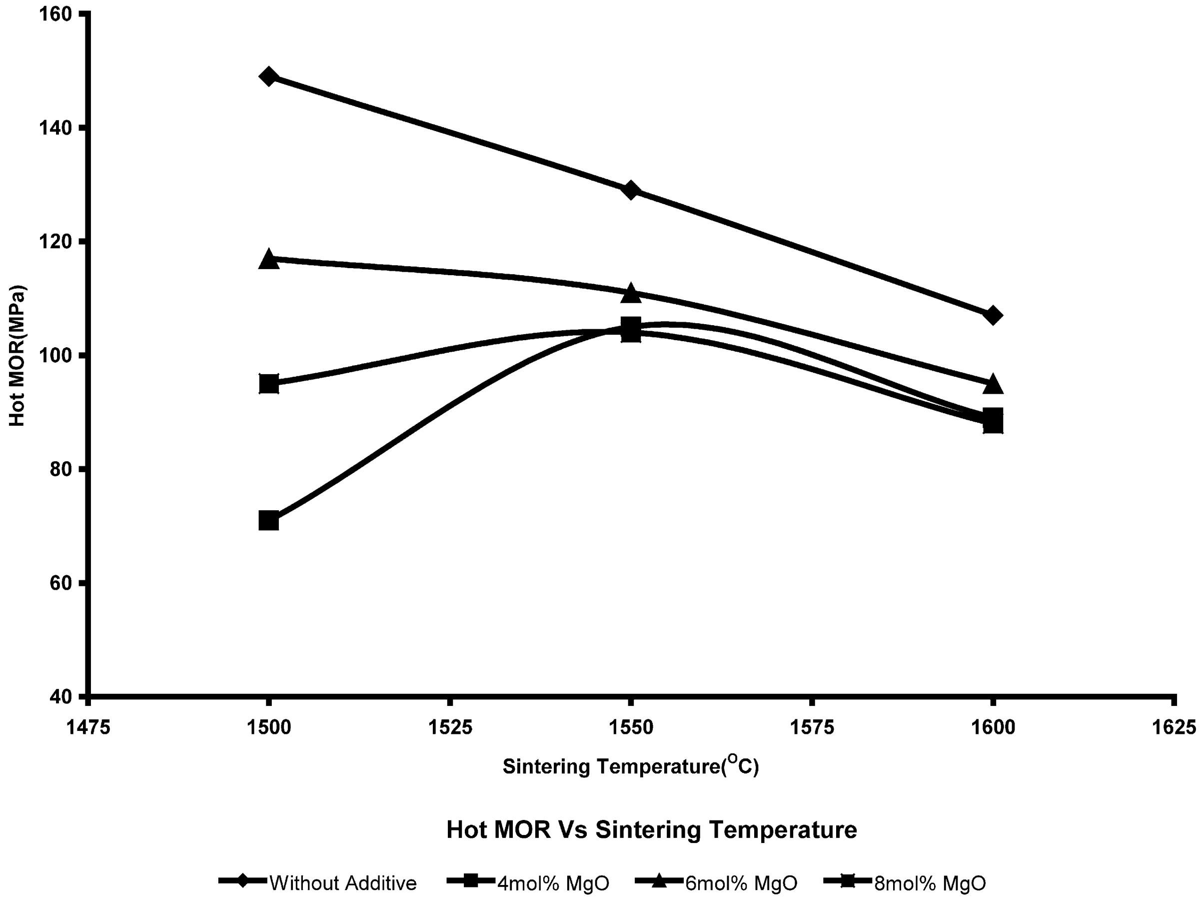

Fig. 3. Hot modulus of rupture (Hot MOR) of sintered composites as a function of sintering temperature.

Table 4
Vicker's Hardness and Fracture Toughness of M6 composite sintered at different temperatures

Sintering temperature (°C)	Hardness (GPa)	Fracture toughness ($MPa.m^{1/2}$)
1500	4.8	2.7
1550	5.3	3.6
1600	5.8	2.5

Table 5
Young's modulus of different composites sintered at different temperatures

Sintering temperature (°C)	Young's modulus (GPa)		
	M4	M6	M8
1500	169	180	133
1550	142	139	132
1600	198	124	125

3. Results and discussions

Chemical analyses of sillimanite sand, zirconia and alumina had been done. Sillimanite beach sand was analysed by following the standard method of silicate analysis. Conventional Na_2CO_3 fusion method used for opening up of the samples. SiO_2 and Al_2O_3 were determined gravimetrically. Titania and iron oxide were determined by spectrophotometric method. Calcium and magnesium oxides were estimated by

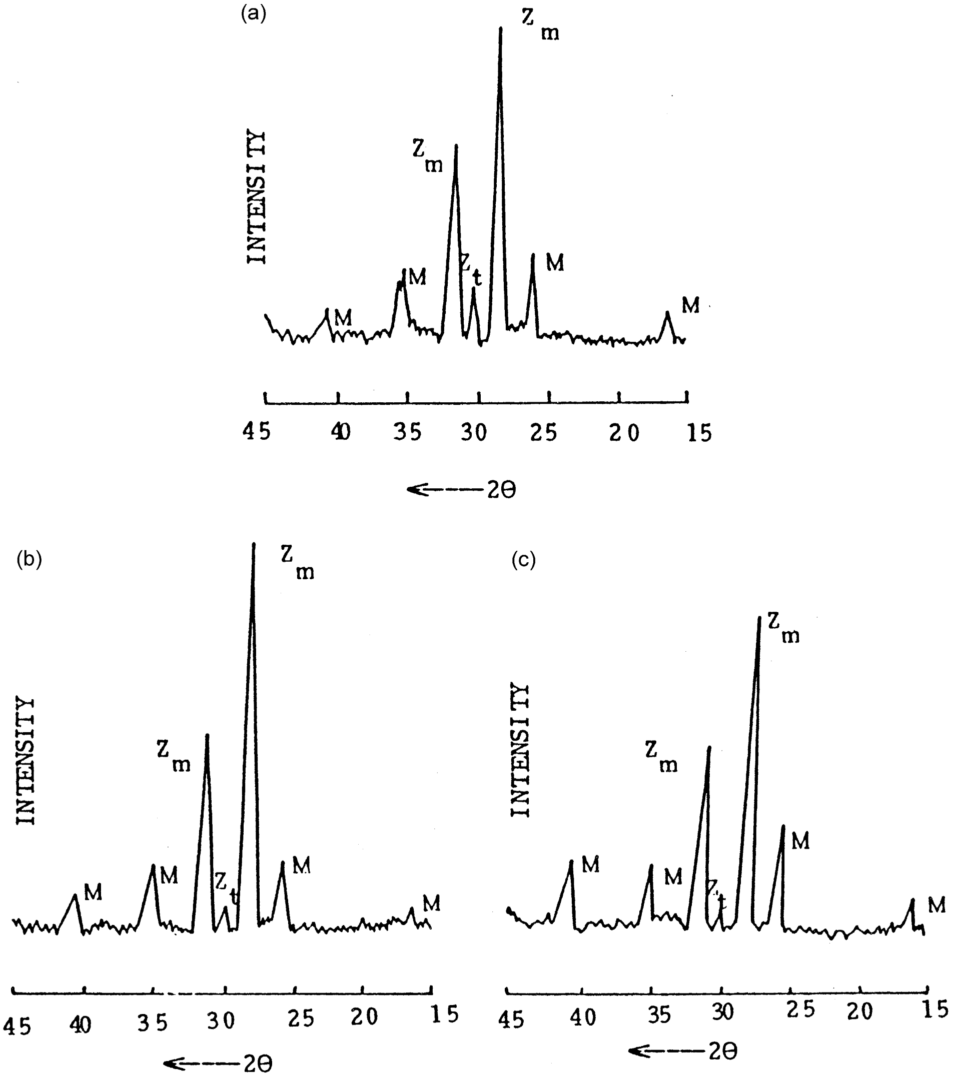

Fig. 4. X-ray diffraction patterns of zirconia–mullite (M8) composite sintered in the temperature range of 1500–1600 °C with 2 h of soaking periods showing the main peaks of zirconia and mullite: (a) M8 sintered at 1500 °C, (b) M8 sintered at 1550 °C, (c) M8 sintered at 1600 °C.

Table 6
Relative tetragonal zirconia(Zt) content(%) of different composites sintered at different temperatures

Sintering temperature (°C)	Zt content (%)		
	M4	M6	M8
1500	13.9	16.0	11.0
1550	11.1	6.3	4.6
1600	6.9	7.9	4.3

following complexometric method of analysis using EDTA, alkali oxides such as Na_2O and K_2O were determined by flamephotometric method. The purity of ZrO_2 and Al_2O_3 were also ascertained by following the standard procedures of gravimetric and complexometric method. Sillimanite sand contains different types of accessories oxides other than Al_2O_3 and SiO_2. The major oxides associated with sillimanite are alkalies, TiO_2, iron oxide. It contains 0.57

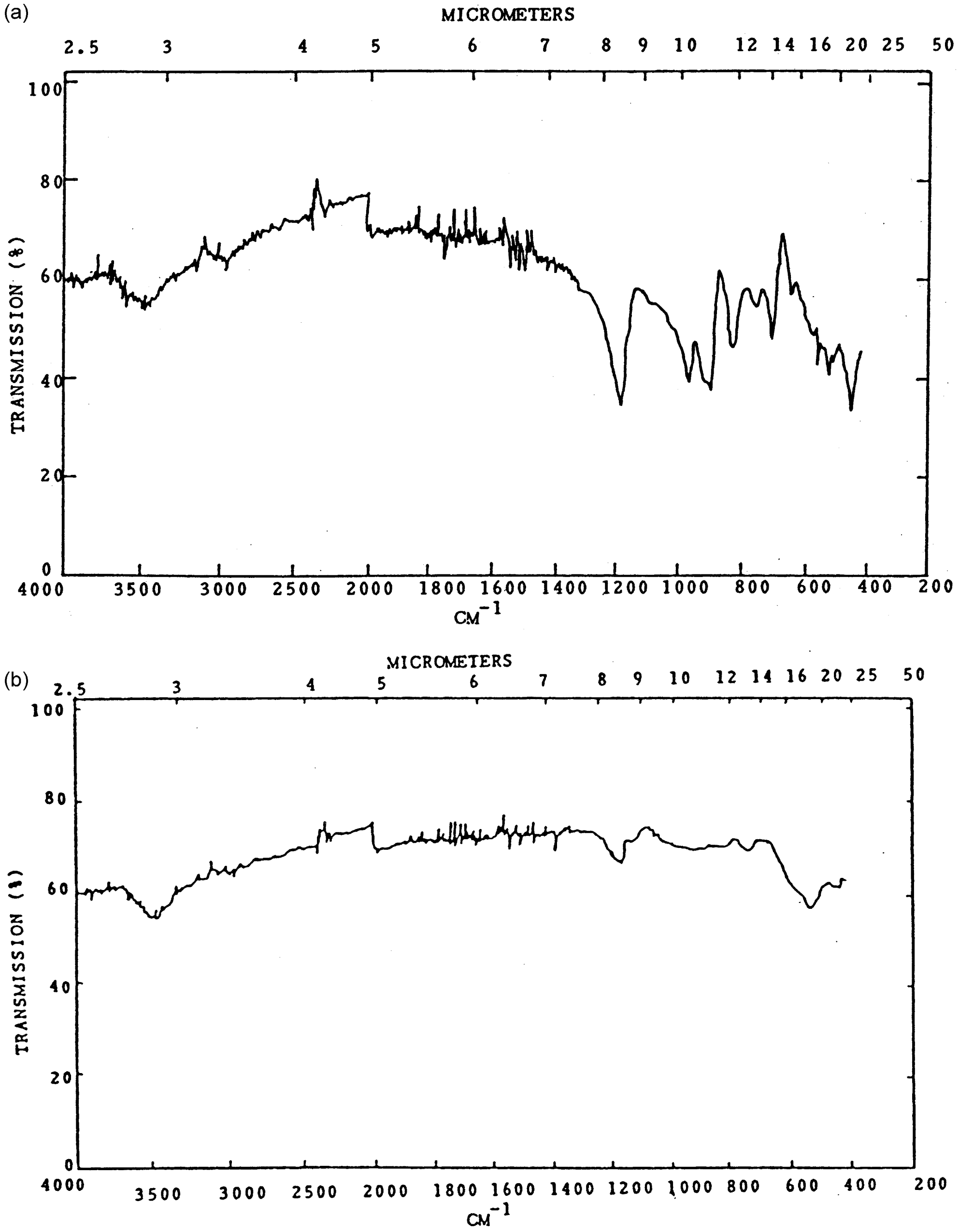

Fig. 5. Infra red spectroscopy of sillimanite sand and zirconia–mullite (M8) composite (sintered at 1600 °C with 2 h of soaking): (a) sillimanite sand, (b) M8.

wt.% iron oxide, zirconia contains 0.28 wt.% iron oxide and alumina contains 0.19 wt.% iron oxide. X-ray diffraction study of zirconia reveals monoclinic zirconia as major phase. In the case of Al_2O_3, α-Al_2O_3 is the sole phase. Table 3 shows the X-ray diffraction analysis of raw materials.

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. 1 shows the

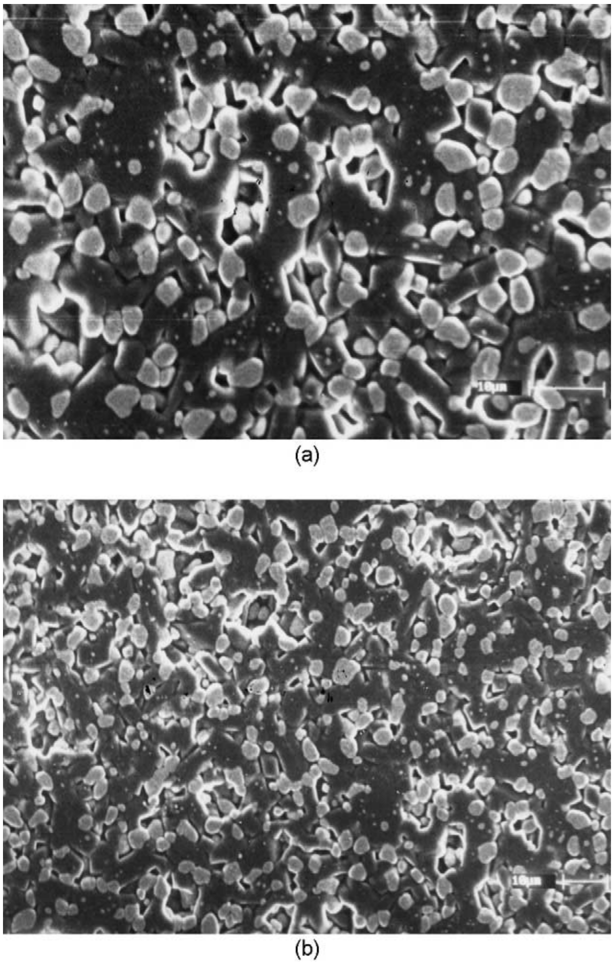

Fig. 6. Scanning electron microstructures of zirconia–mullite (M6) composites (sintered at 1600 °C) showing the mullite (black) and zirconia (white) grains: (a) 1500 °C, (b) 1600 °C.

change in bulk density of the samples with temperature. Here, bulk density of the samples falls with increase in temperature with varying amounts of magnesia. It is believed that magnesia participates in the formation of transient liquid phase which gives rise to a higher reaction rate [14]. Fig. 2 shows the change of linear shrinkage of the composite body with change in temperature. This type of shrinkage mainly arises due to sintering within and between the components present and generated in the system. Fig. 2 shows in case of 4 mol% MgO shrinkage decreases which is due to the formation of mullite. But with the higher content of magnesia (8 mol%) shrinkage/densification increases due to the formation of transient liquid phases [15]. Generation of large volumes of liquid phase with increased amount of magnesia helps in particle rearrangement and effective packing of particles leading to higher shrinkage.

3.2. Mechanical/thermo-mechanical properties

A characteristic feature of zirconia–mullite composites is reduced strength value at high temperatures. Fig. 3 shows the HMOR value at 1250 °C for the composites with sintering temperature. All the composites show lower strength at 1600 °C . Here, the differences in viscosity of grain boundary phases and glass transition temperature are believed to play an important role. The glassy phase becomes more fluid, grain boundary sliding becomes more important than plastic relaxation and can lead to formation of cracks and decohesion of the matrix leading to decreased mechanical strength. Table 4 shows the Vicker's hardness (GPa) and fracture toughness (MPa $m^{1/2}$) of M6 composite sintered at different temperatures. Composites have higher values of fracture toughness than pure mullite ($K_{ic} = 2.0$ MPa $m^{1/2}$). This increase in toughness is believed due to the presence of dispersed zirconia particles in mullite matrix. It has been found [16] that the fracture energy of a ceramic can be increased by a second phase dispersion. Table 5 shows the result of Young's modulus value with change in sintering temperature. The composites showing an overall decreasing trend in modulus of elasticity as the sintering temperature increases. This is may be due to the more glassy phase formation. Fig. 4(a–c) shows the X-R-D of M8 composites sintered at 1500 °C, 1550 °C and 1600 °C for 2 h. Table 6 shows the relative tetragonal zirconia content (%) with change in sintering temperature. An IR spectrums of raw sillimanite sand and M8 composite sintered at 1600 °C for 2 h have been given in Fig. 5(a) and (b). In sillimanite, the perturbation of Si–O vibrations caused by the presence of 4-coordinated Al is quite extraordinary, even in the context of aluminosilicates with which this mineral could well be classified, the stretching frequency at 1200 cm^{-1} is one of the highest observed in the whole field of silicate spectra [17]. Lazarev [18] has given very reasonable general assignments for absorption bands above 700 cm^{-1} in terms of the vibrations of the ribbon anins, consisting of alternating Si and Al tetrahedral, that are present in the structure.

3.3. Microstructural characterisation

Fig. 6(a,b) show the microstructures of zirconia–mullite composites after sintering at 1600 °C for 2 h. Samples have mirror polished and thermally etched before micrographs have been taken. The bright zirconia grains are uniformly distributed throughout the darker mullite matrix. Two types of zirconia grains are present one is intergranular zirconia located between the mullite grains and the other one is intragranular zirconia present within mullite matrix. Fig. 7(a,b) show EDX diagrams of mullite and zirconia phases of composite sintered at 1600 °C.

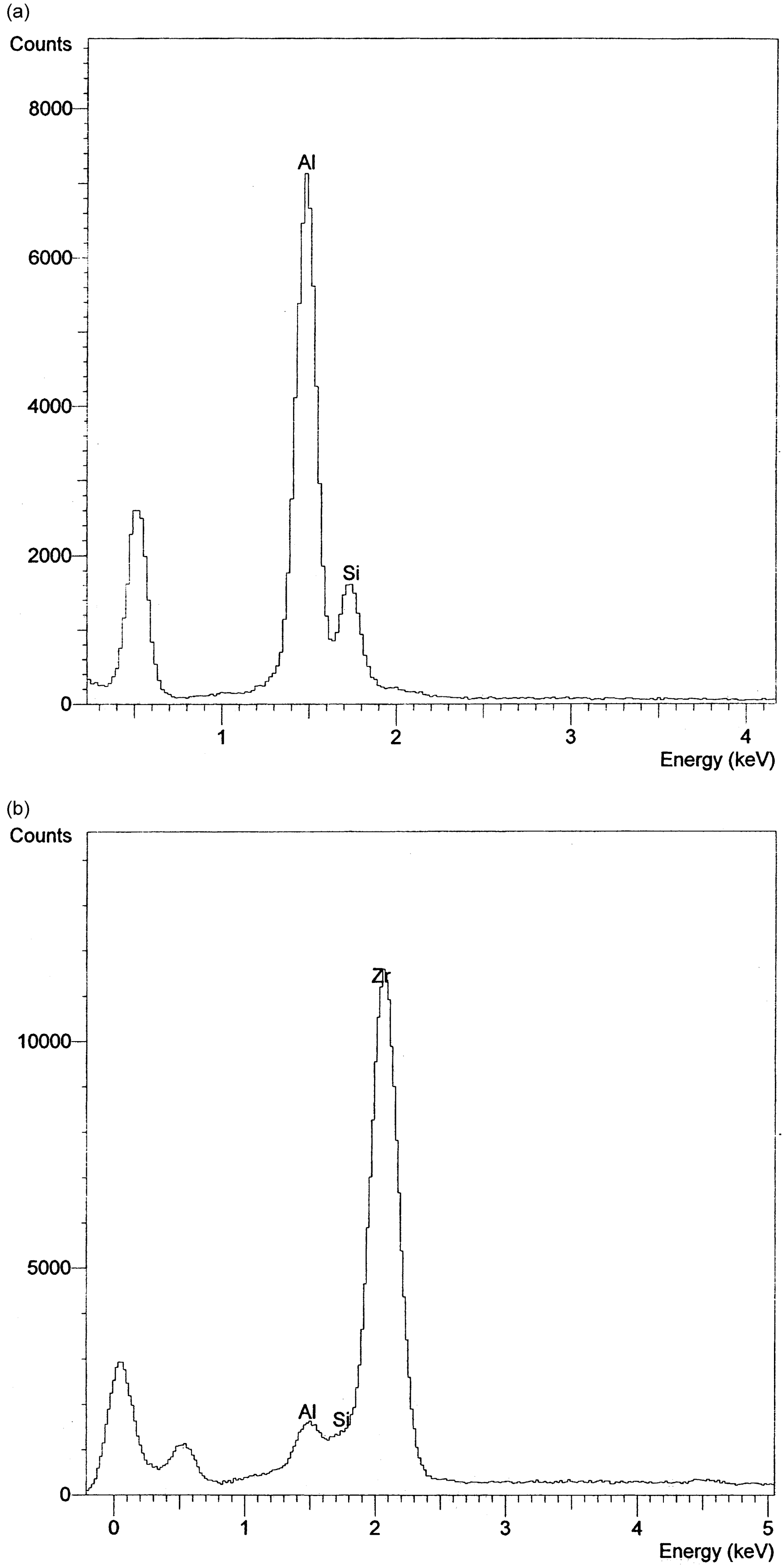

Fig. 7. EDX analysis of zirconia and mullite phases of zirconia–mullite composite (M6 sintered at 1600 °C with 2 h of soaking): (a) mullite, (b) zirconia.

4. Conclusions

Zirconia–mullite composites from Indian coastal Sillimanite beach sand and from zirconia and alumina can be prepared in the temperature range of 1500–1600 °C with magnesium oxide as an additive. The X-ray diffraction shows all raw materials are crystalline in nature. The bulk density of the sintered samples fall with increase in temperature with varying amount of magnesia. The linear shrinkage of the sintered samples increases with higher content of magnesia. The hot modulus of rupture for all samples is showing lower value at 1600 °C. The sintered materials are having higher value of fracture toughness than pure mullite. All the sintered composites are showing an overall decreasing trend in modulus of elasticity as the sintering temperature increases. The scanning electron microstructures of the sintered samples show bright zirconia grains are uniformly distributed throughout the darker mullite matrix.

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