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Preparation of Mullite Nanofibers via sol-gel and Electrospinning Techniques

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Abstract: *Alumina –silica / poly(vinyl alcohol) (PVA) hybrid nanofibers with 300-500 nm diameter were prepared by sol-gel and electrospinning techniques and calcined at high temperatures to obtain ceramic mullite fibers with less than 200 nm diameters. The resulting ceramic fibers were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and FT-IR spectra. TGA showed that the thermal decomposition of hybrid nanofibers was affected by the inorganic content. SEM, XRD and FT-IR results indicated that the morphology, fiber size and crystalline phase evolution of mullite nanofibers depend upon the calcination temperature.*

Keywords: *Mullite ceramics; Nanofibers; Electrospinning; Scanning electron microscopy.*

I. INTRODUCTION

Fibers are useful materials for ceramic composites to enhance the fractural toughness and also thermal shock resistance [1]. SiC fibers such as Nicalon [2] and Sylramic [3] show excellent mechanical strength upto very high temperature. However, since non-oxide ceramics get oxidizes at high temperature in air, they are considered to degrade the excellent properties during long-term use at high temperature in air. It is therefore required to develop fibers with high mechanical strength and oxidation resistance properties. Among the various oxide ceramic fibers, mullite fibers are reported to possess good mechanical strength and creep resistance at high temperature [4,5]. Mullite exhibits some attractive properties like high refractoriness, low thermal expansion and conductivity and excellent mechanical properties at high temperatures [6]. Mullite fibers have attracted considerable attention as a high-temperature ceramic, because of its excellent high temperature strength and creep resistance, thermal and chemical stability and good dielectric properties [7]. There are many reports on the synthesis and characterization of

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mullite powders/whiskers/fibers such as solid-vapor reaction process [8], thermally induced crystallization [9] and sol-gel [10]. Among those methods, sol-gel is the most widely used methods to synthesis mullite ceramics. This technique enables to prepare wide variety of oxide ceramics in forms like powders, films, bulk monoliths, whiskers, fibers by controlling the chemistry of hydrolysis and polycondensation reactions. Oxide ceramics prepared by sol-gel technique can have high purity, homogeneous etc., than those prepared by other methods. Mullite fibers were prepared by sol-gel technique [7,11]. Nowadays, electrospinning technique has been successfully employed in the preparation of some polymer nanofibers for potential applications [12,13]. Several metal oxide nanofibers such as, lead-zirconate-titanate [14]. magnesium titanate [15], nickel titanate [16], alumina-borate [17] have also been prepared by electrospinning method. Though several reports are available on the preparation of mullite powders or fibers, there seems to be no report on the mullite fibers through electrospinning method. Hence for the first time, we demonstrate in this article that mullite nanofibers can be conveniently prepared by electrospinning a nanocomposite solution that contains alimina-silica sol and aqueous PVA solution. Calcinations in a subsequent step leads to the formation pure ceramic nanofibers made of orthorhombic mullite The surface morphology and structural characterization of mullite nanofibers using various physico-chemical methods have also been presented.

II. EXPERIMENTAL

1. Preparation of Nanofibers

Aluminium isopropoxide (AIP, Aldrich, 98 %) and tetraethylorthosilicate (TEOS, Aldrich, 98%) and PVA (Mn = 86000, DC Chemical Co. Ltd) were used as received. An alumina-silica sol with 3:1 mullite composition was prepared from AIP, TEOS, ethanol and water with vigorous stirring at room temperature. A certain amount of alumina-silica sol-gel was dropped into an aqueous PVA solution (10 wt%) and stirred at room temperature for 2 h. A series of viscous solutions with different proportions of alumina-silica sol were obtained as listed in Table 1. The transparent inorganic/organic nanocomposite solution was taken in a plastic syringe. The positive terminal of a variable high voltage power supply was attached to a copper wire inserted into the solution in the syringe, whereas the ground iron drum served as counter electrode. Fig. 1 shows the schematic diagram of electrospinning process. The syringe was placed at an angle of 20° to horizontal in order to get uniform flow of the solution. Under the applied voltage of 19 kV and the tip-to-collector distance of 15 cm, the droplet disintegrated into nanofibers before they reached the ground drum and deposited as non-woven mats consisting of hybrid nanofibers. The as-prepared alumina-silica/PVA hybrid nanofibers were then collected and calcined at high temperatures to get pure mullite nanofibres.

2. Characterization of Nanofibers

The surface morphology of the nanofibers were analysed by a JEOL GSM-5900 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold (Denton

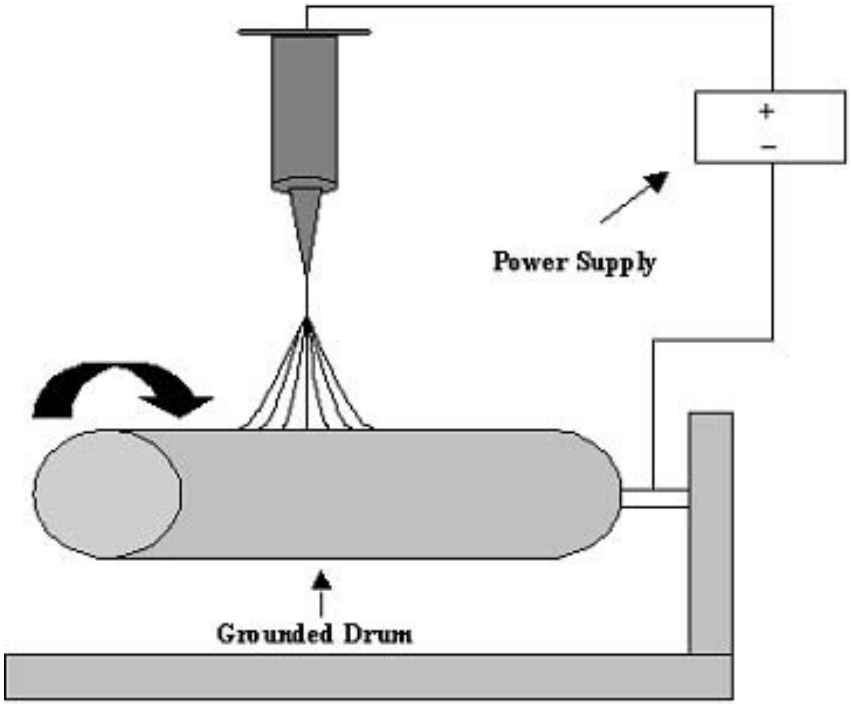

Fig. 1: Schematic Diagram of the Electrospinning Process.

Desk-1 Sputter Coater). Powder X-ray (XRD) patterns were obtained from a Shimadzu Lab-X 600 X-ray diffractometer with a Cu-Ka radiation in the 2q between 12 and 60°. FT-IR spectra of the fibers were taken as KBr discs, at 2000-400 cm^{-1} range using Shimadzu FTIR-8101 spectrophotometer. Thermo gravimetric analysis (TGA) was carried out with a TG 6200 instrument by heating from 50 to 700°C under a nitrogen flow with a heating rate of 10°C/min. The as-prepared inorganic/organic hybrid nanofibres were calcined in air at different temperatures from 800 to 1400 °C at a heating rate of 10°C /min and kept for 2 h at respective temperatures to get pure mullite nanofibres.

III. RESULTS AND DISCUSSION

Fig. 2 shows the SEM photographs of as-prepared hybrid nanofibers with different content of alumina-silica sol. The nature and size of the pure PVA nanofibers were irregular and no longer straight with certain beads formed in them (Fig. 2a). It can be seen from the SEM images that the diameter of the fibers are increased and ranges from 350-500 nm by the addition of inorganic sol (Fig. 2b-e). Moreover, the beads in nanofibers disappeared as the content of alumina-silica- sol was increased and the fibers appeared to be very straight with several micrometer lengths. This change in the fiber morphology and size is due to an increase in the viscosity of the electrospinning solution from 491 to 575 centipoise after the addition of alumina-silica sol (Table 1). Similar observation was made by Reneker *et al.* [18].

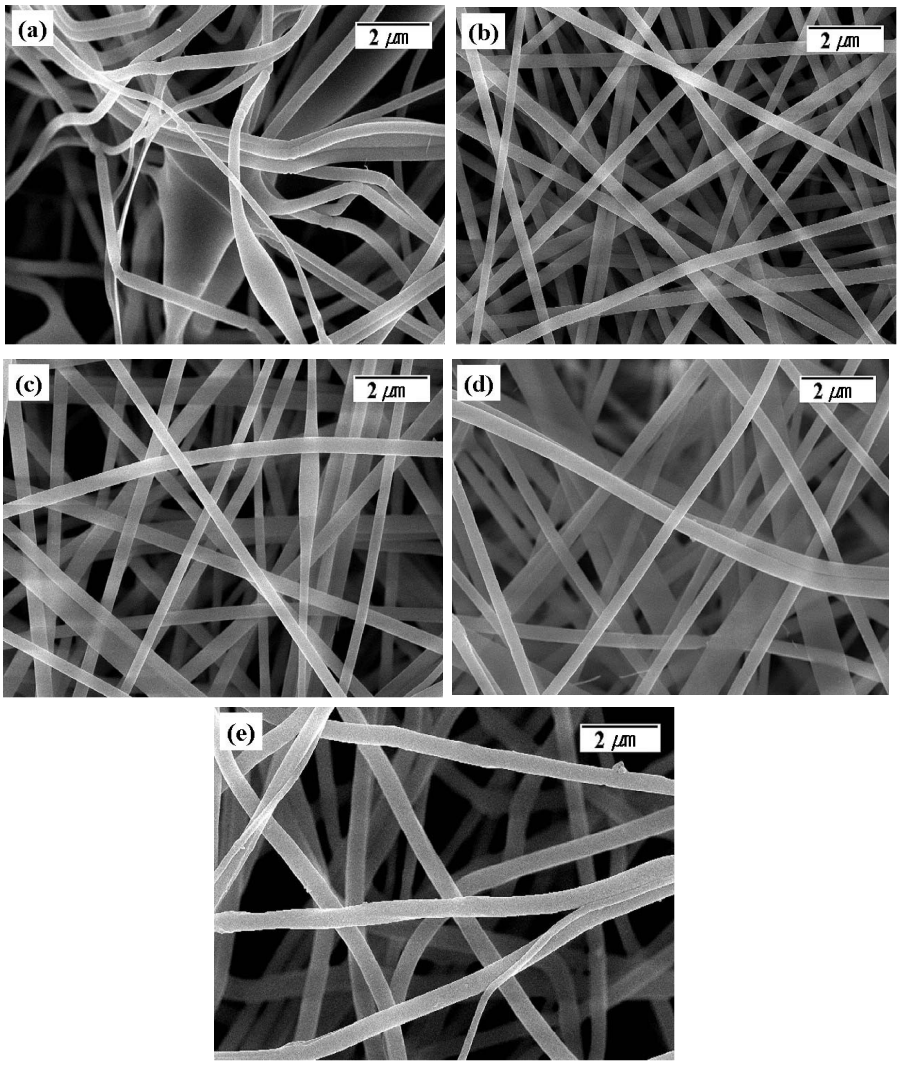

Fig. 2: A SEM micrograph of alumina-silica/PVA hybrid nanofibers with different content of alumina-silica ; (a) 0 g, (b) 1 g, (c) 1.5 g, (d) 2 g and (e) 2.5 g.

Table 1
Composition of Different Electrospinning Solutions

Sample	*Aqueous PVA solution (g)*	*Alumina-silica sol (g)*	*Viscosity (Cps)*
A	10	0	491
B	10	1.0	523
C	10	1.5	536
D	10	2.0	561
E	10	2.5	575

The SEM images of hybrid nanofibers with 2 g of alumina-silica sol after calcination at different temperatures in the lower and higher magnifications were shown in Fig. 3(a-d). From these photographs, it has been observed that the calcined nanofibers

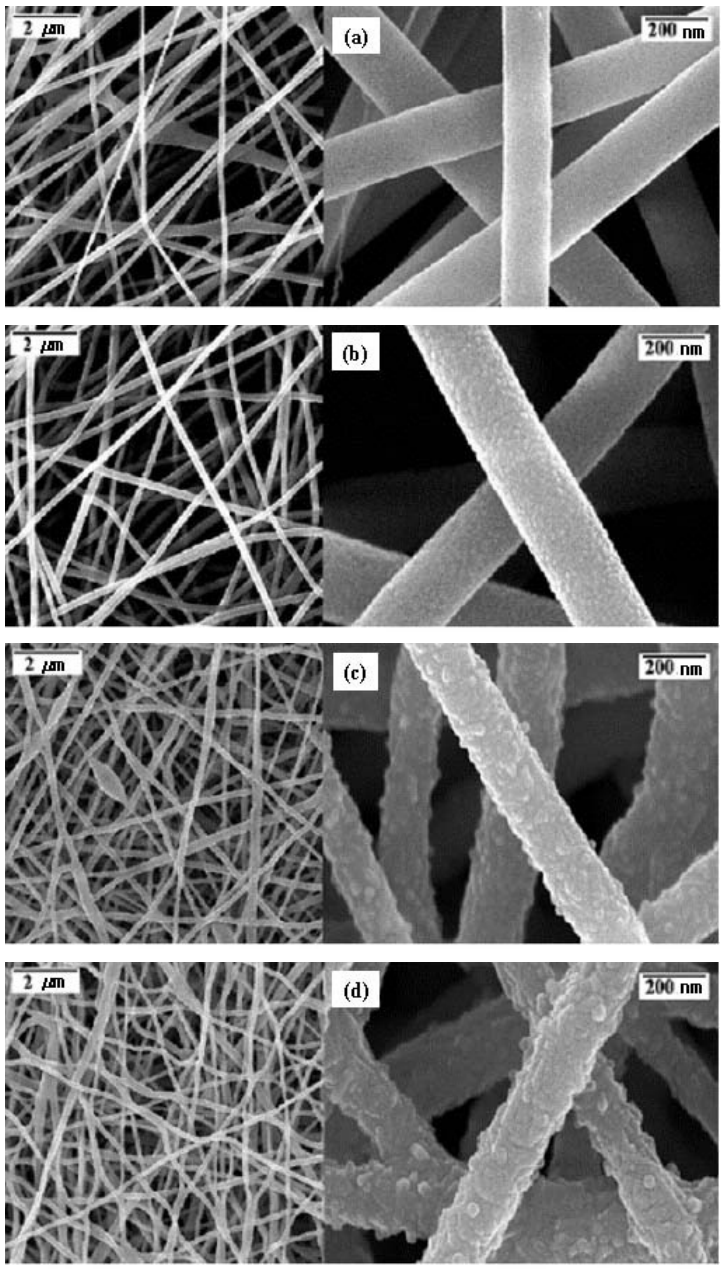

Fig. 3: A SEM micrograph of alumina-silica/PVA hybrid nanofibers with 2 g of alumina-silica content calcined at different temperatures. (a) 800 °C; (b) 1000 °C; (c) 1200 °C and (d) 1400 °C.

haves smooth surfaces after calcinations at 800 and 1000°C, with a reduction in their diameter (around 250 nm) compared with hybrid nanofibers, owing to burning out of PVA , whereas the fibers after calcinations at 1200 and 1400°C showed rough surfaces because of the development of grain boundaries due to mullite crystallization and further shrinkage of fiber diameter to less than 200 nm due to sintering. The size of grains increased with the sintering temperature increasing. In addition, the calcined nanofibers have curved morphology when the calcination temperature increased, which can be attributed to the growth of the mullite grain size.

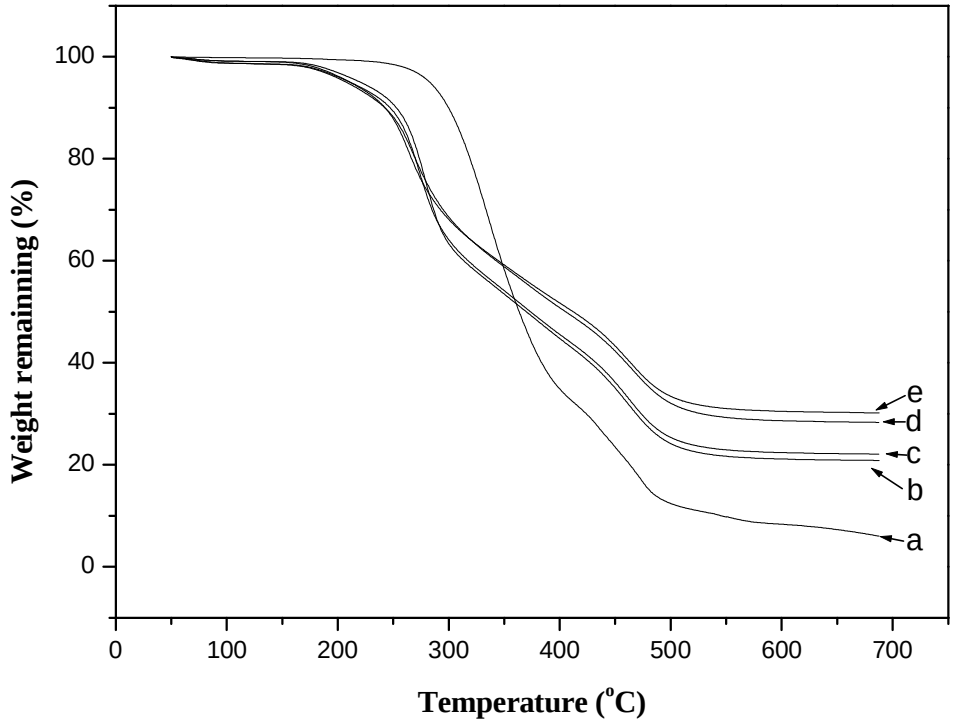

Fig. 4: TGA curves of alumina-silica/PVA hybrid nanofibers with different content of alumina-silica; (a) 0 g, (b) 1 g, (c) 1.5 g, (d) 2 g and (e) 2.5 g.

The thermal decomposition behaviors of the pure PVA, alumina-silica/PVA hybrid nanofibers of varying inorganic contents ranging from 0 to 2.5 g are shown in Fig. 5. As showed in curve (a), pure PVA nanofibers had two weight loss steps in the range 310 to 470 °C . These steps were due to the decomposition of side chain and main chain of PVA, respectively [19]. The as-prepared alumina-silica/PVA hybrid nanofibers showed the weight loss in 3 steps. The first step between 150-270 °C is associated with the loss of water and organic groups and the second step between 270-400 °C corresponds to the degradation of PVA side chain by elimination of water. The third decomposition step above 400 °C is due to the decomposition of PVA main chain. Beyond 480 °C, no

further weight loss takes place unto 700 °C, indicating the complete removal of PVA within this temperature. From the TGA data, we found that the weight remaining after 700 °C increased from 6 to 32% due to the presence of inorganic content in the samples.

Fig. 5 presents the XRD patterns of various nanofiber samples. A broad peak centered around 2θ value 20° corresponding to the (101) plane of semicrystalline PVA [17,19] was found in the XRD patterns of both pure PVA and alumina-silica/PVA hybrid nanofibers (curve (a) and (b)). After calcining the hybrid nanofibers at 800 °C, the above peak due to the semicrystalline PVA disappeared but a new diffuse peak appeared at 2θ value of 24° (curve (c)). These observations revealed that the PVA was completely removed by calcinations at this temperature. A diffuse at peak 2θ = 24° can be assigned to the amorphous SiO_2 [20, 21]. As the calcinations temperature was increased to 1000 °C, the peaks characteristic of mullite were evolved (curve (d)). The mullite peaks became more evident with increasing the calcination temperature from 1000 to 1400 °C (curves (e and f)). The diffraction peaks due to mullite phase were identical in their position to those reported earlier [7,20-23].

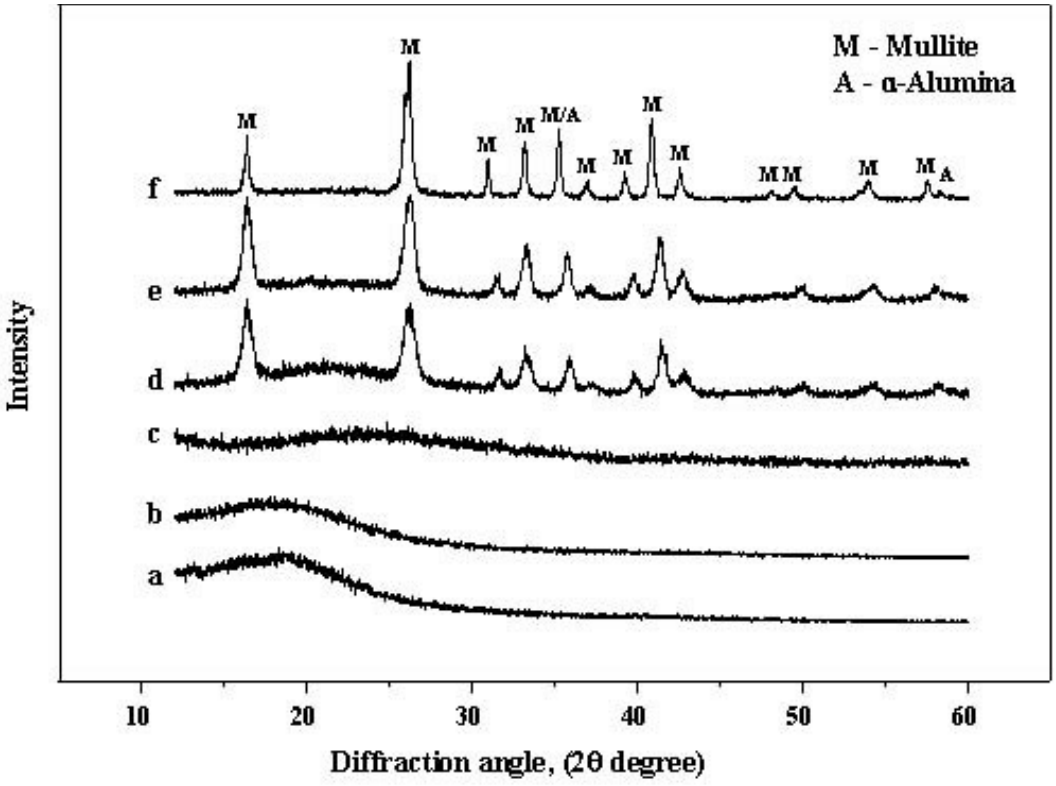

Fig. 5: XRD patterns of various samples: (a) pure PVA nanofibers; (b) alumina-silica/PVA hybrid nanofibers with 2 g of alumina-silica, (c) calcined at 800 °C, (d) calcined at 1000 °C, (e) calcined at 1200 °C and (f) calcined at 1400 °C.

Fig. 6 shows the FTIR spectra of the as-prepared alumina-silica/PVA hybrid nanofibers containing 2 g of alumina-silica sol and those of the fibers calcined at different temperatures. The hybrid nanofibers spectrum has multiple strong absorption bands in the 1000-1700 cm^{-1} range due to PVA (curve (a)) [17]. Upon calcination at 800 °C, the bands due to PVA were disappeared indicating its total decomposition and new broad bands appeared around 1080 and 810 cm^{-1} (curve (b)). These absorptions were assigned as due to the antisymmetric and symmetric vibrations of Si-O in amorphous silica and Si-O-Al networks [22]. When the nanofibers were calcined at 1000, 1200 and 1400 °C, the bands due to Si-O linkage have been shifted to higher wave number indicating the formation of mullite phase (SiO_4 tetrahedra). In addition, the absorptions due to mullite were clearly seen in the spectra of samples calcined at 1000, 1200 and 1400 °C, showing bands at 1100-1180 cm^{-1}, due to AlO_4 and SiO_4 species; in the region 800-900 cm^{-1}, mainly associated with AlO_4 and AlO_6 species; at 735 cm^{-1}, due to AlO_4 and at 565 cm^{-1}, corresponding to AlO_6 species (curves (c, d and e)) [22,23]. A broad band due to a-alumina appeared around 470 cm^{-1} in the spectra of calcined samples [22]. The infrared spectral features shows that the formation of mullite begins at 1000 °C, and remains stable unto 1400 °C.

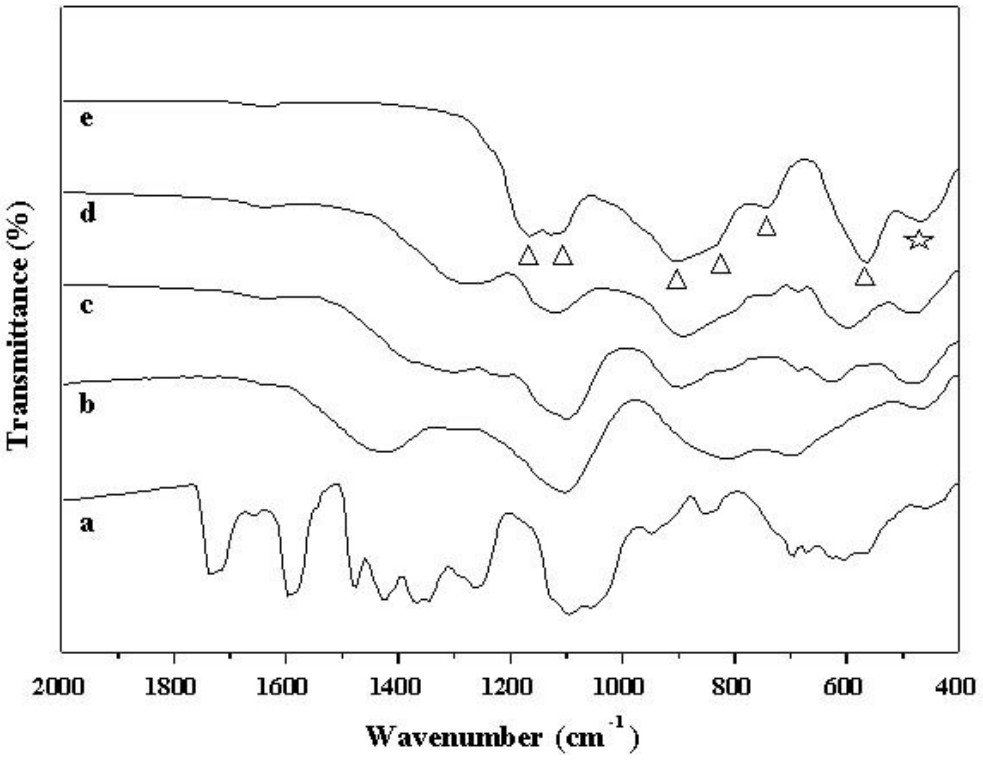

Fig. 6: FT-IR spectra of various samples: (a) pure PVA nanofibers, (b) alumina-silica/PVA hybrid nanofibers with 2 g of alumina-silica, (c) calcined at 800 C, (d) calcined at 1000 °C, (e) calcined at 1200 °C and (f) calcined at 1400 °C.

IV. CONCLUSIONS

A simple method to prepare mullite nanofibers with diameters less than 200 nm using alumina-silica/PVA hybrid nanofibers obtained by sol-gel and electrospinning techniques followed by high temperature calcinations in air was reported in this paper. The change in the fiber morphology and size after high temperature calcinations was studied by SEM. Mullite fibers retained their cylindrical structure even after calcinations at 1400 °C. XRD data confirmed the mullite phase formation at 1000 °C. A good correlation between XRD and FTIR spectra regarding the mullite phase evolution was observed. We suggest that the electrospinning technique described in this article could be extended as a versatile route to prepare nanofibres of other oxides with even smaller diameters by carefully controlling the electrospinning parameters and the composition of the nanocomposites.

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