

An experimental approach for synthesis of Fe-Al-O multiferroic fibrous material

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Abstract: Basic principles of the electro-hydrodynamics are applied for synthesis of solid state Fe-Al-O multi-ferroic fibrous material. For that purpose stable blend spinning solutions comprised of a high molecular assisting organic polymer and salts of iron and aluminum are developed. These solutions are tested under electrospinning conditions and synthesis of homogeneous as spun non-woven mats characterized by fibre mean diameters in the micro- and nano-size range is successfully demonstrated. Multi-step thermal procedure is applied for the consecutive solvent evaporation, polymer pyrolysis and final fibre calcination. Electron-optical imaging technique and XRD are applied for revealing the sample morphology and the phase composition correspondingly. The results obtained outline the wide possibilities for fabrication of multi-ferroics fibrous nano-materials on the basis of Fe-Al-O.

1. Introduction

In the last decade a class of materials named multi-ferroics has attracted great technological and academic interest [1]. The multi-ferroics are materials in which two or all three of the property “ferroelectricity”, “ferromagnetism” and “ferroelasticity” occur simultaneously in the same phase. This multiplicity, combined with relatively simple structure of these materials, makes them suitable object for investigating the general principles that govern these properties. Moreover, the possibility of integration between the ferroelectromagnetic physical properties through the magnetoelectric effects can promote interesting practical advances in many electronic technologies. Therefore, the fabrication of single-phase multi-ferroics materials with appropriate properties for technological application is a provocative challenge for physicists and material scientists.

Among the variety of iron aluminium oxide systems FeAlO₃ is an attractive multi-ferroic material since it exhibits piezo-electricity, ferromagnetism and magnetoelectrical effects at low temperature [2, 3]. Moreover, FeAlO₃ shows an extremely high magnetic anisotropy at temperatures down to 4,2K up to 37T in pulsed magnetic fields [4]. Regardless of this R&D importance only a few activities on the synthesis of single-phase FeAlO₃ have been reported. This is due to the very narrow range of stability of the multi-ferroic phase in the binary equilibrium diagram of Fe₂O₃ - Al₂O₃ [5] and of the extremely high stabilities of both hematite - α -Fe₂O₃ and alumina - α -Al₂O₃, which hinders the reaction. Different experimental approaches are well known for synthesis of single-phase multi-ferroic FeAlO₃ [5], namely: solid-state, sol-gel, co-precipitation and the high-energy ball-milling methods.

In the present paper for the first time a disparate experimental approach for synthesis of FeAlO₃ multi-ferroic fibrous material is applied - electrospinning. Basic principles of the electrohydrodynamics for synthesis of solid state FeAlO₃ multi-ferroic fibrous material are applied and discussed.

2. Experimental

A water soluble polymer polyethyleneoxide – PEO, aluminium acetate - AlOH(CH₃COO)₂ and ferric nitrate - Fe(NO₃)₃·9H₂O are chosen for the preparation of the spinning solution. All chemicals (Fluka - P.A.) are used without further purification. The solutions are prepared with distilled deionized water ($\sigma < 0,5 \mu\text{s/cm}$) from considerations of both purity and electrical conductivity. PEO with an average $M_v = 800\,000$ (800 KD) as determined in distilled water at 30°C, using an Ubbelohde viscometer, by the equation $[\eta] = 1.25 \times 10^{-4} M_v^{0.78}$ is used as high molecular polymer [6]. The starting polymer solution is prepared as 8,0 wt% aqueous PEO. The metal precursors AlOH(CH₃COO)₂ and Fe(NO₃)₃·9H₂O are dissolved separately in distilled water, both salts being in equal concentrations. Afterwards, two AlOH(CH₃COO)₂/Fe(NO₃)₃ mixed solutions are prepared depending on their concentration dissolved in the water. A homogeneous translucent liquid is obtained if the starting solutions are diluted. Besides, an opaque solution – suspension, is produced from the supersaturated mixed solutions of both salts. Thus, two different blend solutions are prepared via drop wise addition of both laboratory prepared water solutions AlOH(CH₃COO)₂/Fe(NO₃)₃ to the corresponding, gently stirred PEO solution. The weight ratio of the blend spinning solutions used displaying optimal visco-elastic properties under electrospinning conditions is 1:1.

The electrospinning process is carried out under carefully controlled conditions. The blend solution is passed through a syringe with a stainless steel needle at the tip. The needle has been electrified using a high-voltage DC supply with an applied voltage of 15-20 kV. A grounded collector of thick aluminum foil served as a counter electrode. The solution has been pumped continuously using a compressed nitrogen and precise valve at an approximately flow rates of 0,1 mL/h. The applied field strength between the capillary tip and counter electrode was of the order of 1,0 kV/cm. Pieces of fused quartz glass arranged over the collector, served as substrates. Brownish colored mat from as-spun hybrid fibers of polymer/metal salts well adhered to these substrates are collected.

In order to obtain PEO free ceramic fibers the hybrid non-woven mats obtained from both blends solutions are further placed in a quartz tubular furnace and thermally modified via specially developed two-step calcination procedure. The latter is performed non-isothermally at 120°C - 360°C for water and PEO removal, in the presence of low pressure oil free compressed air, providing conditions for the efficient removal of the emanating gases from the heated space and controlled PEO pyrolysis [7, 8]. The samples are subjected further to calcination in the presence of low pressure oil free compressed air at 800°C maintaining a constant heating rate of the order of 1,0°C/min.

Scanning electron microscope Jeol SEM T-200 is used for studying the morphology of the thermally processed samples. The samples have been previously coated under high vacuum conditions with carbon layers. Two electron-optical modes of imaging are applied – SEI or BEI-compo for visualization of the samples in morphology and composition contrast respectively. The phase composition of the thermally processed mats is verified by conventional wide angle X-ray diffraction – WAXRD, by means of APD – 15 Philips X-ray diffractometer.

3. Results and discussion

The results obtained demonstrate that applying the electrospinning method and subsequently the two step thermal procedure for calcination of the as spun hybrid fibrous material a non-woven mats could be obtained. Figures 1 and 2 present the electron-optical micrographs of the inorganic fibres fabricated from both precursors. The morphology contrast of the secondary electron image – SEI, reveals the microstructure of the fibrous materials obtained (figures 1a and 2a). It is clearly seen from these micrographs that in both cases the spun non-woven mat is composed from long fibres with nearly homogeneous shape. The morphology of both fibre mats are similar but the fibres cross-section size

differs slightly, that spun from suspension being 20% larger as compared to the fibres spun from homogeneous blend solution. Looking at the backscattered electron image - BEI-compo micrographs (figures 1b and 2b), one can see easily that in both cases the chemical composition of the fibres is uniform at least at the SEM magnifications used in this study.

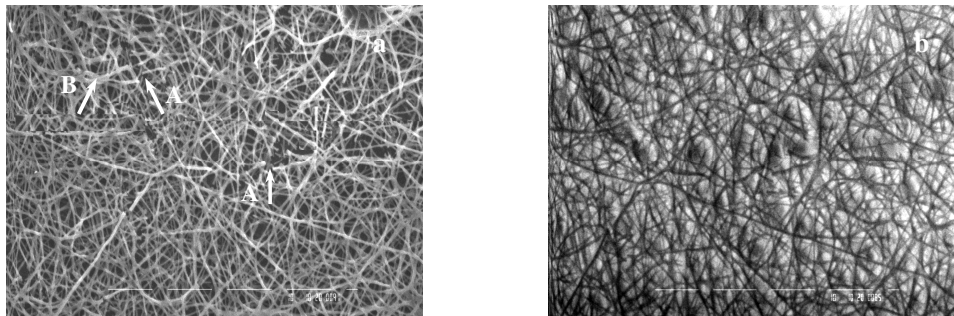


Figure 1. SEI – a and b – BEI-compo micrographs of fibres spun from homogeneous blend solution; bar length 10 μm

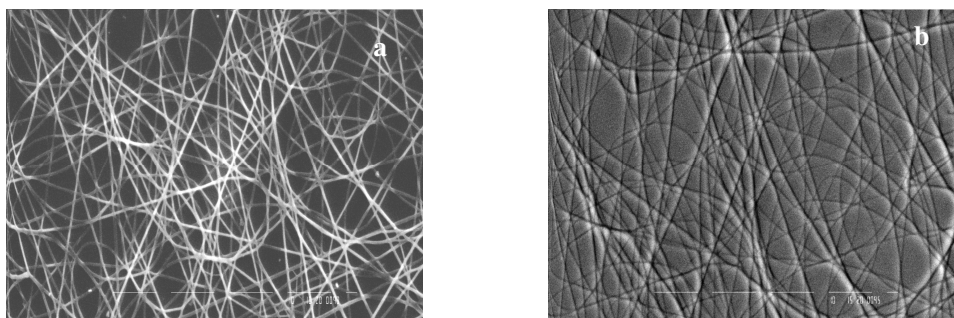


Figure 2. SEI – a and b – BEI-compo micrographs of fibres spun from suspension blend solution; bar length 10 μm

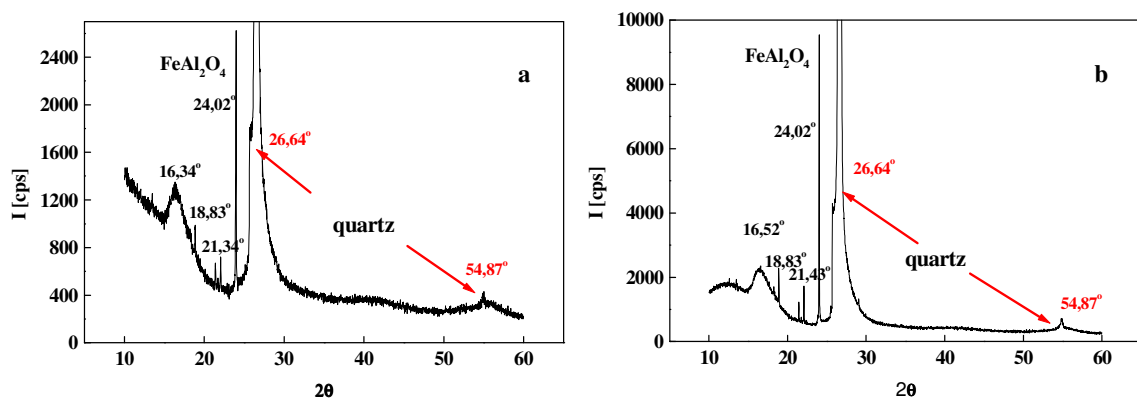


Figure 3. XRD spectra of the non-woven mats spun from homogeneous – a, or b – suspension blend solution

Figure 3 shows the XRD spectra obtained from both kinds of samples. As seen the most intensive peak at $2\theta=26,64^\circ$ as well as this at $2\theta=54,87^\circ$ belong to the quartz material used as substrate. The

second intensive peak in both spectra and at $2\theta=24,02^\circ$ is very sharp and belongs to the FeAl_2O_4 phase and that at $2\theta=18,83^\circ$ - to FeAlO_3 phase. Only these phases are identified among the huge number of Fe-Al-O compounds known from the powder diffraction [8]. Besides, no traces from the very stable hematite $\alpha\text{-Fe}_2\text{O}_3$ or alumina $\alpha\text{-Al}_2\text{O}_3$ are dissolved in these XRD spectra which usually accompany the synthesis of FeAlO_3 with other methods as for instance the solid state reactions [5]. The results from XRD show that in both cases the fibrous material spun at optimal electrospinning conditions and thereafter calcinated during the two step thermal procedure is the multi-ferroic with practically same composition, e.g. – mixture of FeAl_2O_4 with small amount of FeAlO_3 phase.

It should be noted here that rarely some defects along the inorganic fibres spun from homogeneous blend solution are observed: broken – A, or fused B fibres (figure 1a). In some experiments a formation of different fibres defects spindles, knots or drops accompany the spinning process. This could be avoided selecting carefully controlled electrospinning conditions.

4. Conclusion

The present study demonstrates for the first time that applying the electrospinning method it is possible to prepare new class material – multiferroic fibrous non-woven mat from basis material of Fe - Al -O. This new material consists of long fine fibres of FeAl_2O_4 mixed with FeAlO_3 their cross-section diameter being $\leq 1 \mu\text{m}$. Two different blend solutions for electrospinning are used and the fibres prepared are similar in size and shape. Carefully controlled electrospinning conditions are selected in order to fabricate homogeneous and defectless non-woven mats. Further investigations with modified blend solutions for preparation of FeAlO_3 fibres only are in progress.

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