

# Magnetic properties of fibrous Fe–Al–O prepared by electrospinning

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**Abstract.** Recently, we obtained a new Fe-Al-O fibrous material by applying the novel route of electrospinning. Here we report on the properties of the as prepared material established by PPMS magnetometry and X-ray diffraction. X-ray diffractograms revealed the coexistence of the orthorhombic multiferroic phase FeAlO<sub>3</sub> along with traces of unreacted impurities. The structure of the FeAlO<sub>3</sub> phase is described in the orthorhombic Pna2<sub>1</sub> space group and is of great current interest since the compound features piezoelectricity, ferrimagnetism and magnetoelectric effects at low temperatures. In contrast to known bulk material obtained by classical routes the new fibrous material shows a lower value of saturation magnetization and the magnetic transition occurs at a much lower temperature. In the discussion an attempt is made to disclose the reasons for the observed differences.

## 1. Introduction

In the last decade a lot of efforts have been made for obtaining monophase samples of FeAlO<sub>3</sub>. This compound undergoes a ferromagnetic phase transition at about 280 K with strong 180° cation-anion-cation super-exchange antiferromagnetic interactions. Moreover FeAlO<sub>3</sub> is multi-ferroic and at low temperature it shows an extremely high magnetic anisotropy [1,2]. These properties as well as its relatively simple crystal structure make it a perspective material for important technological applications. Additionally, studying the properties could help for clarification of the reason for appearance of magnetoelectric coupling in these compounds. Another important reason for the interest towards FeAlO<sub>3</sub> is that most magnetoelectric materials are based on heavy metal oxides, mainly lead (Pb) and bismuth (Bi). That is why FeAlO<sub>3</sub> is perspective as lead – free multi-ferroic material, showing piezoelectricity and ferrimagnetism at low temperature [1-4]. As is known, in recent years the search of alternative materials with substantial technological impact grows constantly by taking, however, into account their environmental impact to remain acceptably low due to environmental, social and public health reasons [4]. Therefore, the fabrication of single-phase lead-free multi-ferroics (such as



FeAlO<sub>3</sub>) with appropriate properties for the technological application is a provocative challenge for physicists and material scientists.

The standard routes of synthesis of orthorhombic FeAlO<sub>3</sub> are complicated due to the very narrow range of stoichiometry and thermodynamic stability of this phase in the binary equilibrium diagram Fe<sub>2</sub>O<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub>. Different experimental approaches were applied so far for synthesis of single-phase FeAlO<sub>3</sub> such as solid state reaction, sol-gel, co-precipitation and high-energy ball-milling techniques. Recently, we obtained a new fibrous material of Fe-Al-O by applying the novel approach of electrospinning [5]. For the first time it was demonstrated that this method provides the possibility to prepare fibrous Fe-Al-O non-woven material. However, the resulting long fine fibres of multiferroic FeAlO<sub>3</sub> were mixed with FeAl<sub>2</sub>O<sub>4</sub>. This necessitated searching for new precursors and related conditions for the post-heat treatments.

In this study, further investigations with modified blend solutions for preparation of Fe-Al-O fibres are described. The new material was characterized through X-ray powder diffraction and AC susceptibility measurements.

## 2. Experimental details

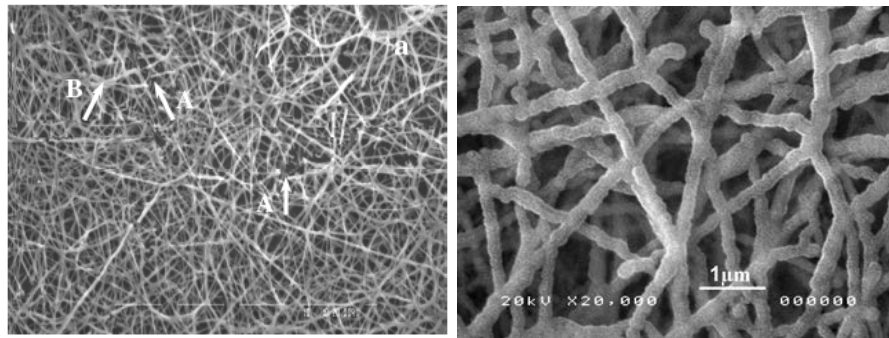
Details of the electrospinning technique and conditions for preparation of the Fe-Al-O material as non-woven mat were reported in [5]. Iron nitrate based precursor was used and the temperature for non-isothermal calcinations was 800 °C. The present fibrous material was obtained by electrospinning of a different liquid precursor, which contains a mixture of blend aqueous solution of aluminum acetate AlOH(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O and iron citrate C<sub>12</sub>H<sub>10</sub>Fe<sub>3</sub>O<sub>14</sub>, dissolved in deionised water in equal molar concentrations. A 10,0 wt% aqueous solution of water soluble polymer polyethyleneoxide-PEO is added in weight ratio 1 : 1 (POE : Fe-Al precursor) in order to assist the electrospinning process. The actual working parameters were as follows: high voltage – 15 kV, working distance - 20 cm, flow rate - 0,3 ml/h and electrospinning time of 10 hours. The samples were deposited onto fused quartz substrates, which thereafter facilitate the calcinating procedure at 1100°C for 2 hours, preceded by stepwise water and PEO removal at 120°C or 360°C, which was accomplished completely for about 6 hours.

The new Fe-Al-O material thus obtained was morphologically inspected using a scanning electron microscope Jeol SEM T-200. In order to amplify the contrast during the SEM observations, the samples were beforehand covered with vacuum deposited carbon and gold films. The phase composition of the thermally processed mats was verified from X-ray powder diffraction (XRD) data collected with a Philips diffractometer, using Cu K $\alpha$  radiation. Temperature dependences of magnetization were measured using a physical properties measuring system (PPMS, Quantum Design) in the temperature range from 2 K to 300 K and applied magnetic field of H<sub>DC</sub> = 1kOe.

## 3. Results and discussion

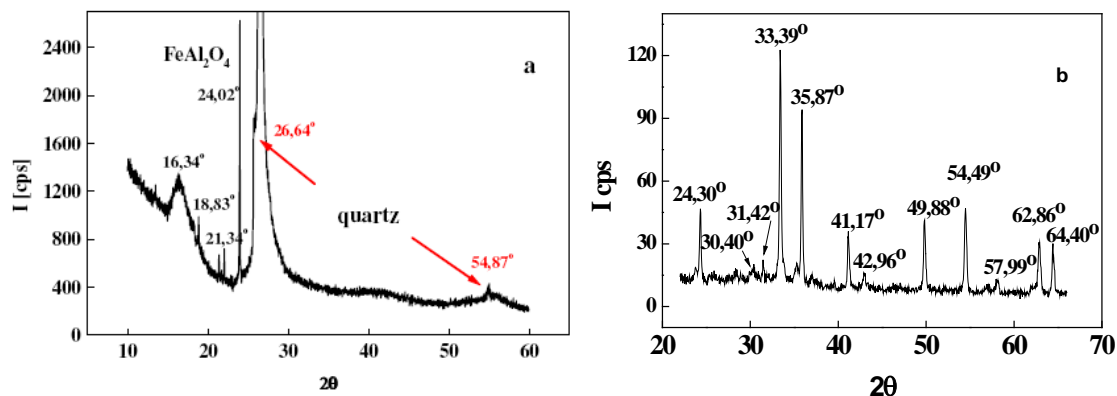
The SEM examinations on the microstructure of Fe-Al-O non-woven mats are illustrated by the images in figure 1. The SEM micrographs revealed morphologically homogeneous fibrous materials composed of long fibers with nearly regular cross sections.

However, the fibres cross-section size is of the order of 30-50 nm for the Fe-citrate based material and is substantially reduced in comparison with the previously estimated cross-section of about 1 $\mu$ m for the Fe-nitrate based material. The micrographs evidenced as well that by following the newly developed procedure the resulting material was of better quality in terms of both morphological and phase quality. Here is to note that the Fe-Al-O non-woven material reported earlier [5] had two major drawbacks: 1) the orthorhombic FeAlO<sub>3</sub> phase was of small amount at the expense of a greater quantity of spinel phase FeAl<sub>2</sub>O<sub>4</sub>; 2) the woven material featured a number of undesirable topological defects such as broken – **A**, fused fibres **B** or knots **a** (figure 1 left panel).



**Figure 1.** SEM images of Fe-Al-O non-woven mats obtained by electrospinning using Fe-nitrate based precursor (left -magnification 2000) and Fe-citrate based precursor (right- magnification 20000).

Figure 2 shows the XRD patterns of Fe-Al-O non-woven mats obtained earlier (left) and at present (right).



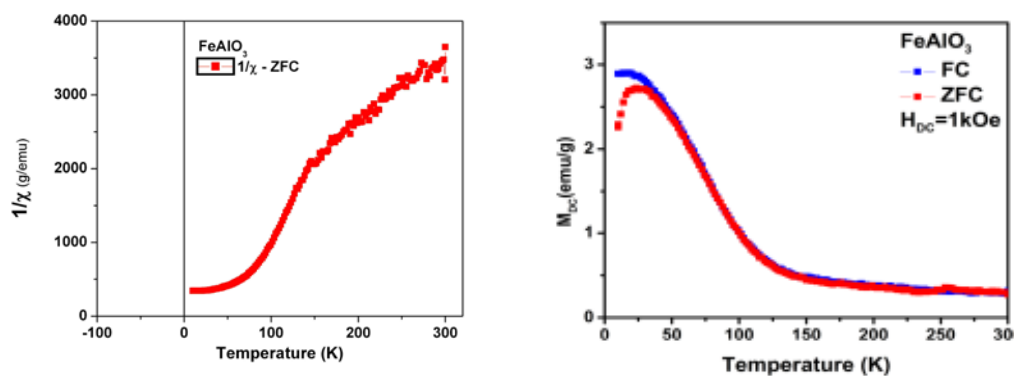
**Figure 2.** Room temperature XRD pattern of Fe-Al-O non-woven mats obtained by electrospinning using ferric nitrate based precursor (left) and ferric citrate based precursor (right).

In figure 2 (left) the peaks at  $2\theta=26,64^\circ$  and  $2\theta=54,87^\circ$  belong to the quartz substrate, the sharp intensive peak at  $2\theta=24,02^\circ$  belongs to the  $\text{FeAl}_2\text{O}_4$  phase whereas the peak at  $2\theta=18,83^\circ$  corresponds to the  $\text{FeAlO}_3$  phase. The orthorhombic perovskite  $\text{FeAlO}_3$  is reported to crystallize in the non-centrosymmetric space group  $Pna2_1$  space group  $Pna2_1$ . The cations are distributed among four types of sites labelled Fe1, Fe2, Al1 and Al2. The three first sites are octahedral and the last one is tetrahedral. The octahedra share edges whereas the nearly regular tetrahedra share oxygen at the corners. There is site disorder among the cationic sites (in fact all sites are occupied by both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions) and site occupancies do not vary with lowering of temperature. The compound presents a classical Néel ferrimagnetism as established by neutron diffraction [6]. The Néel sublattices **A** = Fe1 + Al1 and **B** = Fe2 (+ Al2) are responsible for the strongly antiferromagnetic  $\sim 180^\circ$  bonds Fe1 - O - Fe2 and Fe2 - O - Al2. The direction of easy magnetization is *a*-axis and *c* is the polar axis.

Figure 3 shows a typical plot of inverse susceptibility versus temperature. The curve consists of a linear Curie-Weiss-type region at sufficiently high temperatures (above 200 K). The zero field cooled (ZFC) and field cooled (FC) magnetization (*M*) versus temperature plots are also displayed (zero-field cooling protocol with  $H_{\text{DC}} = 1\text{ kOe}$  applied field). A typical Hopkinson-type maximum exists at about

28K in the ZFC curve and the ZFC and FC curves deviate substantially (such a behavior is often called a spin-glass-like effect). Such behavior has been observed for a number of manganites in the low temperature range [7]. This effect could be a result of different factors—a kind of magnetic disorder, magnetic frustration, the existence of small magnetic particles or clusters, etc. In all cases the main physical reason for it is that the system is energetically degenerate, and the main physical parameter responsible for the effect is magnetic anisotropy. However, more extended and detailed investigations are necessary for a better understanding this effect.

It can be summarized that the magnetic measurements on cooling the samples reveal a magnetic transition ( $T_N$  of about 125 K, taken from the differential maximum of the ZFC  $M(T)$ ) that can be attributed to a transition from the paramagnetic to the ferrimagnetic state. While the spontaneous magnetization is still close to the value of about 0.4  $\mu_B/\text{Fe}^{3+}$  as estimated by Bouree et al. [6] for microcrystalline powder of  $\text{FeAlO}_3$ , the magnetic transition temperature is substantially lower than the values ranging from 250K to 280K reported by different authors for polycrystalline substances of various average grain size produced by commonly used techniques and could be related to the nanosized diameter of the fibres.



**Figure 3.** Non-woven mat Fe-Al-O from ferric citrate based precursor: (Left) Temperature dependence of the inverse magnetic susceptibility  $1/\chi$ ; (Right) ZFC and FC thermomagnetic curves in a field of 1 kOe.

#### 4. Conclusion

It was confirmed that the electrospinning technique with successive steps of calcination of the product provides a reproducible route for fabricating of Fe-Al-O non-woven mats. A new precursor based on ferric citrate was developed and new appropriate conditions for calcinations were implemented successfully for the fabrication of Fe-Al-O substance composed of long filaments of uniform size ranging in diameter between 30 and 50 nm that are more than an order of magnitude thinner than those previously reported [5]. The new material is with much less topological defects, improved morphology and a higher content of the orthorhombic  $\text{FeAlO}_3$  phase. Nevertheless, it shows a lower value of saturation magnetization and the magnetic transition occurs at a much lower temperature as compared to bulk  $\text{FeAlO}_3$  material obtained by classical routes.

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