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# Stabilization of bismuth ferrite suspensions in aqueous medium with sodium polyacrylate characterized by different molecular weights

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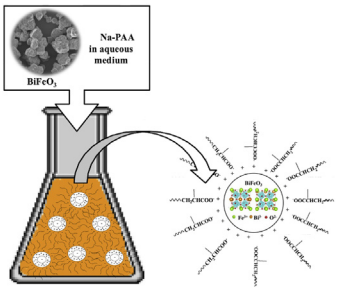
## HIGHLIGHTS

- Electrostatic stabilization of bismuth ferrite $BiFeO_3$ suspensions in aqueous medium.
- Use of polyacrylate as dispersant agent characterized by different $M_w$.
- Influence of BFO conc, dispersant agent conc and $M_w$, and sonication time.
- Dispersion efficiency in terms of sediment percentage and the zeta potential trend.
- Spectrophotometric method to investigate the sediment percentage.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Electrostatic stabilization of bismuth ferrite $BiFeO_3$ (BFO) single phase micronized particles suspended for the first time in aqueous medium, using sodium polyacrylate (Na-PAA) as suspending agent, was investigated to form homogeneous films through electrophoretic deposition technique. The dispersion efficiency was evaluated in terms of the zeta potential trend as a function of pH and sediment percentage, employing a fast and easy spectrophotometric method. All the tests were performed using three suspending agents characterized by the same polyacrylate functional group (-COONa) but with different molecular weights (Na-PAA $M_w = 2100$, 5100, and 20 000). The effect of BFO particles concentration (wt %), suspending agent concentration (wt%), suspending agent molecular weight and sonication time have been evaluated. The results showed that for all the experiments carried out the electrostatic stabilization of the BFO micronized particles in aqueous medium is accomplished in high basic pH range (8.5–9 or 9–11) depending on the molecular weight of the polyacrylate additive.



## 1. Introduction

Bismuth ferrite, $BiFeO_3$ (BFO) has been studied for many years because of its exceptional simultaneous ferroelectric and weak ferromagnetic properties above room temperature [1–4].

The interactions between BFO magnetic and electric polarizations lead to additional functionalities, which make it a promising candidate in a wide range of different applications such as in spintronics magnetic recording media, sensors, photocatalysis and photovoltaic devices [5–9].

Besides the synthetic efforts aimed at the obtainment of bismuth ferrite single phase powder, many publications appeared about the production of electroceramic films and coatings. In fact the growth of a thin layer onto a wafer scale and conformal coverage are required to introduce a multiferroic material for a new generation of ferroelectric devices usable for the above mention applications. In the scientific literature several techniques, such as the pulsed laser deposition (PLD) [10–12], RF-magnetron sputtering (RF-sputtering)

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[13] the chemical vapour deposition (CVD) [14–16] and recently the electrophoretic deposition (EPD) [17] have been proposed for the preparation of thin or thick BFO coatings. This last technique was already used for different kind of nanoparticles such as ZnO [8] or $ZrO_2$ [19] and other metal oxides [20].

To prepare dense and uniform BFO coatings by EPD on conductive substrates stable suspensions are required. In our previous work [18], the electrokinetic properties of bismuth ferrite suspensions in presence of different suspending agents (sodium polyacrylate Na-PAA $M_w$ = 2100, polyethylene glycol, carboxymethyl cellulose and, sodium naphthalene sulfonate), used to provide stable suspension, and the influence of experimental parameters (i.e. deposition time, applied voltage, BFO concentration) on electrophoretic deposition have been investigated. The interaction between suspending agent and BFO surface provide the stability in suspension applied for EPD. This stabilization depends on different factors such as: the BFO concentration; the suspension sonication/stirring time; the amount, the molecular weight and polarity of suspending agent and pH of suspension. Among the different functional groups tested, the polyacrylate one was identified as the most performant additive since it strongly interacts with the BFO particles stabilizing the suspension system. This polyelectrolyte contains ionizable carboxylic (−COONa) groups (one per monomer unit) along its backbone, which dissociate to form negatively charge carboxylate ($-COO^-$) with increase of pH ($pK_a$ ~ 4.5–5) influencing the BFO's solution stability [21,22]. Even though the polyacrylate functional group seems to be employed as suspending agent in many different studies [23], a detailed investigation on the stabilization of bismuth ferrite aqueous suspension is not reported in the literature (to the best of authors knowledge). Hence in the present work the electrostatic stabilization of $BiFeO_3$ suspensions in aqueous media in presence of Na-PAA at different $M_w$ up to 20 000 was investigated in order to find out the optimal conditions. Our aim was to evaluate the effect of the following parameters on the suspension stability: (i) micronized BFO particles concentration (wt%), (ii) suspending agent concentration (wt %), (iii) molecular weight of the suspending agents, and (iv) sonication time of the final suspension. All the other parameters, influencing the suspension behaviour, such as solvent, temperature, and stirring time were kept constant.

## 2. Materials and methods

### 2.1. Materials

Bismuth ferrite submicrometric particles were prepared following the reaction via microwave-assisted hydrothermal process according with the following reaction equation, as detailed elsewhere [24]:

$$Bi(NO_3)_3\cdot 5H_2O + Fe(NO_3)_3\cdot 9H_2O + KOH \rightarrow K_xBi_{1-x}(OH)_3 + Fe(OH)_3 + H_2O \xrightarrow{\Delta} BiFeO_3 + KOH$$

The precipitation of the hydroxides occurs instantaneously during the addition of KOH, while their crystallization to $BiFeO_3$ is a hydrothermal microwave assisted process. The microstructure and the chemical composition of the sample were investigated elsewhere [17,24] and only briefly presented hereafter. All the analytical grade (≥99.7%) chemicals, $Bi(NO_3)_3\cdot 5H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, KOH, were purchased from Sigma–Aldrich (Milan, Italy) and used without further purification for the synthetic step. A MicroMeritics AccuPyc 1330 Pycnometer was used to non destructively determine the density of BFO samples by actually measuring their volume very precisely. The sample mass is measured on a high quality balance and entered into the pycnometer software to give the sample density. The volume is measured using the Gas Displacement Technique.

The sodium polyacrylate (Na-PAA) suspending agent with different average molecular weights, $M_w$ = 2100, 5100, 20 000, the citric acid and the ammonium hydroxide, useful to adjust the pH value, were purchased from Sigma–Aldrich (Milan, Italy), and used as received.

### 2.2. Suspension preparation

The single phase micronized $BiFeO_3$ (BFO) particles obtained by the optimized [24] microwave-assisted hydrothermal reaction were dispersed in bi-distilled water in the presence of Na-PAA agents with different molecular weight ($M_w$) in a concentration range from 0.05 to 0.3 wt% (only for Na-PAA $M_w$ = 2100 from 0.05 to 0.6 wt%). The concentration of BFO particles was varied from 0.1 to 0.4 wt.%. In order to form thoroughly dispersed suspensions, the BFO particles and the suspending agent were vigorously stirred for 24 h and then sonicated for a time ranging from 5 to 45 min.

### 2.3. Zeta potential measurements

The zeta potential, ζ, of bismuth ferrite (BFO) micronized particles at various pH values were measured by a Nano-Zetasizer (Malvern Instruments, Worcestershire, UK). The unit automatically calculates the electrophoretic mobility of the particles and converts it into the zeta potential using the Huckel and Smoluchowski equation [25]. BFO particles are small enough to be detected using Malvern Nano-ZetaSizer ZS because they fall in the size range of 3 nm–10 μm. The ζ values reported in this work have been averaged among 5 measurements.

The suspensions pH was measured by a pHmeter with pentrode probe (Orion 555A), 0.1 M solutions of citric acid and ammonium hydroxide were used for pH adjustments [26]. Zeta potential and electrophoretic mobility were investigated in the pH range 2–13. In all the experiments, the equilibration time, which is the time between reaching the next pH point and the next measurement, was chosen to be 180 s.

### 2.4. Sedimentation rate and sedimentation percentage determination

The sedimentation rates for all the experiments were determined with a spectrophotometer (NANOCOLOR 400 D) at a fixed pH = 8.50–9.50, in which the suspensions were characterized by the higher zeta potential absolute value [17]. A fixed wavelength of 436 nm, corresponding to the maximum BFO adsorption spectra [27], was selected to measure the suspension turbidity. The sedimentation rate for each sample was measured at different time intervals (1, 5, 10, 30, 60 min). The time interval of approximately 30 min, was experimentally found in our previous work [17] to be sufficiently long to allow the obtainment of a good and uniform layer by EPD deposition.

Since the aim of this work is to improve and optimize the stability of water suspension used in EPD process to get uniform and dense BFO film, the sedimentation percentage was calculated by the difference between the initial turbidity (after 1 min) and the final turbidity value (after 30 min) for each sample.

## 3. Results and discussion

### 3.1. Zeta potential of BFO sub-micrometric micronized particles aqueous suspensions in the presence of Na-PAA

The BFO micronized particles presented a single phase perovskite/rhombohedral structure having a space group R3c (JCPDS card