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Crystallization mechanisms and optical properties of BiFeO₃ nano and microparticles

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Abstract— BiFeO₃ nano and micro particles are synthesized via wet-chemical process and conventional solid-state sintering method. Nucleation and crystalline growth of BiFeO₃ nanoparticles are investigated following the Kissinger-Akahira-Sunose approach from calorimetry experiments. For all nano and micro particles we observe different temperature dependences for the effective band gap of different size BiFeO₃ particles, which we relate to vacancies defects. Our work highlights that controlling the phase purity, crystallization and thermal treatments for obtaining BiFeO₃ the particles using optimized soft chemistry synthesis methods is of major interest to control the electronic and optical properties of these compounds.

Keywords—nanoparticles; BiFeO₃; optical properties; vacancies

I. INTRODUCTION

Applying ferroelectrics materials as transducers to convert light into other stimuli such as electrical [1][2], mechanical [3][4] or chemical [5][6] energies, and profit their capabilities for other applications, has received intense research interests at fundamental levels in view to attain new application goals in the fields of photovoltaic, photomechanical or photocatalytic devices [7]. Here we show a detailed study of the crystalline growth mechanisms and the corresponding crystalline, optical and electronic properties of pure phase multiferroic BiFeO₃ nano and micro particles. Applications in the field of photocatalytic processes are presented and discussed.

II. METHODS/RESULTS

BiFeO₃ nanoparticles with average particle size between 30 and 190 nm are synthesized using an optimized wet chemical

methods. Using tartaric acid and ethylene glycol as chelating agents and chemical reagents (Bi(NO₃)₃·5H₂O, Fe(NO₃)₃·9H₂O) and solvents (nitric acid) of analytical grade, we synthesize a 3D network structure that leads to high quality nanopowder samples. We submit the dried precursor solution to controlled heating treatments from 450 °C to 600 °C to tune the nucleation, growth and coalescence of single phase nanoparticles. Moreover, conventional solid state reaction method is used to obtain pure phase micro size particles. Differential scanning calorimetry (DSC) experiments are performed using a TG-DSC 92 SETARAM setup under different temperature ramps in the as-prepared precursors and powders (Figure 1). Crystal phases, structure and phononic fingerprint are determined by x-ray diffraction on a Bruker D2 Phaser diffractometer using Cu K α radiation in theta-theta configuration and by micro-Raman analysis using a Labram-Horiba spectrometer under He-Ne laser excitation (632.8 nm). Atomic scale characterization is performed from high resolution transmission electron microscopy experiments carried out on an FEI Titan ETEM (300 kV of accelerating voltage, equipped with a Gatan OneView CMOS detector, and a Gatan imaging filter Tridiem 965 ER). Optical properties of the particles are studied using UltraViolet-Visible (UV-Vis) diffuse reflectance spectra from a PerkinElmer spectrometer (Lambda 850) equipped with a Harrick Praying MantisTM diffuse reflectance accessory. The photocatalytic activity is evaluated by the degradation of rhodamine-B dye in aqueous

solution under visible-light irradiation (500 W Xe-lamp with a cut-off filter allowing $\lambda > 420$ nm).

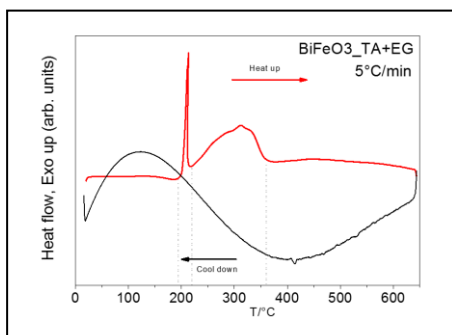


Figure 1. Heating and cooling ramps of DSC experiments using BiFeO₃ precursor powders, synthesized using tartaric acid (TA) and ethylene glycol (EG). The decomposition heat exchange of tartaric acid, ethylene glycol and the esterification network correspond to the exothermic contributions observed in the heating ramp around 200°C and 350°C.

III. DISCUSSION/INTERPRETATION

BiFeO₃ nano and micro particles are synthesized via a facile wet-chemical method based on sol-gel routes. Using calorimetric experiments and advanced analysis, we explicitly get information from the synthesis temperature process, and establish the parameters to obtain single crystalline, phase-pure, BiFeO₃ nanoparticle synthesis conditions. We show that BiFeO₃ nanoparticles undergo a two-step crystallization process [8], deduced from a non-isothermal Kissinger-Akahira-Sunose analysis of the calorimetry data. Through studying the nanoparticles crystallization mechanisms, the particle crystallization process is consequently controlled. The structure and optical, chemical and electronic properties of these systems are studied using X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and diffuse reflectance (Figure 2).

While we determine no striking change in the average structure, nor in the intra bandgap transition related to different Fe 3d states, so-called d-d electron transition, for all nano- and micro- particles we observe different temperature dependences for the effective band gap of different size BiFeO₃ particles, which we relate to vacancies defects [9]. We study the time dependent photo-degradation of the rhodamine-B dye under visible light irradiation while in solution with BiFeO₃ nanoparticles. We observe that rhodamine-B is decomposed under different degradation efficiency depending on the BiFeO₃ nanoparticle size, which we correlate to the different surface properties of smaller nanoparticles compared to larger ones [10].

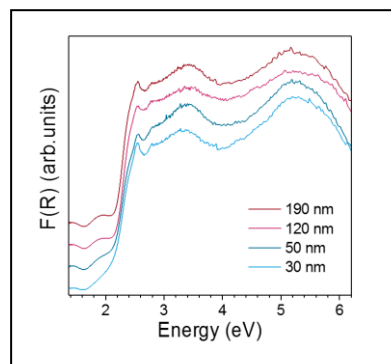


Figure 2. Room temperature UV-Vis absorption spectra of different size BiFeO₃ samples derived from the diffuse reflectance (R) spectra using Kubelka-Munk functions F(R) on pure phase nanopowders nanoparticle size indicated in the legend.

IV. CONCLUSIONS

Our results on BiFeO₃ growth mechanisms highlight the complexity of the crystallization process in these nanoparticles, which is of high importance to widely capture the structure-property relationships and the potential application of these nanoparticles to photocatalytic applications.

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