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$BiFeO_3$ multiferroic nano oxide: Synthesis and Characterization

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Abstract – The control of multiferroic properties is an attractive possibility, but the number of promise materials is limited. One of them, $BiFeO_3$, has critical conditions for synthesizing single phase since the temperature stability range of the phase is very narrow. Hence, nanoparticles of $BiFeO_3$ (< 53.0 nm) were obtained using a wet chemical route (citrate method) that preserved a lot of textural, morphological and surface properties with respect to the same product prepared by solid state reaction. The characterization using X-ray diffraction (XRD); scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) showed the best synthesis conditions.

For the synthesis of $BiFeO_3$ oxide, nitrate type solutions 1.00 M and monohydrate citric acid 2.00 M were used. The precursor solutions were dosed into a reactor equipped with magnetic stirring (150 rpm), temperature control and reflux at 80º C for two hours. The order of addition of precursors, was established by the corresponding hydrolysis constants, so that the total amount of nitrate in solution was 0.01 mol and the addition of citric acid was done in a 4:1 molar ratio, while the pH was adjusted with a ammonia solution between 5.80 and 5.90 based on the analysis and modeling proposed to resolve the potential reactions in aqueous medium using the Hydra-Medusa software[1], this will prevent hydrolysis and precipitation of bismuth cation in the form of insoluble solid complexes type $Bi(cit)_{(s)}$ and $Bi_2O_{3(s)}$ which predominate in a wide pH intervals between $1.00 \leq pH \leq 5.70$ and $5.90 \leq pH \leq 12.00$ respectively (Fig. 1a) . The resulting sol was heat at 120 ºC for 24 hours and then at 250°C, until the obtention of a solid precursor that was calcined at 600ºC for 2 hours using a ramp of $50ºC \cdot hour^{-1}$. The precursor analysis by infrared spectroscopy and thermogravimetric analysis showed the formation of citrate type species as well allowing evaluate the optimum temperature for the consolidation of the crystalline phase (Fig. 1b).

The phase formation, purity and morphology were determined by X-ray diffraction, in a PANAlytical X'pert PRO MPD equipment with ultra-fast X'Celerator detector, using Cu K_α radiation (λ = 1.54186 Å) between 10 and 90° 2θ in Bragg-Brentano configuration with steps of 0.02° 2θ, with irradiations of 40.80 seconds per step; the scanning electron microscopy (SEM), showing that the method allows to generate and maintain in the solid important surface and textural features for potential applications (Fig. 1d). The diffraction results were analyzed and refined using X'Pert High Score® and Cellref3.0® software, indicating that the $BiFeO_3$ has a characteristic grain size distribution proper of synthesis method with preferential orientation in the plane $(00\bar{5})$ (Fig. 1c), with this signal, the determination of the crystalline particle size by Debye-Scherrer equation, yielding a crystal size of 52.3nm. The search in the databases of the ICCD, suggests a classification consistent with the rhombohedric phase reference compound $BiFeO_3$, space group *R3m* (160), with cell parameters $a = b$ = 3.962 Å, c = 3.962 Å, cell volume: 62.180 $Å^3$, ICSD: 028027 and JCPDS: 01-086-1518. The tolerance factor using the SPuDS software [2] confirmed a structural tolerance factor (τ) of 0.9146 at 298 K and an global instability index of 0.000475 for the perovskite type structure.

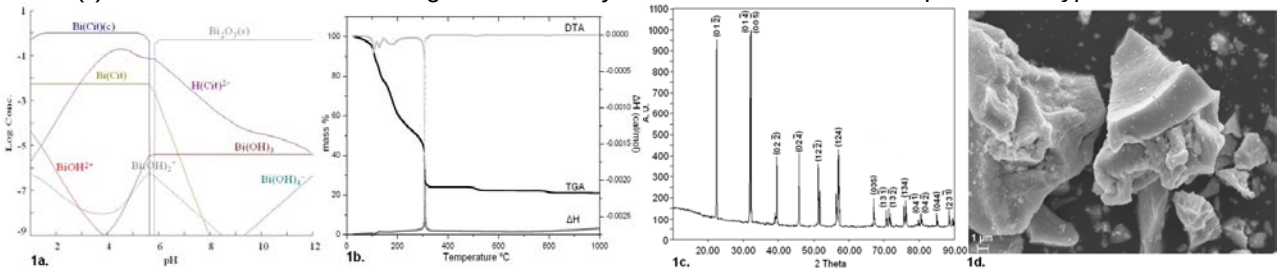

Figure 1: a) Bismuth concentration evolution with respect to pH in form of citrate and hidroxyle species, obtained by Hydra-Medusa® software. **b)** Thermogravimetric analysis of $BiFeO_3$ precursor. **c)** Indexed $BiFeO_3$ XRD pattern. **d)** $BiFeO_3$ scanning electron microscopy at 1µm.

References

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