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Preparation of multiferroic Co substituted $BiFeO_3$ with enhanced coercive force and its application in sorption removal of dye molecules from aqueous solution

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ABSTRACT

Multiferroic Co substituted $BiFeO_3$ ($BiFe_{0.95}Co_{0.05}O_3$) compound was synthesized by complex sol–gel method and its potential application as an efficient magnetic adsorbent in sorption removal of organic contaminants (like Rhodamine B as a model compound) was investigated. The XRD, Raman, and PPMS measurement revealed that Co substituted $BiFeO_3$ enhances magnetic properties dramatically at room temperature without inducing any impurity phase. This aspect is very useful for many applications of Co substituted $BiFeO_3$ especially in magnetic separation of this catalyst after its utilization in water purification. The adsorption kinetics, isotherm, thermodynamic as well as the possible sorption mechanism was studied through batch experiments. Almost no negative effect on the sorption performance (i.e. the sorption rate and saturated sorption capacity) was found after substitution of Co in $BiFeO_3$. In addition, this substitution give rise to much higher coercive force of $BiFe_{0.95}Co_{0.05}O_3$ which can be recycled more easily by magnetic separation technology.

1. Introduction

Nowadays, organic pollutants like dyes which have severe and chronic effects on living organisms have been considered major cause of water contamination [1,2]. Rhodamine B (RhB) is widely used as a colorant in textile industries and is harmful to human beings and animals which could yield potentially carcinogenic aromatic amines under natural reductive anaerobic degradation [3]. So far, many efforts have devoted to remove RhB from aqueous solution by developing new technologies and materials to solve this problem. Based on the results, adsorption process has the advantage of low generation of residues and the possibility of reuse of the adsorbent. Due to these factors, adsorption process has been recognized as an efficient and economic method [4].

Multiferroic materials which exhibit unique ferroic properties such as ferroelectric, ferromagnetic and ferroelastic in a single phase have drawn great attention driven by their potential applications for new electronic devices and intriguing fundamental physics [5,6]. Perovskite-type $BiFeO_3$ with ferroelectric and antiferromagnetic orderings above room-temperature ($T_C \sim 1103$ K, $T_N \sim 643$ K), make it one of the most promising candidate for practical applications [7]. However, weak macroscopic magnetism attributing to canted G-type antiferromagnetic spin structure limited its advancement [8]. Comparing with other methods, ion substitution is an effective mean to improve the multiferroic property. Our previous achievements [9–11] clearly demonstrated that the Co substituted at Fe site could improve room temperature magnetism significantly attributing to the suppression of the spiral spin configuration, which suggests its good application in magnetic separation especially with the concentration of 5% [12]. In terms of environmental remediation, $BiFeO_3$ is being applied as photocatalyst owning to its small band gap and has been studied intensively. However to the best of our knowledge, little work has been focused on adsorption performance of $BiFeO_3$ [13,14].

In this paper, $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$ ceramics were synthesized by a tartaric acid modified sol–gel method. The microstructure as well as the magnetic properties of as-prepared multiferroic oxides was characterized by means of X-ray diffraction (XRD) patterns, Raman spectra and physical property measurements (PPMS). The sorption kinetics, isotherm and thermodynamics were investigated by selecting Rhodamine B (RhB) and multiferroic $BiFe_{0.95}Co_{0.05}O_3$ as a sorbate and sorbent, respectively. Furthermore the possible sorption mechanism has been discussed based on the static-electric adsorption process.

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2. Experimental

2.1. Preparation of $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$ powder

$BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$ ceramics were prepared by a tartaric acid modified sol–gel method. Raw materials of $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ of analytical-grade were dissolved in diluted HNO_3 in proper stoichiometric proportions. Tartaric acid in 1:1 M ratio with respect to metal nitrates was added to the solution, which was heated in 150 °C to form xero gel. After grinded thoroughly, the powder was sintered at 600 °C for 2 h. The obtained $BiFe_{0.95}Co_{0.05}O_3$ sample was leached in diluted far about half an hour, and washed in deionized water repeatedly to remove the trace amounts of impurity.

2.2. Characterization

The crystal structure of both samples was characterized by X-ray diffraction (XRD) with Cu Kα radiation (Rigaku Smartlab). The magnetic properties were investigated by Physical Property Measurement System (PPMS-9, Quantum Design) at room temperature. Raman measurements were carried out on a Horiba Jobin Yvon LabRAM HR 800 micro-Raman spectrometer with 785 nm excitation source under ambient air conditions at room temperature. The zeta potentials as-prepared $BiFe_{0.95}Co_{0.05}O_3$ at different pHs were determined by a zeta potential instrument (Malvern, Great Britain).

2.3. Batch sorption evaluation

All the sorption experiments were conducted under dark conditions in a thermostatic stirrer equipped with water bath. The stirring speed of the magnetic bar was measured at around 150 rpm. The pH of solution was adjusted by diluted HCl or NaOH aqueous solution. After sorption process for certain period, the residual solution without adsorbent was separated through centrifugation. The concentration variation of RhB was monitored by UV–Vis spectrometer (HITACHI U-3900) at wavelength of 554 nm. All the experiments were conducted at least twice and took the average of the results.

3. Results and discussion

Fig. 1 depicts the XRD patterns of $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$. All peaks of $BiFeO_3$ shows the rhombohedral perovskite structure with the space group of R3c, except a small peak of $BiFeO_3$ marked by ∗ which can be attributed to the small amount of impurity of $Bi_2Fe_4O_9$ [15]. After washed by diluted HNO_3 and deioned water, the $BiFe_{0.95}Co_{0.05}O_3$ does not show any impurity phase. The peaks of 5% Co doping at Fe site are similar to pure $BiFeO_3$ indicating that no obvious structure transformation was induced. Magnetic hysteresis loops of both samples as illustrated in Fig. 2 were measured at 300 K by PPMS. The linear curve was observed for $BiFeO_3$ which is in accord with the antiferromagnetic properties. The remnant magnetization and coercivity of $BiFe_{0.95}Co_{0.05}O_3$ (M_r = 0.02 emu/g; H_c = 710.21 Oe) are enhanced significantly by contrast with pure $BiFeO_3$ (M_r = 0.001 emu/g; H_c = 80 Oe). It is worth noticing that the 5% Co doping at Fe site shows significant improvement in magnetic properties without inducing any impurity phase. The improved magnetization effect suggests the application of this material in magnetic separation.

The details of structure evolution induced by Co substituted at Fe site were further studied by Raman spectra (Fig. 3). Theoretically, 13 Raman active modes ($4A_1$ + 9E) are expected for the rhombohedral $BiFeO_3$ [16]. However, with the temperature increasing to higher values, the intensity of many major peaks decreased and higher wavenumber peaks were broadened and merged into single broadened peak and even disappeared [17]. So, only three A_1 modes (A_1-1, A_1-2, A_1-3) could be noticed clearly for both samples at room temperature. It can be noticed that the A_1-1 mode of $BiFe_{0.95}Co_{0.05}O_3$ shifted to lower frequency and the intensity of A_1-2 mode decreased apparently comparing with $BiFeO_3$. The shift of A_1-1 mode which is associated with the vibration of Bi–O bond showed that Co doping produced more structural distortion on Fe site [9,18]. The decrement of A_1-2 mode which could be associated with magnetic transition representing spin reorientation indicates the change in magnetic property [19].

The kinetic curves of adsorption of $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$ measured at 293 K and 303 K are demonstrated in Fig. 4. The Pseudo-first-order dynamic model and pseudo-second-order kinetic model were carried out to fit this data.

Pseudo-first-order dynamic model:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacity at specific contact time and equilibrium; k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the adsorption constants. The related coupling parameters were listed in Table 1. According to the correlation coefficients, the experimental data fits very well to the pseudo-second-order model ($r^2 > 0.94$) better than pseudo-first-order dynamic model which indicates that sorption rate is possibly controlled by chemical sorption and the sorption capacity is proportional to the number of active sites on the sorbent [20]. All the adsorption process reached to equilibrium in 2 h. It is obvious that the substitution of cobalt in $BiFeO_3$ cannot decrease the sorption rate but contrary improve the sorption rate to a certain extent. With the temperature decrease from 303 K to 293 K, the adsorption constants of both samples decreased from 43.579 g mg^{-1} h^{-1} and 254.632 g mg^{-1} h^{-1} to 2.183 g mg^{-1} h^{-1} and 6.371 g mg^{-1} h^{-1}, while the equilibrium adsorption amount (q_e) increased from 0.185 mg g^{-1} and 0.216 mg g^{-1} to 0.516 mg g^{-1} and 0.537 mg g^{-1}. This behavior could be due to the competition result of the molecular diffusion

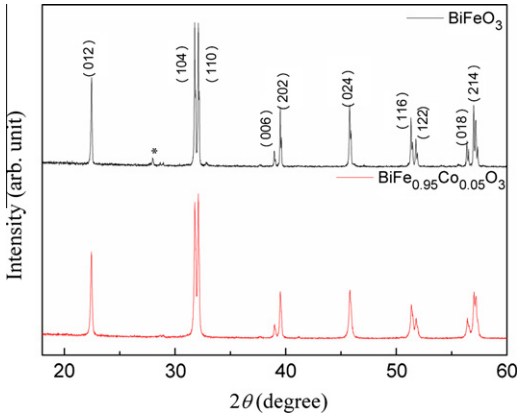

Fig. 1. XRD patterns of $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$. The peak marked by ∗ indicates the impurity phase of $Bi_2Fe_4O_9$.

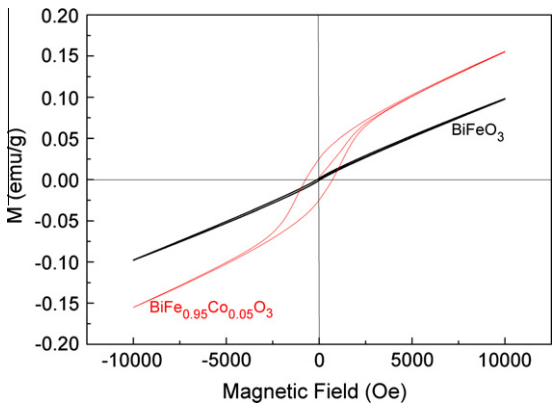

Fig. 2. M–H curves of $BiFeO_3$ and $BiFe_{0.95}Co_{0.05}O_3$ measured at 300 K.