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Probing the local structure of crystalline $NaBiO_3{\cdot}XH_2O$ and its acidified derivatives

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ABSTRACT

Sodium bismuthate is a commercially available, inexpensive, non-toxic and very potent inorganic oxidant and photocatalyst. It is one of the important reagents for oxidative separation of Am^{3+} from the chemically similar lanthanide ions, for its recovery or safe disposal from reprocessed nuclear fuel. While the structure of $NaBiO_3$ has been described from powder and neutron diffraction; the structure of $NaBiO_3{\cdot}XH_2O$, the manufactured form of sodium bismuthate, is currently unknown. Herein, we describe the structure of $NaBiO_3{\cdot}XH_2O$ ($X = 3$) using pair distribution function (PDF) analysis of X-ray total scattering data. In our proposed structure model, $NaBiO_3{\cdot}3H_2O$ is similar to $NaBiO_3$, but with turbostratic disorder in the stacking direction of the alternating Bi-O and Na-O layers. We propose locations for the lattice water, and its role in creating turbostratic disorder. We also used PDF to describe the structural evolution of sodium bismuthate upon exposure to nitric acid, the conditions employed in for nuclear fuel reprocessing. We supported the proposed model for pristine $NaBiO_3{\cdot}3H_2O$ and its acidified derivatives by a variety of techniques including thermogravimetry, powder X-ray diffraction (PXRD), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). By employing both surface and bulk techniques, we hypothesize that the bismuth reduced to Bi^{3+} upon aqueous acid exposure remains in the lattice, rather than completely dissolving and/or depositing on the surface, as prior suggested. Using pretreated acidified sodium bismuthate samples, we delineated the effects of acid strength vs. bismuthate structure/composition on Ce^{3+} to Ce^{4+} oxidation efficacy.

1. Introduction

Bismuth is an inert, inexpensive, non-toxic metal, and the heaviest of all the stable chemical elements. Bismuth has two accessible oxidation states, +3 and +5, respectively. Subsalicylate and subcitrate coordination complexes of Bi^{3+} are routinely used to treat gastrointestinal disorders and peptic ulcers [1]. The structure directing effects of Bi^{3+}'s lone pair is exploited in Pb-free piezoelectrics [2]. On the other hand, the +5 oxidation state bismuthate $[X^{n+}(BiO_3)_n]$ ($X = Li^+$, Na^+, K^+, Ag^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} and Pb^{2+}) is photocatalytically-active, and is as a promising alternative to TiO_2 for degradation of organic pollutants [3–7]. Bismuthate, $[BiO_3]^-$ is a strong oxidizer ($NaBiO_3$: +2.03 V vs SHE) [8], exploited to oxidize and separate valuable elements in the nuclear fuel cycle [9]. Specifically, $NaBiO_3$ oxidizes Am^{3+} to $[AmO_2]^{2+}$ which can then be isolated from other chemically-similar fission products (Ln^{3+}) by solvent extraction with several phosphate and phosphonate ligands [10–12]. The extracted $[AmO_2]^{2+}$ can then be either disposed safely or repurposed in fast reactor fuel.

The reduction of Bi^{5+} to Bi^{3+} paired with americium oxidation in the acidic conditions employed in nuclear fuel reprocessing is not well understood, and there is conflicting data in the literature. Bismuth was proposed to be dissolved in the pentavalent state (Bi^{5+}), as determined by iodometry [9]. However, standard Pourbaix diagrams suggest Bi^{5+} cannot exist in aqueous solution at any pH, and Bi^{3+} persists well above the Eh stability window for water. Mincher et al. described a decrease in the concentration of $[AmO_2]^{2+}$ in solution if the solid $NaBiO_3$ is removed [13]. These observations and studies point towards a heterogeneous oxidation process, in which Bi^{5+} is reduced to Bi^{3+} at the surface of the particles, and it may or may not become a part of the

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evolving solid lattice. Ding and coworkers [7] suggest Bi^{3+} self-dopes the lattice along with co-doped 'holes', responsible for the increasingly dark color with acid treatment. Their X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS) analyses of sodium bismuthate respectively show that the material becomes X-ray amorphous with mild acid treatment, and up to 35% of surface bismuth is trivalent. They additionally noted that Bi^{3+} could be deposited as a hexameric phase, $(Bi_6O_4(NO_3)_5(OH)_5{\cdot}0.5H_2O$ on the surface of the sodium bismuthate particles.

Because $NaBiO_3{\cdot}XH_2O$ is the comercially available form employed by the nuclear energy and photocatalysis communities, an evaluation of its structure is important to understand structure-function relationships. Additionally, since bismuthate rapidly becomes amorphous in its photocatalytic form and in extremely acidic environments of nuclear fuel reprocessing solutions, the structural evolution with acidification is likewise important. Herein, we examine the short range order of both $NaBiO_3{\cdot}XH_2O$ (X = 3)·and its evolution upon acid-treatment. Pair distribution function (PDF) analysis of X-ray total scattering yields structural information, while XPS, wet chemical analysis, and energy-dispersive X-ray spectroscopy (EDX) provide information about the elemental composition and the oxidation states, on both the surface and in the bulk. We document the oxidation efficacy as a function of structural changes of Bi^{5+}/Bi^{3+} evolution, employing the Ce^{3+}/Ce^{4+} redox couple as a surrogate for Am^{3+} oxidation [14]. From these data, we produce a structural model for the hydrated form of sodium bismuthate, and indicates how the local environment evolves as the material becomes X-ray amorphous. Additionally, by pre-acidifying sodium bismuthate prior to performing the Ce^{3+}/Ce^{4+}oxidation studies, we delineate the effects of solution conditions and materials state on oxidation efficacy.

2. Experimental

2.1. Materials and reagents

$NaBiO_3{\cdot}XH_2O$ (Fischer), $Ce(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich, 99%), $(NH_4)_2Ce(NO_3)_6$ (Alfa Aesar, 98 +%) and concentrated HNO_3 (Macron Fine Chemicals) solution were used as received. Deionized water (18.2 MΩ, Millipore) was used to prepare all solutions.

2.2. Acid treatment of $NaBiO_3{\cdot}XH_2O$

$NaBiO_3$ was prepared from $NaBiO_3{\cdot}XH_2O$ by heating at 210 °C for three hours in the air, as described elsewhere [15]. Acidified $NaBiO_3{\cdot}XH_2O$ samples were prepared by suspending 1.00 g $NaBiO_3{\cdot}XH_2O$ in eight, 10 mL volumes of HNO_3 dilutions in water at different concentrations. The $NaBiO_3$:HNO_3 molar ratio and the pH of these suspensions, along with the concentration and the pH of the initial HNO_3 solutions, are shown in Table 1. The suspensions were stirred for two hours at room temperature and a solid phase was isolated from these mixtures by centrifugation, washed three times with water and finally dried under vacuum. The color of these dry samples varied from light orange to dark brown as a function of the $NaBiO_3$:HNO_3 ratio (Fig. S1).

Table 1
Experimental parameters for acid-treatment of $NaBiO_3{\cdot}XH_2O$.

Sample	$NaBiO_3$:HNO_3 molar ratio	$[HNO_3]$ (M)	pH of starting HNO_3 solution	pH of suspension
0	1:0	0	–	> 9
1	1:0.1	0.04	1.85	6
2	1:0.5	0.18	1.22	2.7
3	1:1	0.37	0.85	1.31
4	1:2	0.72	0.55	0.75
5	1:4	1.43	0.11	0.31
6	1:8	2.86	< 0	< 0
7	1:16	5.72	< 0	< 0
8	1:31	11.42	< 0	< 0

2.3. Cerium oxidation studies

$NaBiO_3{\cdot}XH_2O$ (100 mg) and acidified $NaBiO_3{\cdot}2H_2O$ were suspended in 1 M HNO_3, 8 mM $Ce(NO_3)_3$ solutions. The molar ratio $NaBiO_3$:$Ce(NO_3)_3$ in these mixtures was 2:1. The oxidation reactions were halted at different time intervals by passing aliquots through 0.45 µm nylon mesh filters, using plastic disposable syringes, into quartz cuvettes of 1 cm path length. UV–Vis spectra of these filtrates were recorded and the intensity of the absorption band at 380 nm was used to quantify the concentration of Ce^{4+} via a calibration previously obtained with $(NH_4)_2Ce(NO_3)_6$ (Fig. S2).

2.4. Characterization methods

Powder X-ray diffraction (PXRD) was performed on a Rigaku Miniflex diffractometer (Cu-Kα radiation, λ = 1.54 Å) from 5° to 60° 2θ in Bragg-Brentano geometry. To perform pair distribution function (PDF) analysis we used a Rigaku Smartlab X-ray diffractometer with Mo-Kα radiation (λ = 0.71 Å) in the 2θ range of 3–158.6° with Bragg-Brentano geometry. A 0.5°/minute data collection time was used to ensure high resolution scattering data. The theoretical Q-range is up to a Q_{max} of 17.49 $Å^{-1}$. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600. Energy dispersive X-ray spectroscopy (EDX) measurements were performed on Quanta 600 scanning electron microscopy (SEM). Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN). X-ray photoelectron spectroscopy (XPS) was performed utilizing PHI 5600 system with Al Kα X-ray source. UV–visible (UV–Vis) spectra were recorded with Thermoscientific Evolution 220 UV–Visible Spectrophotometer. The Ce^{4+} peak was monitored at 380 nm for quantification and to avoid overlap with other species. Initially, the calibration curve was generated with Ce^{4+} concentration ranging from 1 mM to 9 mM, in relevant solution conditions (Fig. S2).

3. Theory

PDF analysis of the X-ray total scattering data is a powerful characterization method to investigate the structural changes at the atomic-level in the solid-state. These measurements require a high Q-range. The Mo X-ray source (λ = 0.71 Å) employed provides a Q_{max} of 17.49 $Å^{-1}$. PDFgetX3 was utilized to process scattering data into the corresponding PDF [16]. The raw scattering curve (*I(Q)*) is normalized to obtain the structure function, *S(Q)*. Next we define the reduced structure function by applying the operation:

$$F(Q) = Q[S(Q)-1]$$

Q is the momentum vector, *S(Q)* is the structure function and *F(Q)* is the reduced structure function. The reduced structure function is used for Fourier transform, which yields the pair distribution function, *G(r)* (PDF). The pair distribution function is defined by

$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ$$

The resulting PDF is the real space representation of the atomic pair separations. The distribution describes the probability of finding an atomic pair separated by a distance r. A PDF of a crystalline material has a long-range order and will continue to high r, whereas only a few peaks are observed at low r in amorphous materials or solutions, due to lack of long-range order. In this study, we describe the transition from crystalline to amorphous material in detail. All simulations shown were created in PDFgui [17].