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Block Copolymer-Assisted Solvothermal Synthesis of Hollow Bi₂MoO₆ Spheres Substituted with Samarium

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Supporting Information

ABSTRACT: Hollow spherical structures of ternary bismuth molybdenum oxide doped with samarium ($\text{Bi}_{2-x}\text{Sm}_x\text{MoO}_6$) were successfully synthesized via development of a Pluronic P123 ($\text{PEO}_{20}\text{-}\text{PPO}_{70}\text{-}\text{PEO}_{20}$)-assisted solvothermal technique. Density functional theory calculations have been performed to improve our understanding of the effects of Sm doping on the electronic band structure, density of states, and band gap of the material. The calculations for $0 \le x \le 0.3$ revealed a considerably flattened conduction band minimum near the Γ point, suggesting that the material can be considered to possess a quasi-direct band gap. In contrast, for x = 0.5, the conduction band minimum is deflected toward the U point, making it a



distinctly indirect band gap material. The effects of a hollow structure as well as Sm substitution on the absorbance and fluorescence properties of the materials produced increased emission intensities at low Sm concentrations (x = 0.1 and 0.3), with x = 0.1 displaying a peak photoluminescence intensity 13.2 times higher than for the undoped bulk sample. Subsequent increases in the Sm concentration resulted in quenching of the emission intensity, indicative of the onset of a quasi-direct-to-indirect electronic band transition. These results indicate that both mesoscale structuring and Sm doping will be promising routes for tuning optoelectronic properties for future applications such as catalysis and photocatalysis.

INTRODUCTION

Hollow structuring is an effective materials engineering approach that can tailor properties for many different energyrelated applications by increasing the surface-to-volume ratio and reducing charge and mass diffusion lengths.¹⁻³ One reason that hollow structures are interesting for the preparation of complex oxides is that the enhanced surface area can provide more oxygen vacancies and defects that may improve the optical properties of the materials.⁴ Hollow-spherical structures have been prepared using various synthetic techniques.^{2,5} In particular, hard and soft templating methods have been demonstrated as effective approaches to successfully synthesizing these hollow structures.⁶ The latter technique (soft templation) is known to have several advantages over the other methods, such as producing porous shell structures that are attractive candidates for encapsulation among other applications. This allows retention of the mesoscale morphology upon removal of the surfactant, as opposed to the hard templation method in which degradation may occur during or after the template etching process.⁷

Bismuth molybdate is a layered perovskite and one of the members of the Aurivillius oxide family that have perovskite-

like and fluorite-like blocks.⁸ Interesting catalytic, dielectric, and luminescence properties make these materials attractive for further studies, especially examination of their fundamental physical and chemical behaviors.⁹⁻¹³ Several studies have been conducted to control the shape and structure of Bi₂MoO₆ for various applications.^{10,14–16} With regard to hollow structuring, cagelike Bi₂MoO₆ hollow spheres have been synthesized using a hard template of colloidal carbon spheres,¹⁷ and a synthesis of hierarchical flower-like Bi2MoO6 hollow spheres was reported using a template-free solvothermal approach.¹⁵ Because of the thermal and chemical stability as well as the ionic radius of Bi³⁺ that is comparable with those of the lanthanide ions, Bi₂MoO₆ can be considered as a proper host for rare earth dopants. Understanding the physical and chemical processes of such lanthanide ion-doped Bi2MoO6 materials is beneficial as the appropriate design can reduce the need for pure (and scarce) rare earth-based materials.¹⁸ In previous studies, the photocatalytic properties of Bi2MoO6 doped with Gd3+, Ho3+, and

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 Yb^{3+} ions¹⁹ and Eu^{3+} ions²⁰ and their corresponding luminescence properties have been reported.

In the study presented here, we report the modulation of optical properties of Bi2-xSmxMoO6 due to both hollow structuring and alloying with samarium. We have developed a self-assembly technique for synthesizing uniform hollow spheres of Bi_2MoO_6 and $Bi_{2-x}Sm_xMoO_6$ (x = 0.1, 0.3, and 0.5) using Pluronic P123 $(EO_{20}PO_{70}EO_{20})$ as a soft templating agent. The copolymer, inorganic precursors, and solvent interactions were found to favor formation of vesicles, resulting in hollow structures that are obtained under specific thermal conditions and at specific polymer concentrations through chemical self-transformation. The results of this study show a pathway for the synthesis of Bi₂MoO₆-based materials with hollow structures and successful incorporation of lanthanide elements (here Sm) and reveal the importance of certain synthesis conditions that need to be controlled to obtain the desired mesostructure. In addition, density functional theory (DFT) calculations were performed to identify the fundamental mechanisms responsible for the behavior of the material in response to Sm substitution, especially changes in the electronic band structure.

EXPERIMENTAL SECTION

Chemicals. Bismuth(III) nitrate pentahydrate [Bi(NO₃)₃·5H₂O, ≥98.0%], phosphomolybdic acid hydrate H₃[P(Mo₃O₁₀)₄]·xH₂O, 1-butanol (anhydrous, 99.8%), and poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) PEO₂₀-PPO₇₀-PEO₂₀ (Pluronic P123) were obtained from Sigma-Aldrich. Concentrated nitric acid (HNO₃, 68–70%) was obtained from J. T. Baker. All chemicals were used as received and used without further purification.

Synthesis of Spherelike Hollow Bi₂MoO₆ Microspheres. For the preparation of the undoped samples, 1 g of nitric acid (HNO₃) was added to 20 g of 1-butanol at 75 °C and the mixture was stirred for 5 min, after which 8 mmol of bismuth(III) nitrate pentahydrate (3.88 g) was dissolved in the solution described above. Then a stoichiometric amount of phosphomolybdic acid hydrate as the Mo source (0.608 g) was slowly added to the mixture to form a transparent yellowish solution. Subsequently, between 1 and 3 g of P123 was added. After being vigorously stirred for ~ 15 min, the suspension was sealed in a Teflon-lined stainless steel autoclave. The autoclave was kept at 160 °C for 3 h and then cooled naturally to room temperature. The precipitate was obtained by centrifugation and sequential washing with ethanol several times and then dried at 80 °C for 6 h. To remove the soft template, the obtained materials were calcined under air at 450 °C for 4 h with a heating/cooling ramp rate of 2 °C/min. For comparison with the hollow Bi2MoO6 spheres, solid Bi2MoO6 powder was prepared as described above but without the addition of P123.

Synthesis of Hollow Bi_{2-x}**Sm**_x**MoO**₆ **Microspheres.** Bi_{2-x}Sm_xMoO₆ (x = 0.1, 0.3, and 0.5) was prepared by a similar procedure, except that additional dopant ions were added to the solution before the addition of P123. For instance, to synthesize the Bi_{1.9}Sm_{0.1}MoO₆, 0.05 mmol of Sm₂O₃ was added to a solution of 20 g of 1-butanol containing previously described amounts of bismuth(III) nitrate and phosphomolybdic acid hydrate. The formation mechanism and crystal structure are depicted in Scheme 1.

Characterization. Powder X-ray diffraction analyses (XRD) were conducted on a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at room temperature. Brunauer–Emmett–Teller (BET) specific surface areas and Barrett–Joyner–Halenda (BJH) pore size distributions were calculated using nitrogen sorption isotherms measured on a Micrometrics ASAP 2010 instrument. Before each measurement, samples were degassed at 120 °C for 7 h to remove the adsorbed species. A Hi-Res TA 2950 thermogravimetric analyzer with an air flow rate of 60 mL/min was used to perform thermogravimetric analysis (TGA) from 25 to 800 °C at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was conducted on a Φ Physical





^{*a*}Bismuth and samarium atoms are labeled with their chemical symbols, while molybdenum and oxygen atoms are colored gray and red, respectively.

Electronics Industries model 590 spectrometer with multipoles, using Al K α radiation (1486.6 eV). A JEOL 2010 FasTEM instrument and an FEI Talos F200X TEM/STEM instrument at an accelerating voltage of 200 kV were employed to perform phase contrast and scanning transmission electron microscopy (STEM) analysis. Field emission scanning electron microscopy (SEM, FEI Nova Nano SEM 450) was performed at an accelerating voltage of 2.0 kV. Diffuse reflectance spectra were recorded using a Shimadzu UV-2450 UV-vis spectrophotometer; for each measurement, 0.2 g of solid sample was diluted in 2 g of BaSO₄. Raman spectroscopy was performed using a Renishaw 2000 Raman microscope at 514 nm. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Magna 560 spectrometer using a TGS detector. A PerkinElmer Optima 7300DV instrument was used to perform inductively coupled plasma optical emission spectroscopy (ICP/OES), where approximately 0.2 g of the sample was removed, homogenized, and placed into a hot block tube. Trace metal grade hydrochloric (3.6 mL) and nitric (1.2 mL) acids were added to each tube, placed in the hot block, and refluxed for 3 h at 95 °C. The samples were then cooled, and their final volumes were increased to 25 mL with deionized water, after which ICP/OES analysis was performed. A Horiba Jobin Yvon SPEX Fluorolog 3-211 spectrofluorometer with a photomultiplier tube near-IR detector was used to measure the spectra of composite KBr/Bi_{2-x}Sm_xMoO₆ pellets. Photoluminescence (PL) spectroscopy measurements were performed



Figure 1. (a) XRD pattern, (b) SEM images, and (c) low-resolution and (d) high-resolution TEM images of homogeneous, hollow Bi_2MoO_6 spheres.



Figure 2. (a) XRD patterns of Bi_2MoO_6 samples synthesized using different copolymer concentrations. SEM images of Bi_2MoO_6 obtained at 160 °C for 3 h using a solvothermal reaction method (b) without P123 [solid $Bi_2MoO_{6'}$ (b, inset) corresponding TEM image], (c) with 1 g of P123, and (d) with 3 g of P123.

using a Fluorolog 3-211 instrument, where an increment of 2 nm was used to record both excitation and emission spectra.

First-Principles Calculations. The computational method used in this study is DFT as implemented in the Vienna Ab Initio Simulation Package (VASP).^{21,22} The total energies of the examined structural

models, E_{DFT} , were calculated with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (XC) functional,²³ while the Brillouin zones of the models were sampled by a Monkhorst–Pack *k*-point mesh²⁴ of $1 \times 1 \times 5$. The basis set used for our calculations includes all the plane waves with kinetic energies of up to 400 eV. Convergence



Figure 3. (a) XRD patterns of $Bi_{2-x}Sm_xMoO_6$ ($0 \le x \le 0.5$) and (b) the corresponding magnified region in the vicinity of (140) and (131) peaks. (c) Simulated XRD patterns of $Bi_{2-x}Sm_xMoO_6$ at different concentrations.

was assumed when the residual forces were smaller than 10^{-2} eV Å⁻¹. For Bi, Mo, Sm, and O, the valence electrons were taken to be $5d^{10}6s^26p^3$, $4s^25s^24p^64d^5$, $5s^26s^25p^65d^1$, and $2s^22p^4$, respectively. Within these formalisms, the calculated band gap of pure Bi₂MoO₆ is $E_g = 2.25$ eV, which is approximately 20–30% smaller than the experimental value of ~2.74 eV. This systematic reduction is well-known within the framework of DFT with semilocal XC functionals like PBE. Other than this, the dispersion of the calculated band structures is expected to be qualitatively accurate while errors in the lattice parameters from our calculations are within 1–2%.

RESULTS AND DISCUSSION

The composition and phase purity of the as-obtained products were characterized by powder XRD. Figure 1a displays the XRD patterns of hollow sphere Bi_2MOO_6 obtained by the solvothermal method after removing the P123 surfactant. All of the Bragg diffraction peaks in the 2θ range of $4-70^\circ$ can be indexed to the pure orthorhombic phase of Bi_2MOO_6 (JCPDS File Card 21-0102). The strong and sharp diffraction peaks in the pattern indicated that the as-obtained product was well crystallized.

According to the TGA of Bi_2MoO_6 before calcination, weight losses of ~4.64, 11.32, and 3.68% were observed in the temperature ranges of 25–150, 150–336, and 336–470 °C, respectively (Figure S1a). The three weight losses can be attributed to the removal of adsorbed water or butanol, decomposition of $Bi(NO_3)_3$, and oxidation of P123, respectively. These trends can be better understood when compared to the decomposition ranges of pristine $Bi(NO_3)_3$ ·SH₂O (mainly 120–200 °C and partially 200–600 °C), H_3 [P-(Mo₃O₁₀)₄]·xH₂O (30–150 °C), and P123 (180–350 °C) as shown in panels b–d of Figure S1, respectively. In addition, FT-IR results further confirmed that P123 was fully removed after calcination at 450 °C (Figure S1e).

The structures of the Bi_2MoO_6 samples were investigated by SEM and TEM (shown in Figure 1b,c), where hollow Bi_2MoO_6 spheres were observed to have a relatively narrow size distribution of ~300–450 nm. In the TEM images, contrast between the dark edge and the brighter center was due to the large void in the center of the hollow spheres. The shell thickness was observed to be in the range of 60–80 nm, as shown in Figure 1c. The corresponding lattice fringes (Figure 1d) demonstrated highly crystallized samples in agreement with the XRD results. The lattice spacing of 0.265 nm agreed well with the (131) spacing of orthorhombic Bi_2MoO_6 . The effects of various synthesis conditions on the structure of Bi_2MoO_6 hollow spheres were examined to develop a comprehensive understanding of the formation mechanisms. Hence, only the main synthesis variables, polymer concentration and solvo-thermal temperature, were adjusted. It was found that the copolymer concentration has a direct effect on the formation of hollow Bi_2MoO_6 .

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The XRD patterns of the samples synthesized at different copolymer concentrations are shown in Figure 2a and indicate a high degree of atomic ordering in the polycrystalline spheres. SEM images demonstrate the resultant mesostructure is dependent on the surfactant concentration (Figure 2b-d). When the synthesis was conducted in the absence of P123 (the solid Bi₂MoO₆ sample), only crystals with irregular shapes were obtained. The sample with a relatively low P123 concentration of 1 g exhibited a solid sphere structure with no hollow structures. As the amount of P123 was increased to 2 g, hollow Bi_2MoO_6 spheres with diameters on the order of 300-400 nm and shell thicknesses of $\sim 60-80$ nm were obtained. Increasing the amount of P123 to 3 g resulted in the formation of the hollow Bi_2MoO_6 spheres with relatively large diameters (1–1.5 μ m) and a slight increase in shell thickness (~100 nm). P123 includes hydrophilic polyoxyethylene (PEO) blocks on each side of a liner hydrophobic polyoxypropylene (PPO) block with a moderate molecular weight ($M_{avg} = 5800$). We propose that as the concentration of P123 exceeds the critical micelle concentration in water/butanol polar solutions, the conditions favor the formation of inverse micelles with dehvdrated PPO blocks in the cores and hydrated PEO portions in the coronas. $^{25-27}$ The reaction conditions favor the arrangement and then coalescence of the inverse micelles into micellar vesicle aggregations. $^{5,28-30}$ It is likely that the outer surfaces of these formed P123 vesicles interact with the metal precursors through hydrogen bonding, resulting in nanoparticle aggregation to form the hollow spherical shells.⁵ The core portion consisting of polymer and anhydrous solvent is removed after calcination, leaving a vacant region inside the shell made of inorganic materials (as depicted in Scheme 1). The formation process is complicated and governed by parameters such as the polymer concentration, temperature, and pH value. For instance, we observed that at pH 5, 7, and 9 no hollow structures were obtained (see Figure S2) as opposed to the pH we have used in hollow structure formation (pH 3).

To reveal the role of the solvothermal temperature in the formation of hollow Bi_2MoO_6 spheres, the autoclave process was performed at 120, 140, 160, and 180 °C for 3 h (see Figure S3). When the temperature was held at 160 °C, well-dispersed hollow spheres were obtained as shown in Figure 1b. The sample prepared at 120 °C included hierarchically structured

Table 1. Measured and DFT-Calculated Band Gaps and Lattice Parameters of the Hollow Microspherical $Bi_{2-x}Sm_xMoO_6$ Samples

summary of band gap energies				lattice parameters						
			calculated			$measured^b$				
sample	measured optical band gap energy ^a (eV)	calculated band gap energy (eV)	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)	crystallite size (nm)	
Bi ₂ MoO ₆	2.74 ± 0.054	2.25	5.60	16.60	5.63	5.51 ± 0.04	16.21 ± 0.13	5.50 ± 0.00	32.8 ± 1.1	
$\mathrm{Bi}_{1.9}\mathrm{Sm}_{0.1}\mathrm{MoO}_6$	2.61 ± 0.031	1.89	5.50	16.67	5.62	5.48 ± 0.01	16.2 ± 0.04	5.51 ± 0.00	27.9 ± 1.3	
$\mathrm{Bi}_{1.7}\mathrm{Sm}_{0.3}\mathrm{MoO}_6$	2.69 ± 0.042	1.94	5.55	15.99	5.48	5.48 ± 0.00	16.25 ± 0.00	5.51 ± 0.00	24.4 ± 2.9	
Bi _{1.5} Sm _{0.5} MoO ₆	2.76 ± 0.077	2.02	5.58	15.92	5.53	5.51 ± 0.00	16.16 ± 0.01	5.48 ± 0.00	18.1 ± 1.1	

^{*a*}For uncertainty analysis, the mean optical band gap and uncertainty were determined using the *x*-intercept of a linear curve fitted to the linear section of the absorbance data. ^{*b*}For uncertainty analysis, the mean crystallite size is obtained by Scherrer analysis of the full width at half-maximum of the following peaks: [020], [131], [002], [260], and [133]. Mean lattice parameters were obtained using Bragg's law for the orthorhombic phase from the following peaks: [020], [111], [131], [002], and [060]. Uncertainty for both unit cell parameters and crystallite size was defined as one standard deviation above and below the mean.



Figure 4. (a) Low-resolution and (b) high-resolution TEM images of Bi_{1.5}Sm_{0.5}MoO₆.



Figure 5. XPS spectra of Bi_{1.7}Sm_{0.3}MoO₆ for the (a) Mo 3d, (b) Bi 4f, (c) Sm 3d, and (d) O 1s peaks.

Table 2. Measured BET Surface Areas, Precursors, and Measured ICP-OES Concentrations of Bi, Sm, and Mo for the Hollow Microspherical Bi_{2-x}Sm_xMoO₆ Samples

		precurso	r concentration (atom %)	measured ICP-OES (atom %)			
sample	BET surface area $(m^2 g^{-1})$	Bi	Sm	Мо	Bi	Sm	Мо	
Bi ₂ MoO ₆	5.46	66.67	-	33.34	75.63	-	24.37	
$\mathrm{Bi}_{1.9}\mathrm{Sm}_{0.1}\mathrm{MoO}_6$	7.09	63.35	3.30	33.34	68.76	2.65	28.59	
Bi _{1.7} Sm _{0.3} MoO ₆	23.59	56.67	10	33.34	61.89	9.32	28.79	
Bi _{1.5} Sm _{0.5} MoO ₆	29.60	50	16.67	33.34	60.66	16.77	22.56	



Figure 6. STEM/EDS chemical map of Bi_{1.7}Sm_{0.3}MoO₆: (a) HAADF, (b) Bi (L-edge), (c) Mo (L-edge), (d) Sm (L-edge), and (e) O (K-edge).

solids that were formed by self-assembly of nanosheets, and hollow microspheres were not observed. Hollow microspheres were also obtained at 140 and 180 °C, but the morphologies were not as homogeneous as at 160 °C. This can be due to a change in the ability of the metal precursors to adsorb to the vesicle surface, altering the final morphology of the nanoparticles.³¹

Effect of Sm Doping on the Structure and Morphology of $Bi_{2-x}Sm_xMoO_6$. XRD patterns of $Bi_{2-x}Sm_xMoO_6$ (x = 0, 0.1, 0.3, and 0.5) are shown in panels a and b of Figure 3. The results can be indexed to the orthorhombic phase of Bi_2MoO_6 with no diffraction peaks associated with Sm_2O_3 , suggesting the formation of a single-phase bismuth samarium molybdate solid solution. The XRD peaks shift slightly toward the larger angles with increasing x because of the changes in the lattice parameter resulting from the smaller ionic radius of Sm³⁺ (0.958 Å) compared to that of Bi^{3+} (1.03 Å).³² The DFTcalculated XRD patterns shown in Figure 3c are in agreement with the experimental results and the calculated Sm-doped structure (Scheme 1b). Crystallite size calculations were performed using the (131) reflection based on the Scherrer broadening method (Table 1) and indicate a reduction in the crystallite size after Sm doping, which was confirmed by TEM (Figure 4). It can be seen that the hollow structure was preserved and the average sphere diameters approached 120160 nm along with a shell thickness of around 10–30 nm. The corresponding lattice fringes shown in the HRTEM image are indicative of the local crystallinity. The lattice *d* spacing of 0.279 nm corresponded to the (002) plane of the orthorhombic phase within 1.5%. The particle sizes of $Bi_{1.9}Sm_{0.1}MoO_6$ and $Bi_{1.7}Sm_{0.3}MoO_6$ were estimated to be 50–100 and 75–120 nm, respectively, shown in the TEM images in panels a and b of Figure S4, respectively.

XPS analysis was performed to study the bonding nature of the Sm ions as shown in Figure 5 for the x = 0.3 sample and indicates substitutional doping of Sm on Bi atomic sites. The binding energy of $Bi^{3+} 4f_{7/2}$ in $Bi_{1,7}Sm_{0,3}MoO_6$ was ~159.35 eV, which was slightly higher than that of undoped Bii2MoO6 [158.79 eV (see Figure S5b)], but within the range of equipment uncertainty (~0.4 eV). The Sm $3d_{5/2}$ peak centered at 1086.09 eV is far from the binding energy reported for samarium oxide, 1083-1084 eV.³³⁻³⁶ The O 1s core level spectrum (Figure 5d) was deconvoluted into four peaks. The small peak at 534.3 eV was related to the OH groups on the surface of the material. The main peak at 531.5 eV can be attributed to the oxygen in $\mbox{Sm}-\mbox{O}$ groups. 34 The binding energy of O 1s decreases from 529.03 to 528.99 eV, which may be due to the Sm doping, but again this is within instrument uncertainty. The obtained XPS results also suggested the possible formation of the Bi-O-Sm bonds in the

 $Bi_{2-x}Sm_xMoO_6$ samples. The XPS survey and high-resolution spectra of the undoped Bi_2MoO_6 sample are shown in Figure S5.

Chemical concentrations of Bi, Sm, and Mo measured by ICP-OES are listed in Table 2 for each sample. The ICP-OES results indicate that the Sm concentrations were 19.8, 0.07, and 0.0% lower than those of the intended stoichiometric values calculated from the amount of the used precursors for x = 0.1, 0.3, and 0.5 samples, respectively. Furthermore, STEM/EDS analysis of the x = 0.3 sample showed a uniform concentration of each element in the material (Figure 6).

The Raman spectra of $Bi_{2-x}Sm_xMoO_6$ (x = 0, 0.1, 0.3, and 0.5) are shown in Figure 7. For Bi_2MoO_6 , which consists of



Figure 7. Raman spectra of the $Bi_{2-x}Sm_xMoO_6$ samples for x = 0, 0.1, 0.3, and 0.5. The inset shows the region between 700 and 900 cm⁻¹.

 $(MoO_4)^{2-}$ with perovskite-like and $(Bi_2O_2)^{2+}$ with fluorite-like layers, six Raman active modes of vibration were detected in the range of 100-850 cm⁻¹. The vibration peak at 146 cm⁻¹ was related to the lattice mode of Bi³⁺ atoms. The Raman modes near 287 cm⁻¹ were attributed to the E_g bending vibrations, while the peaks at 356 and 408 cm⁻¹ corresponded to E_{μ} symmetric bending. The mode at 717 cm⁻¹ was from the asymmetric stretching vibration mode of the MoO₆ octahedra. The A_{1g} mode at 802 cm⁻¹ and the A_{2u} mode at 852 cm⁻¹ were attributed to the symmetric and asymmetric stretching vibrations of the Mo-O bonds in MoO₆ octahedra.^{37,3} Compared with those of pure Bi2MoO6, the Raman spectra of Sm-doped samples have several different features. The most intense band for pure Bi₂MoO₆ appears at ~803 cm⁻¹, which corresponds to the A_{1g} mode. In the case of $Bi_{2-x}Sm_xMoO_{6}$, as the samarium concentration increases, this mode shifts slightly toward higher wavenumbers. This shift can be attributed to the substitution of Bi ions with Sm ions, and the absence of peaks associated with Sm_2O_3 (344 cm⁻¹ for cubic $\text{Sm}_2\text{O}_3^{39}$), in agreement with the observations from the XRD and XPS data. Furthermore, with an increase in the Sm concentration, the Raman peaks became broader and weaker.

In addition, the optical absorption properties of all samples were studied using UV–vis diffuse reflectance spectroscopy. The absorption of the pure (x = 0) and the doped (x = 0.1, 0.3, and 0.5) samples ranges from 200 to ~440 nm, in agreement with the yellowish color of the samples (Figure S7). Weak light absorption was observed for the undoped solid Bi₂MoO₆ sample, whereas improved absorption behaviors were detected for the hollow structured and Sm-doped cases. The sample with

a doping concentration of x = 0.3 exhibited the strongest absorbance. With a further increase in the doping concentration to x = 0.5, the absorbance intensity decreases by 16%, which is still higher than those of x = 0.1 and pure samples. The estimated optical band gap energies (E_g) of the products were determined using the conversion ratio of $E_g = 1240/\lambda$, where λ is the wavelength of the absorption edge obtained by the intercept of a tangential line fitted on the absorption spectra with the wavelength axis. The measured optical and calculated band gaps are listed in Table 1.

It was observed that the optical band gaps of x = 0.1 and 0.3 samples were 0.11 and 0.02 eV lower (slightly), respectively, than the value of 2.77 eV for the pure Bi2MoO6 sample. However, the band gap of the x = 0.5 sample was 0.04 eV higher than that of pure Bi2MoO6, which can be due to experimental variations. The DFT-calculated band gaps showed a trend similar to that observed experimentally, and the calculated band gap for the x = 0.5 sample was higher than those for the x = 0.1 and 0.3 samples. The calculated electronic band structures of pure Bi₂MoO₆ and three doped models with x = 0.1, 0.3, and 0.5 are shown in Figure 8a, showing that Bi₂MoO₆ is an indirect band gap semiconductor with the valence band maximum (VBM) residing at the Γ point while the conduction band minimum (CBM) is slightly deflected from the Γ point toward the X point. Because the lowest conduction band is very flat near the Γ point, Bi₂MoO₆ can be considered a quasi-direct band gap material. This conclusion is essentially applicable for low doping concentrations (x = 0.1and 0.3), while for x = 0.5, the CBM shifts to the U point, making highly alloyed Bi_{2-x}Sm_xMoO₆ a classic indirect band gap material. Overall, the band gap reduction caused by Sm doping is very small. We then attempted to clarify the roles of the dopants by showing in Figure 8b the electronic densities of states (DOS) of pure and doped models. In pure Bi₂MoO₆, the VBM was dominated by the O 2p states while major contributions to the CBM come from the Mo 4d states and, at a lower level, the O 2p states. Contributions from Bioriginated states were negligible. Presumably, this was why the contributions of Sm dopants to the states near the VBM and CBM of the doped models are also very small. Therefore, the small band gap reduction in Bi_{2-x}Sm_xMoO₆ was a consequence of the small lattice deformation rather than a direct contribution from the dopants. At high Sm concentrations (x= 0.3 and 0.5), the lattice deformations may be partly canceled out, leading to the largest band gap reduction at x = 0.1 as revealed in Table 1 and Figure 8.

Photoluminescence (PL) Properties. The room-temperature photoluminescence spectra of solid and hollow spherical Bi_{2-x}Sm_xMoO₆ are shown in Figure 9 using excitation lines of 363 and 466 nm. All of the samples exhibited emission centered around 436 nm (2.8 eV) followed by shoulder peaks at ~410 nm (3.0 eV). At 466 nm excitation, characteristic emission peaks at 564, 601, 611, and 647 nm were assigned to ${}^{6}\text{H}_{5/2}$, ${}^{6}\text{H}_{7/2}$, ${}^{6}\text{H}_{9/2}$, and ${}^{6}\text{H}_{11/2}$ Sm transitions, respectively.⁴⁰ A comparison between the hollow and solid structured samples indicates an enhancement ratio of 5.79 of the peak intensity at 436 nm, likely due to multiple reflections and scattering in the hollow structures.¹ The emission intensities are enhanced at lower Sm contents (x = 0.1 and 0.3), and a further increase in Sm concentration (x = 0.5) resulted in a sharp decrease in emission intensity. The x = 0.1 sample exhibited the highest intensity, 2.28 times higher than that of the undoped hollow structured Bi₂MoO₆ and 13.2 times higher than that of solid



Figure 8. (a) DFT-calculated electronic band structures and (b) corresponding total and orbital angular momentum projected DOS for pure Bi_2MoO_6 and $Bi_{2-x}Sm_xMoO_6$ (x = 0.1, 0.3, and 0.5).

 Bi_2MoO_6 . On the basis of our DFT calculations, this enhancement for the doped samples likely results from a

large number of electronic states introduced near the CBM of $Bi_{1.9}Sm_{0.1}MoO_6$. The complete emission–excitation spectra of



Figure 9. Emission spectra of $Bi_{2-x}Sm_xMoO_6$ with different Sm concentrations (x = 0, 0.1, 0.3, and 0.5) excited at λ_{ex} values of (a) 363 and (b) 466 nm.

hollow Bi₂MoO₆ spheres showed that maximal emissions were obtained under excitation from 360 to 390 nm (Figure S8). Another factor that should be mentioned is the effect of the surface area on the PL properties of the materials. It has been observed that the PL intensity decreases with an increasing surface area,⁴¹ although these effects were found to be small compared to the other parameters.⁴² This trend is in agreement with the BET surface area of the Sm-doped samples reported in Table 2 and the related N_2 adsorption isotherms (Figure S9). The relative PL intensities for samples with different mean particle sizes are shown in Figure S10 and indicate a lack of correlation between size and peak intensity in our samples. We note it is likely that resonant effects will occur at optimal sizes in these materials, further increasing peak emission intensity, and should be addressed in future work through thorough parametric analysis.

SUMMARY AND CONCLUSIONS

A solvothermal synthesis method involving soft templation by P123 has been demonstrated for the production of hollow spherical structures of $Bi_{2-x}Sm_xMoO_6$ with $0 \le x \le 0.5$. The optical and photoluminescence properties of the hollow structured samples compared to those of the solid sample are remarkably enhanced, with a 1 order of magnitude improvement in the fluorescence intensity for hollow Bi19Sm01MoO6 microspheres compared to that of solid Bi2MoO6. An experimental procedure supported by DFT calculations was used to study the changes in the electronic structure due to the doping, and the results indicate the transition from a quasidirect electronic band gap at a low Sm concentration to an indirect band gap at a high Sm concentration is responsible for fluorescence quenching in the x = 0.5 sample. The results of this investigation have potential applications in the modifications of bismuth molybdate-based materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.6b02854.

TGA analysis of Bi_2MoO_6 samples before calcination, FTIR spectra of hollow Bi_2MoO_6 after the removal of P123, XRD patterns and SEM images of Bi_2MoO_6 samples obtained after removal of P123 at different calcination temperatures, survey and high-resolution XPS of hollow Bi_2MoO_6 , UV–vis absorption spectra of hollow $Bi_{2-x}Sm_xMoO_6$, and an emission-excitation map of hollow Bi_2MoO_6 microspheres (PDF)

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Notes

The authors declare no competing financial interest.

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