# Photophysical and Photocatalytic Properties of Ca<sub>1-x</sub>Bi<sub>x</sub>V<sub>x</sub>Mo<sub>1-x</sub>O<sub>4</sub> Solid Solutions

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New solid solutions with the composition of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  prepared by a solid-state method were found as novel photocatalysts with enhanced activity for O<sub>2</sub> evolution from aqueous solutions containing sacrificial regent AgNO<sub>3</sub> under visible-light irradiation (>420 nm). The obtained solid solutions crystallized in tetragonal crystal structures, except one of the end compounds, BiVO<sub>4</sub>, which crystallized in monoclinic structures. The diffuse reflection spectra of the solid solutions shift monotonically to a long wavelength as the ratio of Bi (V) ions to Ca (Mo) ions increases in the solid solution. The band structure and the dependence of the photocatalytic properties were discussed in relation to the solid-solution compositions and photophysical properties.

#### Introduction

Since the discovery of water splitting on TiO<sub>2</sub> electrodes,<sup>1</sup> heterogeneous photocatalysis based on a semiconductor has attracted extensive interest, because of the potential application in conversion of photon energy into chemical energy and purifying environmental pollutions.<sup>2-5</sup> Many oxides, such as TiO<sub>2</sub><sup>1</sup> and SrTiO<sub>3</sub>,<sup>6</sup> have been reported as active photocatalysts for water splitting under UV-light irradiation. However, these catalysts are limited to UV light, which accounts for only a small fraction (5%) of the solar spectrum. Therefore, development of highly efficient photocatalysts with visible-light response has currently become one of the most important topics in photocatalytic research. The strategy for the design of a novel visible-light photocatalyst can be classified in several ways, among which making a solid solution between semiconductor photocatalysts with wide and narrow band gaps is thought as one efficient method to find new photocatalysts with visiblelight response. Several compounds prepared on the basis of this strategy, such as Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>-Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>,<sup>7</sup> AgInS<sub>2</sub>-ZnS,<sup>8</sup> and SnO<sub>2</sub>-TiO<sub>2</sub>,<sup>9</sup> have been reported as active photocatalysts for water splitting or organic pollution cleaning. While in contrast to those reported visible-light-driven photocatalysts prepared by doping active UV photocatalysts with transited metal ions, the number of active solid-solution photocatalysts is still limited. Further development of new active solid-solution photocatalysts with visible-light response is of great interest.

Recently, some Mo metal oxides, such as  $Bi_2MOO_6^{10}$  and  $(Na_{0.5}Bi_{0.5})MoO_4$ ,<sup>11</sup> have been reported as efficient photocatalysts for  $O_2$  evolution, suggesting the possibility to develop new active photocatalysts containing Mo and Bi ions. Scheelite structures were known as one type of interesting crystal structures for photocatalysts. A few oxides crystallizing in this structure have been reported as active photocatalysts for  $O_2$  evolution or  $H_2$  evolution from aqueous solutions containing sacrificial reagents.<sup>11,12</sup> CaMoO<sub>4</sub> is an important one among the metal molybadate family with a scheelite crystal structure that

has a wide application potential in various fields, such as in microwave application and photoluminescence. The divalent metals in scheelite-type molybates are easily soluble with other elements, which result in a rich family of solid-solution compounds. These facts have motivated us to make new scheelite solid-solution photocatalysts by combining CaMoO<sub>4</sub> with one Bi metal oxide crystallizing in similar crystal structures. Scheelite BiVO<sub>4</sub> was selected as one of the candidates, because of the well-known high activity for O<sub>2</sub> evolution from aqueous silver nitrate solution under visible-light irradiation ( $\lambda > 420$ nm).<sup>12</sup> Oxides in the Bi-Mo-V-O family have been examined extensively before. A narrow stability region for the solidsolution series  $Bi_{1-x/3}Mo_xV_{1-x}O_4$ , where  $0 \le x \le 0.55$  was reported with the partial absence of Bi at the A site of the ABO<sub>4</sub> type oxides.<sup>13</sup> After examining the effect of various cations doping on the crystal structure of scheelite BiVO<sub>4</sub>, Hoffart et al. pointed out that higher-valent cations doping at B sites can stabilize the BO<sub>4</sub> tetrahedra, whereas higher-valent cations doping at A sites may destabilize the rigid BO<sub>4</sub> coordination and reduce the strength of the B–O bonds.<sup>14</sup> Recently, Ramanan et al. attempted to incorporate Na and Mo into the A and B sites of the ABO<sub>4</sub> type oxides BiVO<sub>4</sub>, respectively, and finally observed the formation of a continuous solid solution for the series  $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$  ( $0 \le x \le 1$ ).<sup>15</sup> In this paper, we report the preparation and characterization of a novel active visible-light-driven photocatalyst based on solid-solution series  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  (x = 0-1). The relationship of the photophysical and photocatalytic properties together with the solidsolution compositions is discussed.

#### **Experimental Section**

**Preparation of Photocatalysts.** Powders of  $Ca_{1-x}Bi_xV_x$ -Mo<sub>1-x</sub>O<sub>4</sub> with x = 0, 0.3, 0.5, 0.7, 0.8, 0.9, and 1 were prepared by a solid-state reaction process. CaCO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and MoO<sub>3</sub> were selected as starting metal sources. Stoichiometric mixtures of the starting materials were ground and mixed thoroughly in an agate mortar. The well-mixed powders were preheated at 600 °C for 5 h and then calcined in the temperature range 650-850 °C for 2-5 h after being vigorously reground in a mortar.

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Characterization. The crystal structures of the prepared samples were determined by the X-ray diffraction pattern (JEOL JDX-3500 Tokyo, Japan). UV-vis diffuse reflectance spectra were recorded on a UV-vis spectrometer (UV-2500, Shimadzu) and were converted from reflection to absorbance by the standard Kubelka-Munk method. The specific surface areas of the prepared solid solutions, which were all nearly about 1  $m^2/g$ , were measured by the conventional Brunauer-Emmett-Teller (BET) method (Gemini 2360, Shimadzu). Raman spectrum measurements for the powders were performed using a laser Raman spectrophotometer (Jasco NRS-1000) at room temperature. The photocatalytic  $O_2$  evolution from an aqueous silver nitrate solution was recorded in a closed gas circulation system with a side window Pyrex cell. The light source was a new 300 W Xe arc lamp attached with cutoff filters, the intensity of which was given in Figure 10. The photocatalyst powder (0.5 g) was dispersed in a 270 mL aqueous solution under constant magnetic stirring with 0.85 g of AgNO<sub>3</sub> as an electron scavenger. The evolved O<sub>2</sub> gas was determined by a thermal conductivity detector (TCD) gas chromatograph (Shimadzu GC-8A), which was connected to the system with a circulating line. The apparent quantum yield, the ratio of number of reacted electrons to the number of incident photons, was measured using interference band-pass filters (MIF-W. Kenko).

**Band Structure Calculation.** Castep,<sup>16</sup> an ab initio total energy program, was used for solving the band structure of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions. The calculation was also carried out for BiVO<sub>4</sub> and CaMoO<sub>4</sub> with a monoclinic and a tetragonal scheelite structure, respectively, to obtain more information on the electronic and band structure of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions. All calculations were carried out using the generalized gradient approximation (GGA) with gradient corrected functional PBE.<sup>17</sup> Ultrasoft psudopotentials were applied with a plane wave cutoff energy of 300 eV. The valence electronic configurations for Ca, Bi, V, Mo, and O were  $3s^23p^64s^2$ ,  $6s^26p^3$ ,  $3s^23p^63d^34s^2$ ,  $4s^24p^64d^55s^1$ , and  $2s^22p$ ,<sup>4</sup> respectively.

## **Results and Discussion**

Structural Analysis. X-ray powder diffraction patterns of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions are shown in Figure 1. Consistent with previous reports, the two end compounds of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions, CaMoO<sub>4</sub> and BiVO<sub>4</sub>, are well crystallized with the tetragonal and monoclinic crystal structure, respectively.<sup>18,19</sup> The other  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions are basically single phase with a tetragonal crystal structure except for a small mount of Bi2O3 impurity when calcined at 650 °C, as indicated in Figure 1 for  $x = 0.7 \sim 0.9$ . The content of the impurity in the prepared  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$ solid solutions, which can be evaluated by comparing the area of the strongest peaks of the impurity with that of the solid solutions, is very small. Such a small quantity of the impurity phase could not significantly modify the photophysical and photocatalytic properties of the Ca<sub>1-x</sub>Bi<sub>x</sub>V<sub>x</sub>Mo<sub>1-x</sub>O<sub>4</sub> solid solutions. Further experiments show that the intensity of the impurity peaks decrease with the increasing heat-treatment temperatures and the phase-pure  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions can be obtained when calcined at 700 °C or higher temperature. The needed annealing temperatures for producing the phase-pure solid solutions were strongly dependent on the composition of the solid solutions. For example, calcined at 700 °C is sufficient for preparing Ca<sub>0.1</sub>Bi<sub>0.9</sub>V<sub>0.9</sub>Mo<sub>0.1</sub>O<sub>4</sub> solid solutions, whereas phase-pure Ca<sub>0.7</sub>Bi<sub>0.3</sub>V<sub>0.3</sub>Mo<sub>0.7</sub>O<sub>4</sub> solid solution can only be obtained when the annealing temperature increases to 850 °C.



**Figure 1.** (a) XRD patterns of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  (x = 0-1) solid solutions heat treated at 600 °C for 5 h and then calcined at 650-850 °C for 2 h; (b) the enlarged part of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  XRD patterns ranging from  $2\theta = 30-36^\circ$ .

However the photocatalytic activities of the solid solutions were found to be drastically decreased with the increase of the sintered temperature of the catalysts. For example, although the XRD patterns and Raman spectra of the Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>4</sub> solid solution show no significant difference when the annealing temperature increases from 650 to 800 °C, the rate of O2 evolution from the aqueous AgNO<sub>3</sub> solution with Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>- $Mo_{0.2}O_4$  photocatalyst under visible-light irradiation (>420 nm) decreased from 100.7 to 57 µmol/h (Supporting Information Figures S1–S3). Similar results have been found on many other photocatalysts containing Bi, V, and Mo ions, which were attributed to the easily volatilized Bi, V, and Mo oxides at high temperature, resulting in many defections (working as recombination sites for photogenerated charges and holes) formed in the sample and then a decrease of the activity of the photocatalysts. Furthermore, the decrease of the activities can also be attributed to the changes in the crystal structure of the photocatalyst or the decrease in the surface area at higher temperatures. In the rest of this paper, the photocatalytic properties of the solid solutions were mainly carried out by using the  $Ca_{1-r}Bi_rV_rMo_{1-r}O_4$  solid solutions prepared by being pretreated at 600 °C for 5 h and then by being calcined at 650 °C for 2 h as the model photocatalysts.

To show it clearly, the enlarged parts of the XRD patterns for the obtained pure solid-solution series calcined at 800 °C or higher temperatures were displayed in Figure 1b from 30° to 36°. It is noteworthy that the 004 and 200 diffraction peaks of the prepared solid solutions have a clearly a monotonically blue and red shift, respectively, with the increase of Bi (V) content in the solid solutions. The observed peak shifts in the XRD patterns were assumed to be caused by the different ion radii of Ca<sup>2+</sup> (0.1 nm), Bi<sup>3+</sup> (0.103 nm), V<sup>5+</sup> (0.036 nm), and Mo<sup>6+</sup> (0.041 nm) in the solid solutions, which can slightly modify the crystal structure or distortion of the metal-oxide

TABLE 1: Lattice Parameters and Photocatalytic Activities of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  (x = 0-1) Solid Solutions

compounds	crystal structure	space group	lattice params (nm)	cell vol (nm <sup>3</sup> )	band gap (eV)	<sup>b</sup> rate of O <sub>2</sub> evolution (μmol/h)
<sup>a</sup> BiVO <sub>4</sub>	monoclinic	I 112/b	a = 0.5197 b = 0.5096 c = 1.1702 $\beta = 90.4$	0.3099	2.34	33.8
$Ca_{0.1}Bi_{0.9}V_{0.9}Mo_{0.1}O_4$	tetragonal	I 4 <sub>1</sub> /a	a = 0.51432(8) c = 1.1673(3)	0.3088(1)	2.37	78.9
$Ca_{0.2}Bi_{0.8}V_{0.8}Mo_{0.2}O_4$	tetragonal	I 4 <sub>1</sub> /a	a = 0.5155(3) c = 1.165(1)	0.3098(4)	2.38	100.7
$Ca_{0.3}Bi_{0.7}V_{0.7}Mo_{0.3}O_4$	tetragonal	I 4 <sub>1</sub> /a	a = 0.5160(3) c = 1.165(1)	0.3104(3)	2.42	121.4
$Ca_{0.5}Bi_{0.5}V_{0.5}Mo_{0.5}O_4$	tetragonal	I 4 <sub>1</sub> /a	a = 0.5206(5) c = 1.145(1)	0.3109(6)	2.51	82.2
$Ca_{0.7}Bi_{0.3}V_{0.3}Mo_{0.7}O_4$	tetragonal	I 4 <sub>1</sub> /a	a = 0.5223(1) c = 1.1423(7)	0.3116(1)	2.7	79.2
<sup>a</sup> CaMoO <sub>4</sub>	tetragonal	I 4 <sub>1</sub> /a	a = 0.52235 c = 1.14298	0.3118	3.64	

<sup>*a*</sup> The lattice parameters of BiVO<sub>4</sub> and CaMoO<sub>4</sub> are taken from ICSD #33243 and ICSD #62219, respectively. <sup>*b*</sup> The photocatalytic O<sub>2</sub> evolution from aqueous AgNO<sub>3</sub> solutions was detected under visible-light irradiation (>420 nm).



**Figure 2.** Diffuse reflectance spectra of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  (x = 0-1) solid solutions.

polyhedrons.<sup>20</sup> The lattice parameters of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions were refined by the least-squares method. As represented in Table 1, in good agreement with the observed peak shift in the XRD patterns, the lattice parameter (a) decreases while the lattice parameter (c) increases monotonically with the increasing value of *x* in the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions. The obtained regular shift of the XRD peaks and the changes of the lattice parameters indicate the prepared powders should be a solid solutions rather than a mixture of BiVO<sub>4</sub> and CaMoO<sub>4</sub>.

UV-Visible Diffuse Reflectance Spectra of  $Ca_{1-x}Bi_xV_x$ -Mo<sub>1-x</sub>O<sub>4</sub> Solid Solutions. The photoabsorption abilities of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions were examined by the UVvis diffuse reflectance spectra. As shown in Figure 2, the UVvisible absorption spectra of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions possessed steep edges in the profile, indicating that the visible-light response of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions is not caused by impurity donor levels but by a directed energy band gap from the valence band to the conduction band. The band gaps of CaMoO<sub>4</sub> and BiVO<sub>4</sub> were estimated to be 3.64 and 2.34 eV from the onsets of the absorption, respectively, which are rationally in accordance with previous reports.<sup>12a,21</sup> The absorption edges of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions



**Figure 3.** Raman spectra of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions.

were notably located in a position between those of CaMoO<sub>4</sub> and BiVO<sub>4</sub>, and the absorption spectra were red-shifted monotonically as the value of *x* increased, indicating that the obtained powders were solid solutions rather than simple mixtures of BiVO<sub>4</sub> and CaMoO<sub>4</sub>. The band gaps of the Ca<sub>1-x</sub>Bi<sub>x</sub>V<sub>x</sub>Mo<sub>1-x</sub>O<sub>4</sub> solid solutions were estimated to be 2.37-2.7 eV from the onsets of the absorption edges, when *x* decreased from 0.9 to 0.3, as shown in Table 1.

**Raman Spectra of Ca**<sub>1-x</sub>**Bi**<sub>x</sub>**V**<sub>x</sub>**Mo**<sub>1-x</sub>**O**<sub>4</sub> **Solid Solutions.** As shown in Figure 3, Raman spectra of the prepared solid solutions were similar, and all showed three characteristic vibrational features below 1000 cm<sup>-1</sup> similar to that of other tetrahedral metal oxides.<sup>22</sup> Raman spectra of scheelite structure crystals have been examined extensively before. It has been established that in scheelite ABO<sub>4</sub> (A = Ca, Sr, Bi; B = W, Mo, V) crystals, four oxygen atoms are in tetrahedral coordination around a B atom thus forming rather tightly bound molecular BO<sub>4</sub> anions, which bonded to the metal A cations in the lattice via relatively weak long-range ionic forces. As a result of this difference, modes within the BO<sub>4</sub> anions are greater than those of external modes corresponding to vibrations between lattice ions (pure lattice modes). In other words, the Raman



Figure 4. Energy band structures and DOS for (a)  $CaMoO_4$  and (b)  $BiVO_4$ ; density contour maps of the LUMO and HOMO for  $CaMoO_4$  (c) and  $BiVO_4$  (d).

spectrum of the scheelite ABO<sub>4</sub> structure crystals mainly reflect the structure of the BO4 tetrahedrons in the scheelite crystals.<sup>23</sup> As to the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions, the disordered distribution of V and Mo at the B-sites of the scheelite structure is expected to be similar to that found in the  $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$  series. For the typical solid solution  $Ca_{0.1}Bi_{0.9}V_{0.9}Mo_{0.1}O_4$ , the intense bands ~882 and ~815 cm<sup>-1</sup> are assigned to the internal vibrational modes of the MO<sub>4</sub> tetrahedra for the symmetrical  $v_1$  and antisymmetrical  $v_3$ stretching motions. The peaks at lower wavenumbers ( $\sim$ 340 and  $\sim$ 375 cm<sup>-1</sup>) are for the symmetrical and antisymmetrical bending motions, corresponding to the  $\nu_2$  and  $\nu_4$  frequencies.<sup>23e</sup> In the very low frequency domain, the obtained lines are due to lattice modes. While it is noteworthy that the symmetrical and antisymmetrical stretching motions,  $v_1$  and  $v_3$ , slightly shift with the increasing content of Ca (Mo) ions in the solid solutions, for Ca<sub>0.7</sub>Bi<sub>0.3</sub>V<sub>0.3</sub>Mo<sub>0.7</sub>O<sub>4</sub> solid solution, the symmetrical and antisymmetrical stretching motions were detected at 876 and 822 cm<sup>-1</sup>, respectively, suggesting the crystal structure changes with the increasing content of Ca and Mo ions in the solid solutions, which is consistent with the XRD patterns and UV-visible absorption spectra of the solid solutions.

**DFT Electronic Structure Calculation.** Figure 4a,b shows the band dispersion relation and the densities of states (DOS) for scheelite tetragonal CaMoO<sub>4</sub> and monoclinic BiVO<sub>4</sub>. The density contour maps for the lowest unoccupied band (LUMO) and the highest occupied band (HOMO) of CaMoO<sub>4</sub> and BiVO<sub>4</sub> are shown in Figure 4c and 4d, respectively. The valence band maxima and conduction band minima of CaMoO<sub>4</sub> and BiVO<sub>4</sub>

are located at the G point and Z-V regions, respectively, suggesting both of the two compounds should be direct-gap materials. The HOMO and LUMO of CaMoO<sub>4</sub> are composed mainly of O 2p and Mo 4d orbitals, respectively, as shown in Figure 4c. Mo and V ions are known to be tetragonally coordinated in the scheelite structural  $CaMoO_4$  and  $BiVO_4$ compounds. For a metal in tetragonal symmetry, the metal d orbitials can be split into two parts, t2g and eg states, because of the crystal field effect. As shown in Figure 4a, the lower part of the conduction band of CaMoO<sub>4</sub>, which is composed primarily of eg states associated with the Mo 4d, is separated by approximately 0.75 eV from the upper part of the conduction band formed from the Mo  $t_{2g}\xspace$  states and 3d states of Ca. It was reported from another calculation by using the LAPW technique with the WIEN97 code that the Ca 3d states contribute to a high density of states 3~4 eV above the bottom of the conduction bands.<sup>24</sup> These results were in good agreement with our results obtained by using the Castep program. In the case of monoclinic BiVO<sub>4</sub>, the HOMO is composed mainly of Bi 6s and O 2p as shown in Figure 4d. The contribution of the Bi 6s to the HOMO band was calculated as 10% by using the projected weights of wave functions at the valence band top. On the other hand, the conduction band of monoclinic BiVO<sub>4</sub> ranges from 1.5 to 7.4 eV. The upper conduction band in the range of 5-7.4 eV is mainly composed of Bi 6p and O 2p. However, the band below 5 eV is mainly composed of V 3d orbitals, where the contributions of Bi and O are very small. The V 3d orbitals are also found divided into two peaks in the range of 1.5-3.5 eV and of 3.5-5 eV as a result of the crystal field splitting in the tetragonal VO<sub>4</sub> environment (Figure 4b).



**Figure 5.** Structural models for (a) CaMoO<sub>4</sub> and (b–d) Ca<sub>0.75</sub>Bi<sub>0.25</sub>V<sub>0.25</sub>-Mo<sub>0.75</sub>O<sub>4</sub> solid solutions. In model b, Bi atoms located at the nearest neighbor's sites of V ions. In models c and d, Bi atoms locate at the lattice plane of the supercell and gradually far from the V ions. Models b–d preserve *P*1 symmetry.

To further explore the band structures of the solid solutions, the electronic structure of one solid solution Ca<sub>0.75</sub>-Bi<sub>0.25</sub>V<sub>0.25</sub>Mo<sub>0.75</sub>O<sub>4</sub> was calculated as a typical result. The model<sup>25</sup> consisted of four (CaMoO<sub>4</sub>) units as a supercell with the center Mo atom substituted by the V atoms as shown in Figure 5. The stoichiometry of the superlattice cell is Ca<sub>0.75</sub>- $Bi_{0.25}V_{0.25}Mo_{0.75}O_4$ , which falls within the range of the x = 0-1in the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions. As shown in Figure 5, this supercell consisted of three distinct sites for Bi atoms when compared with that of the substituted V atom. To test the validity of the calculation results, geometry optimization of these models was carried out to minimize the system energy. Model b gave the lowest total energy of -17990.326 eV, and relative energies measured from model b were 0.919 and 1.025 eV lower than that from model c and model d, respectively. Therefore, the optimized model b was selected as the stable structure of the solid solution for the further band structure calculations.

The calculated band structure and DOS of  $Ca_{0.75}Bi_{0.25}V_{0.25}$ -Mo<sub>0.75</sub>O<sub>4</sub> solid solutions are shown in Figure 6. The valence band contained two parts, the lower one is composed of the O 2p, V 3d, and Mo 4d orbitals; however, the upper part is composed primarily of O 2p (together with a little contribution of Bi 6s) orbitals. The HOMO (No. 48) is made up primarily of O 2p as shown in Figure 6. On the other hand, the conduction band is rather broad. The lower part in the range of 2.7-6.36eV is mainly composed of V 3d and Mo 4d orbitals (No. 49 to No. 70) (together with a little contribution of Bi 6p and O 2p orbitals), which are divided into two peaks in the range of 2.7-4.3 eV and 4.3-6.36 eV for the crystal field splitting in the tetragonal environment. Similar to that of CaMoO<sub>4</sub> compounds,<sup>24</sup> an unoccupied band caused by Ca 3d orbitals that contribute to a high density of states then appears at the higher energy side in the conduction band. It is known that a wide density-of-states distribution in the conduction band is helpful for the mobility of the excited electrons, which is related to a better photocatalytic performance. The photophysical properties and DFT calculations indicate the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions to be new photocatalysts with visible-light response.

Band Structure Model of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  Solid Solutions. With all taken into consideration, a possible band structure model of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions can be illustrated schematically as shown in Figure 7. For the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions, the valence band should be composed of hybrid orbitals of Bi 6s and O 2p similar to that of BiVO<sub>4</sub>, and the contribution of Bi 6s orbitals to the valence band may increase with the increasing content of Bi ions in the solid solution. On the other hand, the V 3d orbitals mixed with Mo 4d orbitals contributed to forming the bottom of the conduction band, and the lowest unoccupied band (LUMO) should be composed of hybrid orbitals of V 3d and Mo 4d as suggested by the DFT calculated results (Figure 6). In accordance with the continuous shifts in the UV-vis absorption spectra (as shown in Figure 2), the valence and conduction band levels of the solid solutions should be located between those of CaMoO<sub>4</sub> and BiVO<sub>4</sub>, and band levels could be shifted with the change in the ratio of Ca and Mo ions to that of Bi and V ions. These results indicated that the band structure of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions could be easily controlled by changing the ratio of the starting metal oxides, suggesting that the band-engineering method is one of the promising methods for designing novel photocatalysts with visible response.



Figure 6. Energy band structures, DOS, and density contour maps of the LUMO and HOMO for Ca<sub>0.75</sub>Bi<sub>0.25</sub>V<sub>0.25</sub>Mo<sub>0.75</sub>O<sub>4</sub>.



Figure 7. Band structure of  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solution,  $CaMoO_4$ , and  $BiVO_4$ .



**Figure 8.** Formation rates of O<sub>2</sub> evolution from an aqueous AgNO<sub>3</sub> solution with Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>4</sub> and BiVO<sub>4</sub> photocatalysts under visible-light irradiation ( $\lambda > 420$  nm) (catalyst, 0.5 g; AgNO<sub>3</sub>, 0.85 g).

Photocatalytic Reactions. The formation rates of O<sub>2</sub> from an aqueous silver solution under visible-light irradiation ( $\lambda >$ 420 nm) with  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid-solution photocatalysts were examined. Figure 8 shows a typical reaction time course of O2 evolution over Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O4 photocatalysts. The activity for O<sub>2</sub> evolution over the monoclinic BiVO<sub>4</sub> photocatalyst prepared with similar conditions was given for a comparison. The initial rate of the O<sub>2</sub> evolution was 100.7 and 33.8 µmol/h for Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>4</sub> and BiVO<sub>4</sub> catalysts, respectively, under the present condition. The apparent quantum yield at  $\lambda = 420.4$  nm was measured to be  $\sim 10\%$  and  $\sim 2.7\%$ for  $Ca_{0.2}Bi_{0.8}V_{0.8}Mo_{0.2}O_4$  and  $BiVO_4$ , respectively, by using an interference band-pass filter ( $\lambda_0 = 420.4$  nm,  $T_{\text{max}} = 44.8\%$ ,  $\Delta\lambda/2 = 14.7$  nm) together with a water filter. It is notable that the rate of  $O_2$  evolution decreases with the reaction time (as shown in Figure 8). After 5 h of reaction time, the O<sub>2</sub> evolved rate decreased remarkably. This phenomenon can be attributed to the metallic silver formed by the reduction reaction, which was deposited on the surface of the catalysts and shielded the catalysts from the incident light. Therefore, the initial rate of the  $O_2$  evolution was selected as the activity of the reaction. The crystal structure of the photocatalyst was examined again after photocatalytic O<sub>2</sub> evolution. Figure 9 shows the XRD patterns of Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>4</sub> solid solutions before and after the photocatalytic O<sub>2</sub> evolution. It can be seen that the XRD patterns of the Ca<sub>0.2</sub>Bi<sub>0.8</sub>V<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>4</sub> solid solutions did not change except that several new metallic Ag peaks (marked by the arrows) appear, suggesting that the solid-solution crystals are stable for the O<sub>2</sub> evolution reaction. The photocatalytic



Figure 9. XRD patterns of  $Ca_{0.2}Bi_{0.8}V_{0.8}Mo_{0.2}O_4$  solid solutions before and after the photocatalytic  $O_2$  evolution. The arrow marks indicate the peaks of the metallic Ag, which was photodeposited on the surface of the solid solution from the AgNO<sub>3</sub> solution.



**Figure 10.** Wavelength dependence of  $O_2$  evolution on the cutoff wavelength of incident light, and UV–vis diffuse reflectance spectrum of  $Ca_{0.5}Bi_{0.5}V_{0.5}M_{0.5}O_4$  solid solutions. The insert shows the wavelength dependence of light intensity with different cutoff filters (catalyst, 0.5 g; AgNO<sub>3</sub>, 0.85 g; 270 mL of H<sub>2</sub>O).

process for H<sub>2</sub> evolution in aqueous CH<sub>3</sub>OH solution with Pt cocatalyst was also attempted. However no H<sub>2</sub> evolution was detected after 10 h of work with constant visible-light irradiation. These results indicate that the potential of the top of the valence band for the solid solutions, which is composed primarily of O 2p, should be more positive than the redox potential of  $O_2/H_2O$ (1.23 V vs SHE, pH = 0). But for the bottom of the conduction band, which mainly contained V 3d and Mo 4d orbitals, the potential should not be enough for the H<sub>2</sub> evolution by H<sub>2</sub>O reduction. Therefore the solid-solution photocatalysts cannot be used for water splitting under visible-light irradiation. Similar results have been obtained for BiVO4 and Bi2MoO6 photocatalysts, whose conduction bands were mainly composed of V 3d and Mo 4d, respectively. Although they all have high activities for O<sub>2</sub> evolution in AgNO<sub>3</sub> or FeCl<sub>3</sub> solution under visiblelight irradiation,<sup>10,12</sup> neither of them are suitable for pure water splitting.

The wavelength dependence of the rate of  $O_2$  evolution from aqueous AgNO<sub>3</sub> solution with  $Ca_{0.5}Bi_{0.5}V_{0.5}Mo_{0.5}O_4$  photocatalysts was investigated by using different cutoff filters, as shown in Figure 10. The rates were determined in the early stages of the reaction (first 1–2 h). The intensity variation of the incident light with different cutoff filters is given as an insert figure for reference. It is notable that the rates of  $O_2$  evolution decreased with increasing cutoff wavelength, which is in good agreement with the UV–vis diffuse reflectance spectra of  $Ca_{0.5}Bi_{0.5}V_{0.5}$ -



**Figure 11.** Composition dependence of the  $O_2$  evolved rate over  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions under visible-light irradiation (>420 nm).

 $Mo_{0.5}O_4$  solid solutions, indicating the present reaction is driven by a visible-light absorption. The light-irradiation dependence of the reaction for  $O_2$  evolutions was examined. No additional  $O_2$  evolution was detected when the Xe lamp was turned off, also suggesting the  $O_2$  evolution on the solid solutions should be driven by the visible-light irradiation. It is reliable to conclude that the  $O_2$  evolution from aqueous AgNO<sub>3</sub> solution over the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid-solution compounds is a photocatalytic reaction.

The composition dependence of the photocatalytic activities for O<sub>2</sub> evolution on the solid solutions was detected. As shown in Figure 11, the prepared solid solutions all exhibited activities for O2 evolution from aqueous AgNO3 solutions under visiblelight irradiation, suggesting the potential of the valence band of the solid solution should be more positive than the oxidation potential of H<sub>2</sub>O to form O<sub>2</sub>. The two end compounds of the solid solutions, BiVO4 and CaMoO4 synthesized under similar conditions, showed lower activities for O2 evolution under visible-light irradiation. The CaMoO4 did not show activities for O<sub>2</sub> evolution under visible-light irradiation, because of the large band gap (3.64 eV). The activity for  $O_2$  evolution over the monoclinic BiVO<sub>4</sub> photocatalyst prepared by the solid-state method is about 33.8 µmol/h, which is consistent with that reported by other groups.<sup>12</sup> In contrast,  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions showed higher photocatalytic activities for O2 evolution under visible-light irradiation. Photocatalytic activities of BiVO<sub>4</sub> powders that had been reported strongly depended on the crystalline phase. The scheelite monoclinic structural BiVO<sub>4</sub> crystals exhibit a high activity for O<sub>2</sub> evolution from aqueous AgNO<sub>3</sub> solution under visible-light irradiation, whereas the photocatalytic activities of the tetragonal sheelite and zircon structural BiVO<sub>4</sub> for O<sub>2</sub> evolution were reported negligible under visible-light irradiation,<sup>12</sup> indicating that the observed higher photocatalytic activities of the prepared Ca<sub>1-x</sub>Bi<sub>x</sub>V<sub>x</sub>Mo<sub>1-x</sub>O<sub>4</sub> solid solutions cannot be attributed to the generated tetragonal BiVO<sub>4</sub> impurities if there are any present in the solid solutions. The rates of O<sub>2</sub> evolution over the solid-solution photocatalysts are listed in Table 1. It is noteworthy that all the solid solutions show high activities for O2 evolution, which are nearly 2-fold higher than that of BiVO<sub>4</sub>, even when the ratio of Bi ions to the solid solution decreases to 0.3. The highest activities were obtained for the solid solutions when x values reach to 0.7, whereas further decrease of the x values will reduce the photocatalytic activities for O2 evolution. The mechanism of the observed composition dependence of the solid-solution photocatalytic activities is not clear at the present stage. It may be caused by the changes in the band structure of the solid solutions. As indicated by the DFT results (Figures 4 and 6), the valence bands of the solid solutions are mainly composed of O 2p orbitals with a little contribution of the Bi 6s orbitals. The position of the valence band, in other words the potential of the valence band, should be dependent on the ratio of the Bi 6s to O 2p orbitals in the valence band, which should be an important factor for the increase of the photocatalytic activities of the solid solutions. Furthermore, as previously stated, a wide density-of-states distribution in the conduction band is presumed to be formed on the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions, which may be helpful for the mobility of the excited electrons and may result in higher photocatalytic activities. On the other hand, the increase of the band gap, which means that the number of available photons decreased with the same light source, is a possible reason for the decrease of the photocatalytic activity of the solid solution when x values are smaller than 0.7. It is noteworthy that the present photocatalysts prepared by the solidstate method had a quite small surface area ( $<1.5 \text{ m}^2/\text{g}$ ). It is reliable to conclude that a significant increase of the photocatalytic activities can be obtained by increasing the surface areas of the solid solutions as that observed in BiVO<sub>4</sub> catalysts.

## Conclusions

 $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions were found as active photocatalysts for O<sub>2</sub> evolution from aqueous AgNO<sub>3</sub> solution under visible-light irradiation (>420 nm). The photocatalytic activity of the solid solutions was found to be strongly dependent on the composition, and  $Ca_{0.3}Bi_{0.7}V_{0.7}Mo_{0.3}O_4$  with a 2.42 eV band gap showed the highest activity for O<sub>2</sub> evolution. Photophysical properties and DFT calculations indicated that the band gap of the  $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$  solid solutions was controllable by a change in composition. The present results suggested that band engineering is an efficient method to develop novel photocatalysts with visible-light response. Therefore, the finding of novel photocatalysts based on solid solutions is encouraging. Further research on other solid-solutions photocatalysts is also necessary for revealing the essential factors of active solidsolution photocatalysts.

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**Supporting Information Available:** The effect of treating temperatures on the XRD patterns, Raman spectra, and detected photocatalytic properties of one typical solid solution  $Ca_{0.2}$ -Bi<sub>0.8</sub> $V_{0.8}Mo_{0.2}O_4$ . This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) At the present stage, the exact atomic position of the solid solution is not clear. The obtained Raman spectra suggested the tetrahedral sites of the scheelite structure are probably randomly occupied by vanadium and molybdenum atoms similar to that found in the  $Na_{x/2}Bi_{1-x/2}Mo_xV_{1-x}O_4$  series and  $Bi_{1-x/3}Mo_xV_{1-x}O_4$  series solid solutions. Because of the limited computing condition and also to simplify the calculation process, here we selected four CaMoO<sub>4</sub> units as a supercell to simulate the complicated crystal structure of the solid solutions.