PAPER

Gamma-Bi$_4$V$_2$O$_{11}$ – a layered oxide material for ion exchange in aqueous media

Peiwen Lv[a] and Feng Huang [iD] *[ab]

Layered perovskite oxides have attracted considerable attention due to their potential application in photoelectricity and catalysis. The unique character of layered perovskites as ion-exchange materials provides the possibility of creating structural diversity. A new ion-exchange reaction in aqueous solution was observed in layered oxide gamma-Bi$_4$V$_2$O$_{11}$. When employed in ion exchange, gamma-Bi$_4$V$_2$O$_{11}$ is converted into the scheelite-type phase (ABO$_4$) by selectively discarding Aurivillius-type sheets, and is also converted into the A2X3 phase by selectively dissolving perovskite-like layers. Metal-doped BiVO$_4$ and Bi$_2$O$_3$ were obtained using such an ion-exchange reaction.

Recently, perovskite oxides and layered perovskite oxides have been widely and thoroughly studied because of their structural simplicity and flexibility, good stability, and their promising applications in solar cells, photocatalysts, and fuel cells, for example.[1–3] Perovskite oxides are a type of oxide with the chemistry formula ABO$_3$, where A is a large cation and B is a smaller cation. The skeleton of perovskite oxides comprises corner-sharing BO$_6$ octahedra, where the B-site cation is located in the center of an octahedron of oxygen anions with a coordination number of 6, and the A-site cation is located at the center of eight corner-sharing BO$_6$ octahedra. Layered perovskite oxides are stacks of perovskite oxide layers interspersed with other metal oxide layers. The layered perovskite oxides are well known as The Dion–Jacobson phases, A′[A$_{n-1}$BnO$_{3n+1}$]; the Ruddlesden–Popper phases, A2′[A$_{n-1}$BnO$_{3n+1}$]; and the Aurivillius phases, Bi$_2$O$_2$[A$_{n-1}$BnO$_{3n+1}$].[4–6] Unlike the perovskite oxides, the layered perovskite oxides have the unique characteristic of undergoing soft chemical reactions, such as intercalating molecules into their interlayer space, ion-exchange reactions, and exfoliation to nanosheets.[6,7] Many soft chemical reactions of layered perovskites have been reported, with the unique characteristic of replacing or modifying the interlayer cations under mild conditions.[7–9]

BIMEVOX materials are a group of compounds obtained by doping Bi$_4$V$_2$O$_{11}$ with other metallic ions. These materials exhibit high oxide ion conduction and have potential application at the membrane for oxygen separation.[10,11] Among BIMEVOX materials, the gamma phase of Bi$_4$V$_2$O$_{11}$ consists of Aurivillius-type Bi$_2$O$_2$$^{2+}$ sheets alternating with perovskite-like

oxygen-deficient layers (VO$_{3.5-0.5}$)$^{2-}$.[12] Encouraged by the soft chemical reactions, and using the layered structure of Bi$_4$V$_2$O$_{11}$ as templates, it is feasible to design perovskites that retain the structural features of the precursor layered phases. Interestingly, we found that it is possible for Bi$_4$V$_2$O$_{11}$ to be converted by soft chemical reactions. Moreover, the compound is converted in alkaline solution, and the high crystal symmetry is inherited from the parent compound. We believed that this approach would provide a rational route to the design of materials with high symmetry at high temperatures, using soft chemical reactions at room temperature.

Gamma-Bi$_4$V$_2$O$_{11}$ is synthesized by a standard solid-state reaction. Bi$_4$V$_2$O$_{11}$ possess three polymorphs: alpha, beta, and gamma. The phase-transition temperature of gamma-Bi$_4$V$_2$O$_{11}$ is 840 K (ref. 13). Gamma-Bi$_4$V$_2$O$_{11}$ can be synthesized by quenching in liquid nitrogen after sintering at 1073 K for 48 h or doping with a transition metal to stabilize the high-temperature phase. Gamma-Bi$_4$V$_2$O$_{11}$ constituted with Aurivillius-type Bi$_2$O$_2$$^{2+}$ sheets alternating with perovskite-like oxygen deficient layers (VO$_{3.5-0.5}$)$^{2-}$. The X-ray diffraction (XRD) pattern of gamma-Bi$_4$V$_2$O$_{11}$ is shown in Fig. 1.

Inspired by the ion-exchange mechanism in layered perovskites, in which the Ruddlesden–Popper phases, Dion–Jacobson phases, and Aurivillius phases can be inter-converted,[6] we conjectured that the interlayer cations in the layered structure of gamma-Bi$_4$V$_2$O$_{11}$ have the potential to be replaced. After ion exchange with protons (0.6 M HNO$_3$), gamma-Bi$_4$V$_2$O$_{11}$ is converted into a red powder. The red powder is indexed as the space group *I*21/*a*, with cell parameters of $a = 5.1950$, $b = 11.701$, $c = 5.0920$, and beta = 90.3800. These cell parameters are highly consistent with BiVO$_4$.[14] However, according to the structure of gamma-Bi$_4$V$_2$O$_{11}$, which consists of Bi$_2$O$_2$$^{2+}$ sheets and (VO$_{3.5-0.5}$)$^{2-}$ layers, the sheets of Bi$_2$O$_2$$^{2+}$ are thought to be removed in the ion exchange. Thus, the overall reaction could be represented as follows:

[a]CAS Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. E-mail: fhuang@fjirsm.ac.cn

[b]School of Materials, Sun Yat-sen University, Guangzhou 510275, China. E-mail: huangfeng@mail.sysu.edu.cn
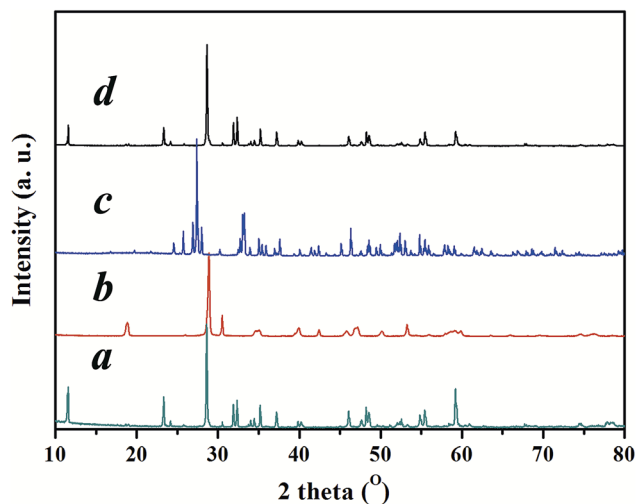
Fig. 1 XRD pattern of (a) gamma-$Bi_4V_2O_{11}$, (b) $BiVO_4$, and (c) Bi_2O_3 converted from gamma-$Bi_4V_2O_{11}$, (d) the product of a solid-state reaction between $BiVO_4$ and Bi_2O_3 converted from gamma-$Bi_4V_2O_{11}$.

$$(Bi_2O_2)_2(VO_{3.5})_2 + 2HNO_3 \rightarrow V_2O_5 + 2H_2O$$

When examining the structure of gamma-$Bi_4V_2O_{11}$, we find that there are two Wyckoff positions for the Bi-atom: the 4e and 16m positions, respectively. Among the $Bi_2O_2^{2+}$ sheets, the Bi-atom at the 4e position is connected to the oxygen atom in the sheets with a bond length of 2.3149 Å.[15] The distance between the Bi-atom (4e) and the oxygen atoms in the $(VO_{3.5-0.5})^{2-}$ layers is as far as 2.7699 Å, which deviates from the typical Bi–O bond length.[16] Thus, the Bi-atom at the 4e position and the oxygen atom in the sheets can be regarded as an integral part of the $Bi_2O_2^{2+}$ sheets. For the Bi-atom at the 16m position, the distance between the bismuth and the oxygen atom in the $Bi_2O_2^{2+}$ sheets is 2.6005 Å. Meanwhile, the Bi-atom (16m) connects to the oxygen atoms in the $(VO_{3.5-0.5})^{2-}$ layers with a bond length of 2.4193 Å. Compared with Bi-atoms at the 4e position, the Bi-atom at the 16m position prefers connecting $(VO_{3.5-0.5})^{2-}$ layers to $Bi_2O_2^{2+}$ sheets. We believe the different Wyckoff positions for the Bi-atom leads to different behaviors when extracting $Bi_2O_2^{2+}$ sheets in acidic solution. Consequently, $BiVO_4$ nanosheets, shown in Fig. 2, are obtained after ion exchange in acid solution.
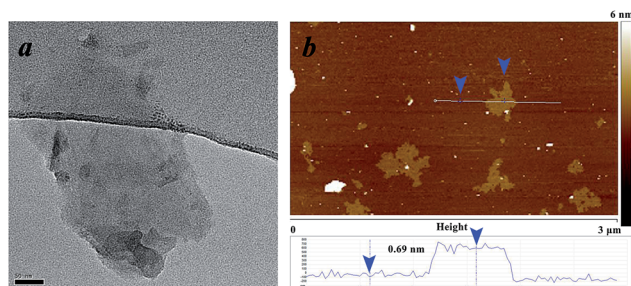

Fig. 2 Transmission electron microscopy (TEM) image (a) and atomic force microscopy (AFM) image (b) of $BiVO_4$ nanosheets.

Traditional ion exchange often occurs under acidic conditions or through solid-state reactions with alkali or BiO_x at elevated temperatures. Interestingly, we find that the layered structure of gamma-$Bi_4V_2O_{11}$ is not only convertible under acidic conditions, but also in alkali solution. After reaction with 20 M KOH solution at room temperature, gamma-$Bi_4V_2O_{11}$ was converted to a light green powder. The powder was identified with XRD, and was composed of the alpha phase of Bi_2O_3 and a small fraction of the gamma phase of Bi_2O_3. Consistent with $BiVO_4$ leached from the acid treatment of gamma-$Bi_4V_2O_{11}$, Bi_2O_3, which can be regarded as perovskite-like layers $(VO_{3.5-0.5})^{2-}$, along with partial bismuth was removed from the layer structure. We believe that the $Bi_2O_2^{2-}$ layers which lacked MO_x octahedra would keep growing under a high concentration of alkaline solution, which is regarded as a minimizer, and boost the crystal growth of Bi_2O_3. In this respect, most of the $Bi_2O_2^{2+}$ layers leached from gamma-$Bi_4V_2O_{11}$ kept growing in the alkaline solution and formed the thermodynamically stable phase – alpha Bi_2O_3. As a result of crystal growth, the scanning electron microscope (SEM) image of Bi_2O_3 in Fig. 3 shows the micromorphology of a single crystal.

The structural evolution is demonstrated in Fig. 4, and the overall reaction is:

$$Bi_2O_3(BiVO_4)_2 \xrightarrow{HNO_3} 2BiVO_4$$

$$Bi_2O_3(BiVO_4)_2 \xrightarrow{KOH} Bi_2O_3$$
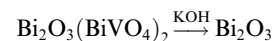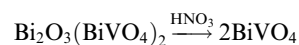
Considering the structural evolution and the overall reaction, the reaction could form a closed loop, as shown in Fig. 5. The Bi_2O_3 and $BiVO_4$ are obtained by ion exchange from gamma-$Bi_4V_2O_{11}$, introducing further dopant, and form gamma-$Bi_4V_2O_{11}$, again by solid-state reaction:

$$2BiVO_4 + Bi_2O_3 \xrightarrow{\Delta} Bi_4V_2O_{11}$$
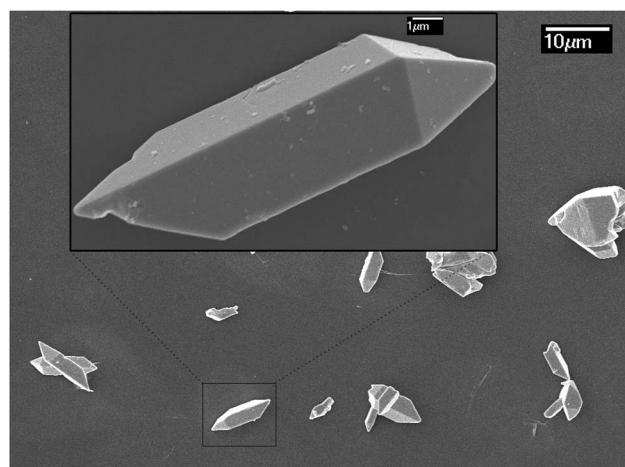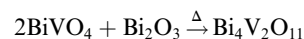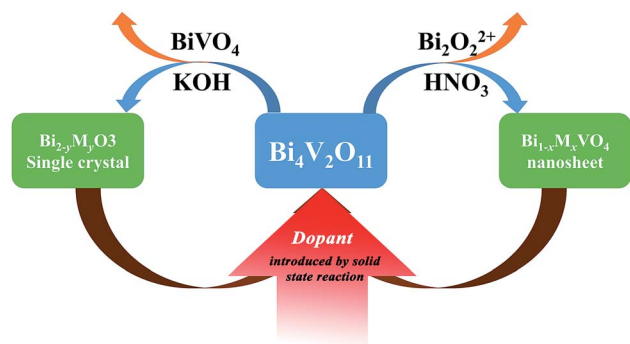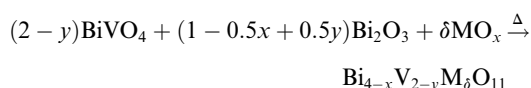

Fig. 3 SEM image of a Bi_2O_3 single crystal prepared via the ion-exchange mechanism.
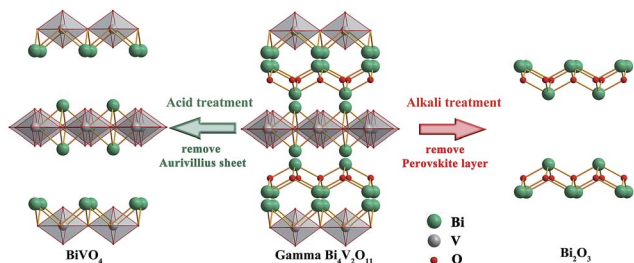
Fig. 4 Structural evolution of gamma-$Bi_4V_2O_{11}$.

Fig. 5 Toolbox of metal-doped Bi_2O_3 and $BiVO_4$ derived from gamma-$Bi_4V_2O_{11}$.

$$(2 - y)BiVO_4 + (1 - 0.5x + 0.5y)Bi_2O_3 + \delta MO_x \xrightarrow{\Delta}$$

$$Bi_{4-x}V_{2-y}M_\delta O_{11}$$

Regarding the large solid solution regions of metal-doped $Bi_4V_2O_{11}$ and the availability of most cations in the periodic table,[17,18] such a toolbox could construct a diverse set of structural architectures, with certain specific morphologies.

Moreover, the toolbox provides the possibility to design $BiVO_4$ and Bi_2O_3 with dopants exceeding the equilibrium solid
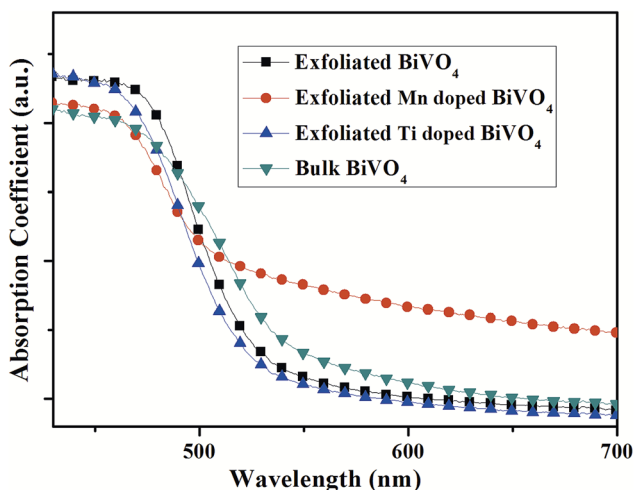
Fig. 6 UV-vis absorption spectra of metal-doped $BiVO_4$.
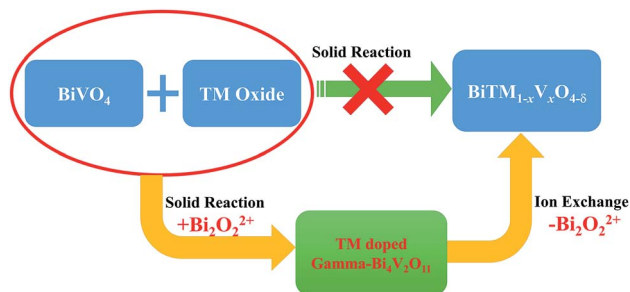
Fig. 7 Introducing dopant into $BiVO_4$ nanosheets by the modified two-step reaction.

solubility. We first doped Mn into $BiVO_4$ and tuned the doping level at a wide range from 0 to 18% (mole ratio of Mn) by the modified two-step reaction shown in Fig. 7. Moreover, titanium-doped $BiVO_4$ was also realized. Accordingly, many transition metal-doped $BiVO_4$ materials were available by the two-step reaction, which could be employed to insert other elements to trigger various capabilities in the $BiVO_4$ mother compound. Fig. 6 shows the UV-vis absorption spectra of metal-doped $BiVO_4$. The bandgap as well as the band structure could be modified.

Conclusions

In summary, gamma-$Bi_4V_2O_{11}$ could be directly converted into the scheelite-type phase (ABO_4) by selectively discarding Aurivillius-type sheets. At the same time, gamma-$Bi_4V_2O_{11}$ could be converted into the A2X3 phase by selectively dissolving the perovskite-like layers. This ion-exchange reaction, along with a solid-state reaction, formed a closed loop and enabled the formation of a diverse array of structural architectures with certain specific morphologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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