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Gamma-Bi₄V₂O₁₁ – a layered oxide material for ion exchange in aqueous media

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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-Bi₄V₂O₁₁. When employed in ion exchange, gamma-Bi₄V₂O₁₁ is converted into the scheelite-type phase (ABO₄) by selectively discarding Aurivillius-type sheets, and is also converted into the A2X3 phase by selectively dissolving perovskite-like layers. Metal-doped BiVO₄ and Bi₂O₃ 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 ABO₃, where A is a large cation and B is a smaller cation. The skeleton of perovskite oxides comprises corner-sharing BO₆ 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 BO₆ 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, Bi₂O₂[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 Bi₄V₂O₁₁ 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 Bi₄V₂O₁₁ consists of Aurivillius-type Bi₂O₂²⁺ 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 Bi₄V₂O₁₁ 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 Bi₄V₂O₁₁ 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-Bi₄V₂O₁₁ is synthesized by a standard solid-state reaction. Bi₄V₂O₁₁ possess three polymorphs: alpha, beta, and gamma. The phase-transition temperature of gamma-Bi₄V₂O₁₁ is 840 K (ref. 13). Gamma-Bi₄V₂O₁₁ 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-Bi₄V₂O₁₁ constituted with Aurivillius-type Bi₂O₂²⁺ sheets alternating with perovskite-like oxygen deficient layers (VO_{3.5–0.5})^{2–}. The X-ray diffraction (XRD) pattern of gamma-Bi₄V₂O₁₁ 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-Bi₄V₂O₁₁ have the potential to be replaced. After ion exchange with protons (0.6 M HNO₃), gamma-Bi₄V₂O₁₁ 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 BiVO₄.¹⁴ However, according to the structure of gamma-Bi₄V₂O₁₁, which consists of Bi₂O₂²⁺ sheets and (VO_{3.5–0.5})^{2–} layers, the sheets of Bi₂O₂²⁺ are thought to be removed in the ion exchange. Thus, the overall reaction could be represented as follows:

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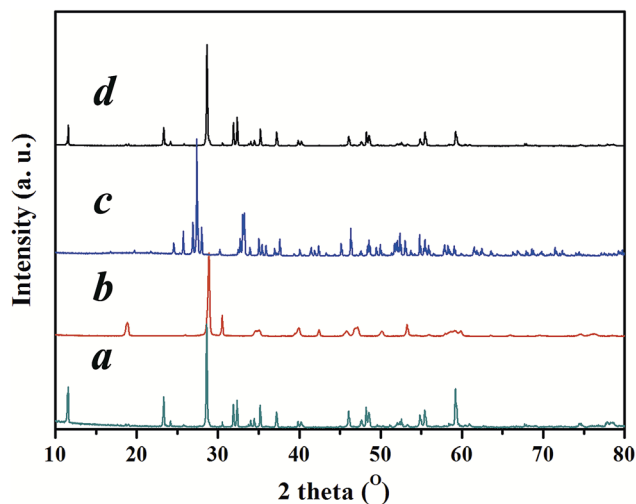


Fig. 1 XRD pattern of (a) gamma-Bi₄V₂O₁₁, (b) BiVO₄, and (c) Bi₂O₃ converted from gamma-Bi₄V₂O₁₁, (d) the product of a solid-state reaction between BiVO₄ and Bi₂O₃ converted from gamma-Bi₄V₂O₁₁.



When examining the structure of gamma-Bi₄V₂O₁₁, we find that there are two Wyckoff positions for the Bi-atom: the 4e and 16m positions, respectively. Among the Bi₂O₂²⁺ 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 Bi₂O₂²⁺ sheets. For the Bi-atom at the 16m position, the distance between the bismuth and the oxygen atom in the Bi₂O₂²⁺ 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 Bi₂O₂²⁺ sheets. We believe the different Wyckoff positions for the Bi-atom leads to different behaviors when extracting Bi₂O₂²⁺ sheets in acidic solution. Consequently, BiVO₄ nanosheets, shown in Fig. 2, are obtained after ion exchange in acid solution.

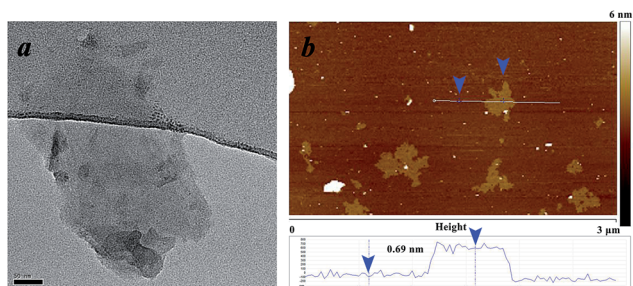
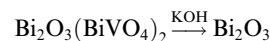
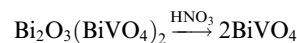


Fig. 2 Transmission electron microscopy (TEM) image (a) and atomic force microscopy (AFM) image (b) of BiVO₄ nanosheets.

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-Bi₄V₂O₁₁ is not only convertible under acidic conditions, but also in alkali solution. After reaction with 20 M KOH solution at room temperature, gamma-Bi₄V₂O₁₁ was converted to a light green powder. The powder was identified with XRD, and was composed of the alpha phase of Bi₂O₃ and a small fraction of the gamma phase of Bi₂O₃. Consistent with BiVO₄ leached from the acid treatment of gamma-Bi₄V₂O₁₁, Bi₂O₃, 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 Bi₂O₂²⁻ 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 Bi₂O₃. In this respect, most of the Bi₂O₂²⁺ layers leached from gamma-Bi₄V₂O₁₁ kept growing in the alkaline solution and formed the thermodynamically stable phase – alpha Bi₂O₃. As a result of crystal growth, the scanning electron microscope (SEM) image of Bi₂O₃ in Fig. 3 shows the micro-morphology of a single crystal.

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



Considering the structural evolution and the overall reaction, the reaction could form a closed loop, as shown in Fig. 5. The Bi₂O₃ and BiVO₄ are obtained by ion exchange from gamma-Bi₄V₂O₁₁, introducing further dopant, and form gamma-Bi₄V₂O₁₁, again by solid-state reaction:

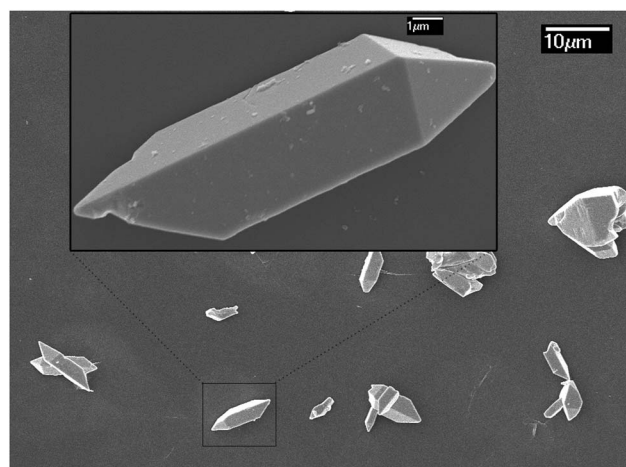
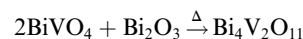
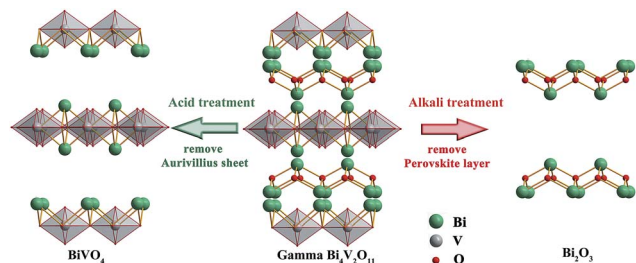
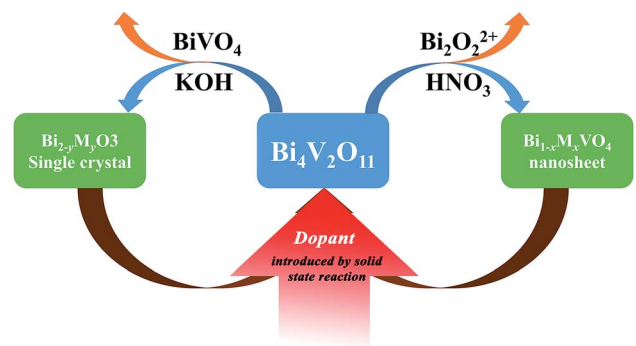
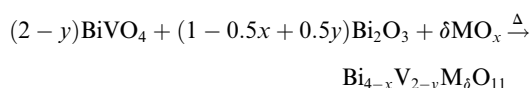


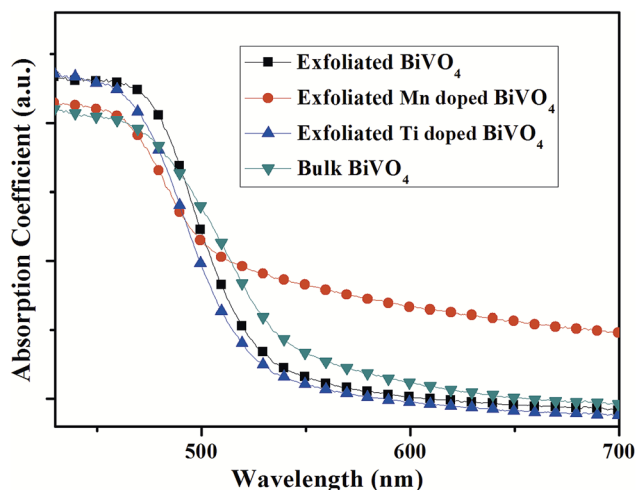
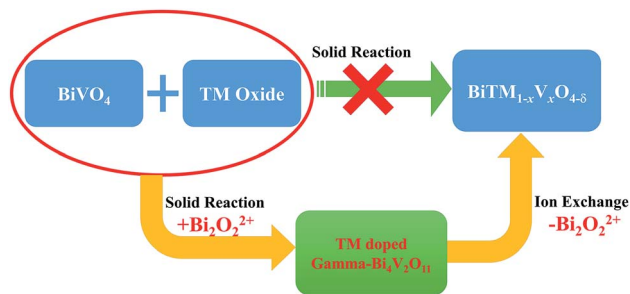
Fig. 3 SEM image of a Bi₂O₃ single crystal prepared via the ion-exchange mechanism.



Fig. 4 Structural evolution of gamma-Bi₄V₂O₁₁.Fig. 5 Toolbox of metal-doped Bi₂O₃ and BiVO₄ derived from gamma-Bi₄V₂O₁₁.

Regarding the large solid solution regions of metal-doped Bi₄V₂O₁₁ 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 BiVO₄ and Bi₂O₃ with dopants exceeding the equilibrium solid

Fig. 6 UV-vis absorption spectra of metal-doped BiVO₄.Fig. 7 Introducing dopant into BiVO₄ nanosheets by the modified two-step reaction.

solubility. We first doped Mn into BiVO₄ 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 BiVO₄ was also realized. Accordingly, many transition metal-doped BiVO₄ materials were available by the two-step reaction, which could be employed to insert other elements to trigger various capabilities in the BiVO₄ mother compound. Fig. 6 shows the UV-vis absorption spectra of metal-doped BiVO₄. The bandgap as well as the band structure could be modified.

Conclusions

In summary, gamma-Bi₄V₂O₁₁ could be directly converted into the scheelite-type phase (ABO₄) by selectively discarding Aurivillius-type sheets. At the same time, gamma-Bi₄V₂O₁₁ 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.

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