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Short communication

Synthesis peculiarities of $BiVO_3$ perovskite

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Abstract

We have experimentally investigated the synthesis of $BiVO_3$ perovskite. We identified the solid-state redox reaction as a process that averts the formation of $BiVO_3$. At elevated temperatures, Bi^{3+} oxidizes V^{3+} to yield metallic Bi and V^{5+} species. This process prevails over the formation of $BiVO_3$. The $BiVO_3$ perovskite structure requires a strong orbital coupling between Bi^{3+} and VO_6 octahedra but this facilitates the electron transfer between V^{3+} and Bi^{3+}. At the investigated temperatures (>400 °C), the activation energy for the electron transfer from V to Bi is exceeded and the structure is destabilized, but the synthesis of $BiVO_3$ might be possible at lower temperatures for which the activation energy for the redox reaction is not exceeded.

Keywords: B. X-ray methods; D. perovskites; P. powders: solid state reaction

1. Introduction

Over the last decades, bismuth-based compounds have been extensively studied because of their extraordinary properties that originate from electronic and/or steric influences of the $6s^2$ lone pair of Bi^{3+} and their relatively low toxicity compared to other related compounds that contain heavy metals with a similar electronic structure (e.g., Hg, Cd, Sn, Tl or Pb). In the last years, the interest in the Bi-compounds, especially perovskites, have further escalated because of their potential as lead-free piezoelectrics ($BiAlO_3$, $BiScO_3$, $BiFeO_3$, $BiCoO_3$, $BiGaO_3$ and modified versions of these compounds) [1–5], photocatalysts ($BiFeO_3$, Ga-doped $BiFeO_3$) [6–8], and multiferroics ($BiFeO_3$, $BiMnO_3$, $BiCoO_3$, $BiCrO_3$) [9–15]. As a consequence, these compounds have been thoroughly investigated and significant amount of knowledge has been accumulated. Also for other Bi-perovskites, interesting properties have been discovered such as negative thermal expansion and giant magneto-optical Kerr effect in $BiNiO_3$ [16,17]. In addition to the mentioned compounds, there is a group of simple Bi-perovskites that has not been synthesized yet. There is no information available in the literature about the existence of $BiVO_3$, $BiTiO_3$ or $BiCuO_3$ [18]. It would be wrong to assume that the lack of the literature reports on these compounds indicates that they are not stable. For instance, $BiAlO_3$ has not been synthesized for a long time but, only after an ab-initio computational study predicted its thermodynamic stability and promising piezoelectric properties, enough experimental efforts have been made to synthesize it [1,19].

The present study focuses on $BiVO_3$ perovskite, for which promising photocatalytic and/or multiferroic properties are expected by analogy to similar $BiFeO_3$ and $BiMnO_3$ systems. Bi^{3+} is regarded as a good choice for photocatalytic materials because its $6s^2$ lone electron pair hybridizes with the O 2p orbitals, resulting in an increase in the valence band level [20]. This is why the Bi-based oxide semiconductors exhibit untypically low band gaps (e.g., the band gaps of $Bi_2Ti_2O_7$ [21], $BiFeO_3$ [6] or $BiVO_4$ [22] are 2.8, 2.5, and 2.4 eV, respectively). The Bi 6s–O 2p hybridization is responsible for distortion of the Bi coordination environment, which results in ferroelectricity, while the partially filled d orbitals of V^{3+} are available to induce ferromagnetism. A coupling of the ferroelectricity with the ferromagnetism gives rise to the multiferroic properties, which are of a high fundamental importance

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for material scientists as well as of a high applied value for modern technologies.

Empirical approaches that are used to estimate stability of perovskites predict that $BiVO_3$ should be stable. The Goldschmidt tolerance factor (t) [23] for $BiVO_3$ is 0.892 (for ionic radii reported by Shannon [24]), which falls well within the stability limit that is approximately in the range of 0.78–1.05. For the stability of the perovskites, the octahedral factor (r_B/r_O) is as important as the tolerance factor. For $BiVO_3$ this value was found to be 0.457, which again falls within the stability range that is between 0.414 and 0.732 [25]. Although these numbers predict a stable $BiVO_3$ perovskite structure, no successful synthesis of $BiVO_3$ has been reported yet. Only one unsuccessful attempt has been published so far. In the 1970s, Ramadass et al. [26] fired the stoichiometric mixture of Bi_2O_3 and V_2O_3 in a sealed evacuated silica tube. The product was not the $BiVO_3$ perovskite but described as a cubic defect pyrochlore structure with a $Bi_2V_2O_{7-y}$ composition. Unfortunately, the report on the structural analysis of this pyrochlore is very deficient and does not allow us to judge the correctness of the conclusions.

Because of the high technological interest for this material, we have performed a systematic experimental analysis to find reasons why the $BiVO_3$ perovskite cannot be synthesized by the solid-state reaction. We have identified chemical processes and interactions that prevent formation of $BiVO_3$ at elevated temperatures. We present these findings in order to enable synthetic chemists to build on this knowledge and, eventually, perform a successfully synthesis of this compound.

2. Experimental

The stoichiometric mixture of starting reagents, Bi_2O_3 (Alfa Aesar, 99.975%) and V_2O_3 (Alfa Aesar, 97%), was homogenized dry in an agate mortar. The homogenized mixture was pressed into pellets and heat-treated at temperatures ranging from 300 to 900 °C in a sealed tube furnace under N_2 (99.999%). In a separate experiment the mixture was inserted into quartz ampoules and vacuum-sealed at a pressure of $\sim 10^{-6}$ bar. Reference samples consisting of only Bi_2O_3 or V_2O_3, were heat-treated separately under the same conditions as the stoichiometric mixtures. For the wet chemistry synthesis, a green solution containing $Bi(NO_3)_3 \cdot 5\,H_2O$ (Alfa Aesar, 98%) and $V(C_5H_7O_2)_3$ (Alfa Aesar, 97%) in a 1:1 M ratio was first heated at 90 °C and then further processed at temperatures ranging from 400 to 900 °C in a N_2 atmosphere.

The phase characterization was carried out by X-ray powder diffraction using a PANalytical X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm), a step size of 0.017° and collection time of 25.8 s per step. The diffraction patterns were recorded in the range $2\theta = 15–80°$. The quantitative analysis of the phases was done using the PANalytical X'Pert HighScore Plus software.

3. Results and discussion

The previous efforts of researchers [18] and our own efforts to synthesize the $BiVO_3$ perovskite by the solid-state reaction from Bi_2O_3 and V_2O_3 have yielded multiphase samples. Our results indicate that the phase composition of nominal $BiVO_3$ after heat treatment depends on the heat treatment conditions and involves phases such as metallic Bi, V_2O_5, $BiVO_4$, $Bi_4V_2O_{10.5}$, and $Bi_{1.62}V_8O_{16}$. The phases with vanadium in different oxidation states are formed, even if a special care has been taken to perform the synthesis in an oxygen-free atmosphere. It is important to note that the same phases were formed when, instead of oxide precursors, we used bismuth(III) and vanadium(III) precursors for the wet-chemical synthesis. This shows that the observed phases are formed as a result of a thermodynamic equilibrium at the applied conditions and their formation is not subjected to a choice of the precursors. It is evident that the synthesis of $BiVO_3$ cannot be accomplished by the direct reaction of Bi^{3+} and V^{3+} at elevated temperatures due to thermodynamic reasons.

Since no Bi_2O_3–V_2O_3 phase diagrams or any other information regarding their interactions are available in the literature, our further research has been directed into the studies of these interactions in order to identify the processes that avert the formation of $BiVO_3$. First, two reference samples, Bi_2O_3 and V_2O_3, were separately heat-treated in N_2 under atmospheric pressure and in the vacuumed quartz ampoules. The XRD analysis after the thermal treatment showed partial oxidation of V_2O_3 to VO_2 and, in both cases, partial amorphisation (see Fig. 1). The partial oxidation of V_2O_3 could have been caused by the residual oxygen in the atmosphere and/or oxygen species adsorbed on the surface of the V_2O_3 oxide. In the case of Bi_2O_3, no chemical changes were noticed after the heat treatment. Further experiments were performed on the equimolar mixtures of V_2O_3 and Bi_2O_3 that

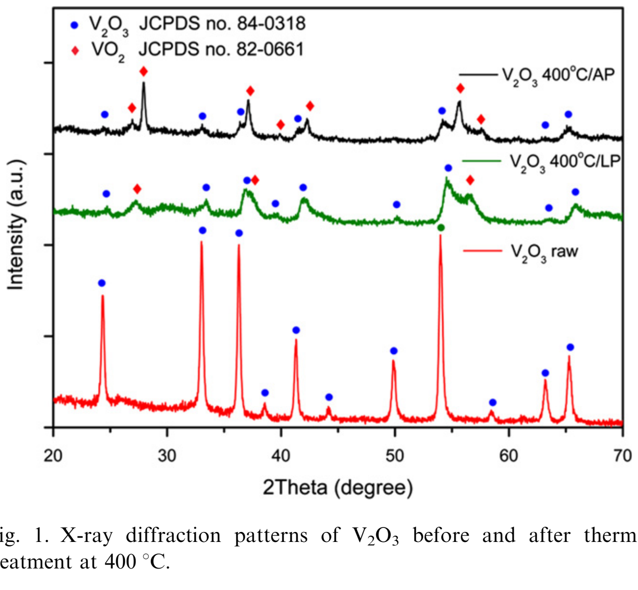

Fig. 1. X-ray diffraction patterns of V_2O_3 before and after thermal treatment at 400 °C.

were heat-treated at different temperatures from 300 to 900 °C. The experiments were again performed in N_2 and vacuum; however, no significant influence of the atmosphere was detected. At 300 °C, no interaction between the two oxides was observed. The product contained some VO_2 in accordance with the reference experiment. At 400 °C, the first interaction between both phases was observed. The new phases that formed were metallic Bi and $BiVO_4$ (see Fig. 2). At the same conditions of the thermal treatment, the reference Bi_2O_3 sample was not reduced to metallic Bi, but in the presence of V_2O_3, metallic Bi appeared as a reaction product. In addition, the reaction yielded $BiVO_4$ phase with vanadium in +5 valence state. This indicates that the direct reaction of Bi_2O_3 and V_2O_3 does not occur. The reaction is sequential. Initially it is induced by an electron transfer from V^{3+} onto Bi^{3+}, i.e., solid-state redox reaction that yields Bi^0 and V^{5+}:

$$2/3Bi_2O_3+V_2O_3 \rightarrow 4/3Bi^0+V_2O_5 \quad (1)$$

At these conditions, V_2O_5 reacts further with unreduced Bi_2O_3 to yield $BiVO_4$ phase:

$$V_2O_5+Bi_2O_3 \rightarrow 2BiVO_4 \quad (2)$$

Bi_2O_3 oxidizes V_2O_3, but also reacts competitively with newly formed V_2O_5. As a consequence, the redox reaction stops before all V-oxides are consumed. Unfortunately, the much lower electron density and the consequent lower X-ray scattering factors for the V-oxides compared to Bi compounds make the XRD analysis of small concentrations of the V-oxides difficult. In these cases we have not been able to reliably detect and identify the remaining V-oxide phases.

At temperatures above 500 °C, other bismuth vanadates appear (see Fig. 3): predominantly $Bi_{1.62}V_8O_{16}$ and polymorphs of $Bi_4V_2O_{10.5}$ in which vanadium is again in the oxidation state lower than +5. As we have seen, Bi_2O_3 and VO_2/V_2O_3 do not react directly into the binary compounds but rather undergo the described redox process; therefore, the only reaction path that can yield the binary Bi-vanadates with V^{3+} or V^{4+} must go through the reduction of V^{5+} from $BiVO_4$.

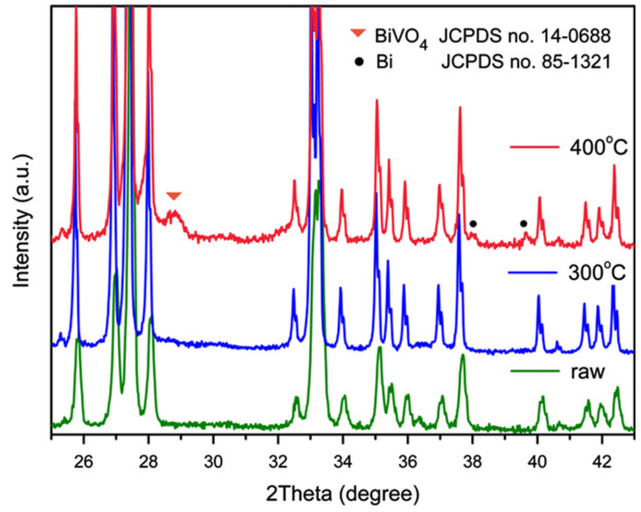

Fig. 2. X-ray diffraction patterns of the equimolar Bi_2O_3–V_2O_3 sample before and after the thermal treatment at 300 and 400 °C. The magnification shows a region where the diffraction peaks of the new phases appear.

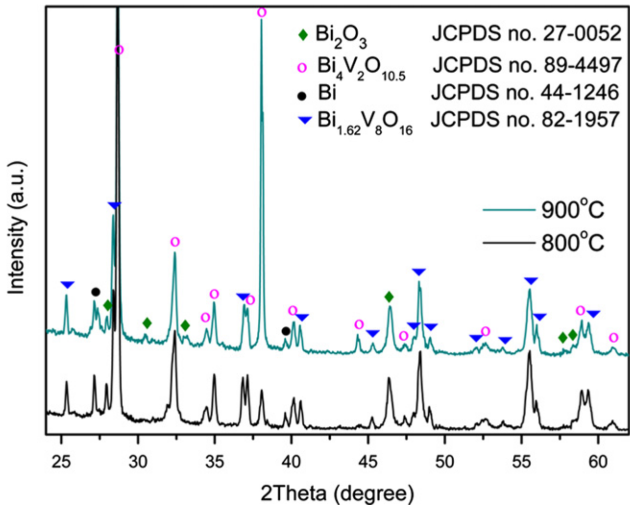

Fig. 3. X-ray diffraction patterns of the equimolar Bi_2O_3–V_2O_3 sample heated at 800 and 900 °C.

$$5.62BiVO_4+4.38VO_x \xrightarrow{T>600^{\circ}C} Bi_4V_2O_{10.5}+Bi_{1.62}V_8O_{16} \quad (3)$$

The coefficients in Eq. (3) are approximate because the amount of V-oxides was not quantitatively determined.

The experiments show that the reduction–oxidation reaction occurs between Bi^{3+} and V^{3+} already at a very low temperature, around 400 °C. This solid-state redox reaction is a consequence of tendency for covalent bonding between the Bi^{3+}, V^{3+} cations and oxygen. To stabilize the $BiVO_3$ structure and facilitate the short Bi–O bonds (calculated by ab-initio modeling to be ~2.2 Å—will be reported elsewhere), a strong orbital interaction between Bi^{3+} and VO_6 octahedra is necessary. This reduces the activation energy and facilitates the charge transfer between V^{3+} and Bi^{3+} at fairly low temperatures. The situation is different in the hollandite-type $Bi_{1.62}V_8O_{16}$ phase (where Bi is in +3 and V in +3 and +4 oxidation states, respectively) wherein the electron transfer between Bi^{3+} and V^{3+} does not take place even at high temperatures (of 800 °C). This indicates higher activation energy for the reduction of Bi^{3+} to the metallic state, probably because in the hollandite-type structure the Bi cations occupy much larger channels (here the Bi–O distance is ~2.5 Å) and interact with the VO_6 octahedra only weakly and with much less covalent contribution to the bonding.

4. Conclusions

Our experimental study of $BiVO_3$ synthesis has identified the reduction–oxidation reaction between Bi^{3+} and V^{3+} as a process that averts the formation of $BiVO_3$.

The formation of $BiVO_3$ requires a strong orbital coupling between Bi^{3+} and VO_6 octahedra. At such electronic state and at the elevated processing temperatures (> 400 °C), the activation energy for the electron transfer from V to Bi is exceeded and the structure is destabilized. The interaction yields metallic Bi and V_2O_5 instead of $BiVO_3$. However, this result does not necessarily disprove the stability of $BiVO_3$ or possibility of its formation at lower temperatures. We suggest that a successful synthesis of $BiVO_3$ might be accomplished by low-temperature synthesis methods (such as hydro(solvo)thermal or even ammonothermal) for which the activation energy for the reduction-oxidation process is not exceeded.

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