Preparation and phase transformation of Ag or Bi ion-exchanged layered niobate perovskite and their photocatalytic properties

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Ag-intercalated and Bi-intercalated layered perovskite were fabricated by ion-exchanged process. The XRD and XPS confirm the phase transformation of the Ag-ion exchanged layered perovskite from Dion–Jacobson to Ruddlesden–Popper phase by heating at higher than 200°C. In the case of Bi ion-exchange perovskite, the product remained Dion–Jacobson phase during the heat treatment. For the Ag-intercalated sample, Ruddlesden–Popper type photocatalyst by heating at 500°C can degrade 20 ppm phenol solution to 6 ppm in 3 h under Xe light, which has superior photocatalytic activity to Dion–Jacobson phase Ag0.67H0.33LaNb2O7. For the Bi-intercalated sample, Dion–Jacobson type photocatalyst can degrade phenol from 20 to 12 ppm in 3 h. From first principle DFT simulation, high photocatalytic activity may be due to the new Ag 4d, O 2p and Nb 4d hybridized band at the highest of the valence band for Ag-included, and to the new Bi 6p band at the lowest of the conduction band for Bi-included samples.

Key-words : Photocatalyst, Layered perovskite, Ion-exchange, Phenol degradation, Phase transformation, DOS calculation

Concerning the global environmental issues and energy crisis, photocatalysis technology using semiconductors has been attracting more and more consideration. Over the past several decades, researchers have been searched for effective methods for chemical waste removal. Several contaminants are of particular threatened to the health of human being, such as phenolic compounds, various dyes, etc. However, removal of phenol presents serious challenges, because this molecule is not biodegradable and could hardly undergo direct photolysis by sunlight or removed by conventional water treatment processes. Layered perovskite as an ideal green chemistry photocatalyst is undoubtedly advantageous over the other conventional catalysts.

Layered perovskites are intergrowths of perovskite and other structures, and they consist of two-dimensional perovskite slabs interleaved with cations or cationic structural units. The Dion–Jacobson series of layered perovskites has one interlayer cation per formula unit. Ruddlesden–Popper phases have two interlayer cations per formula unit and possess twice the interlayer charge density of the Dion–Jacobson phase. Aurivillius phase are intergrowths of perovskite and bismuth oxide and have a coherent network of Bi2O25+ between the two-dimensional perovskite slabs.

For photocatalytic reactions, control of the band structure is very important for improvement of the activity. Especially, Li et al. reported that Ag2ZnGeO4 has the valence band in which top is composed of Ag 4d and O 2p hybrid orbital. Lin et al. reported that Bi 6s and O 2p forms hybrid orbital in the Bi2SbO5. We have been reported that preparation of partially-substituted RblaNb2O7 for Nb5+ by W5+ and Ti4+ and its phenol degradation activity by change of conduction band. On the basis of Li and Lin’s results, the present work reports a study on the photocatalytic performance of interlayered perovskite from a layered perovskite structural oxides HLaNb2O7 as host, Ag or Bi as guest by control of top in the valence band. Therefore, we study the hybridization of layered niobate perovskite with Ag or Bi in detail. Such structure is expected to not only change the valence band but also inhibit the recombination of charge carriers effectively, and the photocatalytic activity of semiconductor can be enhanced.

All reagents were purchased from Kanto kagaku Ltd. Japan. Layered compound RbLaNb2O7 was synthesized by a solid-state reaction at 1000°C in air for 6 h, using an intimate mixture of reagent-grade Rb2CO3, La2O3, Nb2O5 with a mole ratio of Rb:La:Nb = 1.25:1:2 as starting materials. HLaNb2O7 was prepared by proton exchange reaction of RbLaNb2O7 with 2M HCl solution at 40°C for 24 h 5 times. Then put the AgNO3 aqueous solution or Bi(NO3)3 nitric acid solution into HLaNb2O7 aqueous solution, with twice of the equimolar ratio. Then the suspension liquid solution was shaking at 40°C. After 24 h, solution was filtered at room temperature, washed strongly and then dried at 50°C. Then we can get Ag1xH1-xLa2-xNb2O7 or Bi1yH1-yLa2-yNb2O7. After that, Ag1xH1-xLa2-xNb2O7 was sintered at different temperature to get the final product. For the Bi ion exchanged product, same experiment procedure was taken.

The structure samples were examined by monochromated X-ray diffraction (XRD) pattern (RINT-2000, Rigaku). The chemical compositions of these samples were measured by X-ray fluorescence (XRF) (ZSX Primus II, Rigaku). The chemical states of these samples were measured by X-ray photoelectron spectroscopy (XPS) (Kratos Axis-Ultima, Shimadzu). The electronic structures of these samples were examined for optical band gap by UV–vis spectrum (V-550, Jasco) and for calculation by first-principle density functional theory. The calculations were carried out by PAW potentials. The calculation have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien.

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The hybrids with Bi were analyzed by synchrotron X-ray diffraction using Debye–Scherrer camera at BL02B2 in Spring-8. The sample was filled in borosilicate glass tube with a radius of 0.2 mm. The X-ray wavelength used is 0.496071 Å determined by CeO₂ as reference. The refinement of the crystal structure was carried out by Rietan-FP.²¹)

The photocatalytic activity was evaluated by the phenol degradation. For consideration of practical application, Xe light was used as irradiation resource. Phenol aqueous solution at a concentration of 20 ppm was prepared from ultrapure water, and the sample was dispersed into the phenol solution at a concentration of 3 g/L. Solution was stirred in dark condition (no irradiation of visible light) for 1 h to examine the adsorption balance of phenol. After 1 h, the solution was photo-irradiated by ultraviolet light from 300 W Xe lamp (UXR-300DU, Ushio Inc.) with continuous stirring. The solution of 2 mL was extracted at 90, 120, 150, 180, 210 and 240 min of elapsed time. The concentration of phenol in solution was measured by high-performance liquid chromatography (co-2065, Jasco) with ODS column.

In this research, we use Dion–Jacobson phase layered perovskite RbLaNb₂O₇ as mother compound. Figure 1 shows XRD patterns of (a) RbLaNb₂O₇, (b) HLaNb₂O₇, (c) Ag₁₋ₓHₓLaNb₂O₇, sintered Ag ion-exchanged sample at different temperature (d) 500°C, (e) 1000°C, (f) Bi₁₋ₓHₓLaNb₂O₇, and (g) Bi₁₋ₓHₓLaNb₂O₇ powder sintered at 500°C.

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In-situ measure tends to disarrange the orientation by dehydration in the layered structure.

We measured the synchrotron XRD patterns omitted in this paper. There are no Ag metal diffraction lines for Ag-included samples. However, for Bi-included samples, mass % of α-Bi2O3 can be detected as an impurity by Rietveld refinement. In order to determine the amount of Ag and Bi in compound, the X-ray fluorescence of sample was measured. From the result we can see that there is no Rb exists in protonated sample. Such vanishment results from success of the protonation. After Ag ion-exchanged treatment, the ratio of Ag/La is 0.67 which means more than two thirds of Ag site exists in compound. Consequently, chemical formula of (Ag,H)LaNb2O7 and that heated at 500°C can be regarded as Ag0.67H0.33LaNb2O7 and Ag0.67LaNb0.67O6.84, respectively. In the case of Bi0.09H0.88LaNb7O7 the ratio of Bi/La is 0.09. The chemical formula was Bi0.09H0.88LaNb0.67O6.84 in light of α-Bi2O3 existence. Since the crystal structures of each sample are Dion-Jacobson and Ruddlesden-Popper type, these samples are designated as ALNO(DJ) for Ag0.67H0.33LaNb2O7, ALNO(RP) for Ag0.67LaNb0.67O6.84 samples at 500°C, and BLNO(DJ) for Bi0.09H0.88LaNb0.67O6.84, respectively.

For analysis of Ag and Bi chemical state, samples were examined for XPS spectra. Figure 4 shows the narrow XPS spectra for Ag 3d and Nb 3p of (a) ALNO(DJ), (b) ALNO(RP) heated at 500°C, and (c) BLNO(DJ). In Fig. 4(a) for ALNO(DJ), the binding energy of state for Ag 3d3/2 is 367.8 eV, and for Ag 3d5/2 is 374.0 eV. These energies indicate existence of cationic Ag+. The binding energies 365.3 and 381.3 eV are correlated to Nb 3p3/2 and 3p1/2 in NbOx. The smaller peak at 369.9 eV might be of metallic Ag. In Fig. 4(b) for ALNO(RP), the binding energies of 367.7 and 373.9 eV belong to the Ag 3d3/2 and Ag 3d5/2, for Ag+ cation. The other peaks with binding energies around 365.1 and 380.7 eV belong to Nb 3p. In comparison between ALNO(DJ) and ALNO(RP), state of Ag is very similar: most of Ag exists as cation within interlayer space, and small amount of Ag metal lied on the outside of the perovskite particle. From Fig. 4(c) we can see that small amount of Bi exist as Bi2O3. The binding energy of state for Bi 4f7/2 is 158.87 eV and for Bi 4f5/2 is 164.07 eV. These energies illustrated that around half of Bi exist as Bi cation. The binding energies 159.97 and 164.97 eV are attributed to Bi2O3 as an impurity.

Optical bandgap of ALNO(DJ) and ALNO(RP) were estimated by tauc plots of Kubelka–Munk transformed UV–vis spectra omitted in this paper. The estimated band gap energies of ALNO(DJ) and ALNO(RP) are 3.16 and 2.99 eV, respectively. These band gaps demonstrate that transformation of Ag+-included layered perovskite from Dion–Jacobson to Ruddlesden–Popper phase shrink the apparent optical bandgap.

Figure 5 shows DOS curve calculated by first principle density function theory (DFT) simulation of (a) ALNO(DJ), (b) ALNO(RP) heated at 500°C, and (c) BLNO(DJ). At first ALNO(DJ) and ALNO(RP) were formed as Fig. 2 and the stress was related by molecular dynamics simulation. Then, DOS curves were calculated. From DOS curve of the Dion–Jacobson phase, we can see that valence band and conduction band are composed of O 2p and Nb 4d, respectively. For Ruddlesden–Popper phase, the simulation was performed by temporal structure because relaxation of stress in the structure seems to be quasi-converged, and then tends to charge Dion–Jacobson type after the convergence. In this stage, the new Ag 4d, O 2p and Nb 4d hybridized band emerges in top of the valence band. In this model, the conduction band spreads toward low energy. Such tendency corresponds to the measured bandgap mentioned above.

In the case of (c) BLNO(DJ), it is different from ALNO(DJ) and ALNO(RP), no hybridized band emerges in the valence band, by contrast, the edge of conduction band spreads to low energy by Bi 6p.

Figure 6 shows the relationship between elapsed time and normalized concentration of phenol by (a) RbLaNb2O7, (b) ALNO(DJ), (c) ALNO(RP), and (d) BLNO(DJ). All the products were stirred in dark for 1 h to get adsorption balance of phenol. From these plots we can see that RbLaNb2O7 did not show significant photocatalytic activity in this research. After 3 h irradiation by Xe light, the normalized concentrations of phenol with ALNO(DJ), ALNO(RP) were around 1 and 0.3, respectively. In the case of Ruddlesden–Popper phase, emergence of new orbital at the top of valence band results in shrink of the band gap. Based on the above-mentioned, ALNO(RP) presented...
the excellent photocatalytic ability superior to ALNO(DJ). For the ALNO(RP), the degradation curve is not linear because the degradation may advance by three stages, adsorption, diffusion on the surface of the particle, and decomposition. In the diffusion stage, the slope of the curve is prone to small as a plateau. In this stage, the diffusion to the small amount of Ag metal may occur and the Ag metal might work as a promoter. From Fig. 6, we can also see that BLNO(DJ) has higher photocatalytic activity compared to ALNO(DJ) maybe because that the conduction band spread to low energy, thus the band gap was shrunk.

In conclusion, Ag ion-exchanged perovskite of Dion–Jacobson phase and Ruddlesden–Popper phase and Bi ion-exchanged perovskite have been synthesized. The photocatalytic activity was evaluated using the degradation of phenol for 3h. At last, the normalized concentrations of phenol are 1 for Dion–Jacobson phase Ag ion-exchanged perovskite, 0.3 for Ruddlesden–Popper phase perovskite at 500°C, and 0.6 for Bi ion-exchanged products, respectively. To clear such difference of photocatalytic activities, the samples were examined for the crystal structure and electronic structure. The XPS spectra indicate that Ag cation was intercalated into interlayer space for both Ruddlesden–Popper and Dion–Jacobson phase. For the electronic structures, the band gap of layered perovskite photocatalyst tends to shrink after sintered. Consequently, Ruddlesden–Popper phase could increase the photocatalytic activities efficiently. For Ruddlesden–Popper phase, on one hand, the new Ag 4d, O 2p and Nb 4d hybridized band distributes nearby the Fermi level, on the other hand, the conduction band spreads toward low energy. In the case of Bi ion-exchanged product, only conduction band was spread to low energy by Bi 6p. In conclusion, sintering of Ag ion-exchanged perovskite can change the photocatalyst crystal structure and furthermore improved the photocatalytic activities efficiently.

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