

Intercalation of Tris(2,2'-bipyridine)ruthenium(II) into a Layered Perovskite Derived from Aurivillius Phase $\text{Bi}_2\text{SrTa}_2\text{O}_9$

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Intercalation of tris(2,2'-bipyridine)ruthenium(II), $\text{Ru}(\text{bpy})_3^{2+}$, into a layered perovskite derived from Aurivillius phase $\text{Bi}_2\text{SrTa}_2\text{O}_9$ was successfully achieved by a guest ion-exchange method using $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ hybrid compound as an intermediate. X-ray diffraction analysis revealed that the structure of the perovskite-like slabs in $\text{Bi}_2\text{SrTa}_2\text{O}_9$ was retained after the intercalation reactions. $\text{Ru}(\text{bpy})_3^{2+}$ shows pronounced spectral red shifts in both its absorption and emission spectra (relative to those in water) when it is incorporated into the perovskite-like slabs.

Considerable research effort has recently been devoted to the study of inorganic layered solids.¹ Intercalation of various photosensitizer into functional layered compounds would be expected to provide novel series of photocontrollable layered materials. Nanostructured materials obtained by intercalation of ruthenium chelates have been investigated with the purpose of exploring photoprocesses and catalytic reactions in restricted media. The layered systems intercalated by $\text{Ru}(\text{bpy})_3^{2+}$ and related ruthenium derivatives have included smectite clays,² layered zirconium phosphates,³ titanate/niobates,⁴ and layered sulfides.⁵

Aurivillius phases ($\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$), a series of layered perovskites, consist of perovskite-like slabs and bismuth oxide sheets. Various members of these families are known to show a wide variety of chemical and physical properties such as ion exchange and intercalation,⁶ photocatalysis,⁷ and ferromagnetism and giant magnetoresistance.⁸ In this study, we used a soft-chemical method for preparation of ion-exchangeable thin film, then, prepared $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ hybrid compound as one of the potential photofunctional materials by means of a guest ion-exchange technique. To the best of our knowledge, this is the first study of $\text{Ru}(\text{bpy})_3^{2+}$ intercalation into a layered perovskite derived from Aurivillius phase.

Aurivillius phase $\text{Bi}_2\text{SrTa}_2\text{O}_9$ is characterized by a layer structure built up of $(\text{SrTa}_2\text{O}_7)^{2-}$ sheets bound together by one layer of $(\text{Bi}_2\text{O}_2)^{2+}$ with 1.25 nm interlayer spacings, as shown in Figure 1. In the perovskite layer, Sr^{2+} ions locate in the A site and Ta^{5+} ions

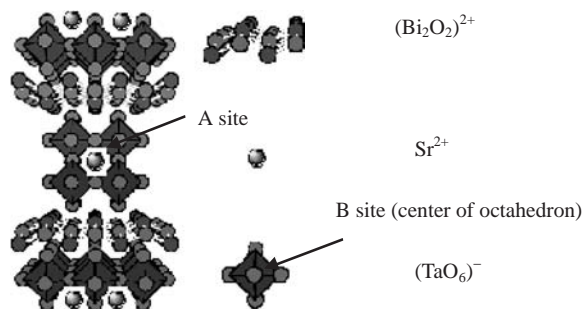


Figure 1. Structure of $\text{Bi}_2\text{SrTa}_2\text{O}_9$ ($n = 2$).

locate in the B site. Upon reaction with HCl, the interlayer $(\text{Bi}_2\text{O}_2)^{2+}$ of $\text{Bi}_2\text{SrTa}_2\text{O}_9$ is leached and replaced with two protons to form the layered Ruddlesden–Popper phase $\text{H}_2\text{SrTa}_2\text{O}_9$.⁹ The $\text{H}_2\text{SrTa}_2\text{O}_9$ can accommodate *n*-alkylamines in the interlayer space via the acid–base reaction. It has been long believed that the $\text{Bi}_2\text{SrTa}_2\text{O}_9$ was not possible to substitute other cations into the $(\text{Bi}_2\text{O}_2)^{2+}$ layers, because as it forms caps of BiO_4 square pyramids.¹⁰ The goal of this study is to achieve a synthetic procedure to obtain a $\text{Ru}(\text{bpy})_3^{2+}$ immobilized into a perovskite-type layers $(\text{SrTa}_2\text{O}_7)^{2-}$.

$\text{Bi}_2\text{SrTa}_2\text{O}_9$ was prepared by the solid-state reaction of a stoichiometric quantities of high-purity mixture of Bi_2O_3 , SrCO_3 , and Ta_2O_5 , using a method similar to that employed for $\text{Bi}_2\text{SrNb}_2\text{O}_9$.¹¹ The intimately mixed materials were heated in air at 900 °C for 12 h, 1000 °C for 12 h, and 1200 °C for 24 h with intermittent grinding. The sample was slowly cooled in air. The crude product was washed with distilled water for 3 times and dried at 100 °C. A protonated form $\text{H}_2\text{SrTa}_2\text{O}_7$ was prepared by the treatment of $\text{Bi}_2\text{SrNb}_2\text{O}_9$ with 6 M HCl for 24 h three times at room temperature (200 mL HCl per gram $\text{Bi}_2\text{SrNb}_2\text{O}_9$). The product was centrifuged and washed with distilled water until free of Cl^- , then dried in air, and further dried at 100 °C, leading to the formation of a single-phase anhydrous phase ($\text{H}_2\text{SrTa}_2\text{O}_7$). $\text{H}_2\text{SrTa}_2\text{O}_7$ was modified with *n*-hexylamine by acid–base reactions. One gram of $\text{H}_2\text{SrTa}_2\text{O}_7$ was sealed in an ampoule containing a 20 mL of aqueous *n*-hexylamine solution 50% (v/v) which was allowed to stand for two weeks at 70 °C. An aqueous colloidal dispersion of the $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ hybrid powder was obtained by suspending 0.2 g of the powder $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compounds, which had been milled in advance, in 20 mL of H_2O . The 200 μL of colloidal suspension was cast onto a conventional quartz glass plate (20×40 mm) and was allowed to dry at room temperature for two days. The intercalation of $\text{Ru}(\text{bpy})_3^{2+}$ into the interlayer space of the $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ hybrid thin film was conducted through facile guest–guest ion exchange in aqueous solutions. Air-dried thin film was fully immersed in 3 mM of aqueous $\text{Ru}(\text{bpy})_3^{2+}$ solutions for 72 h at room temperature with constant stirring. The film was then carefully washed with distilled water until the $\text{Ru}(\text{bpy})_3^{2+}$ absorption could no longer be detected at 452 nm in the filtrate solution. The elemental analysis of the $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ showed a 30% $\text{Ru}(\text{bpy})_3^{2+}$ ion exchange with $\text{H}_2\text{SrTa}_2\text{O}_7$ (Observed: C, 14.32; H, 1.24; N, 3.33%. Calculated for $[\text{Ru}(\text{bpy})_3^{2+}]_{0.3}\text{H}_{1.4}\text{SrTa}_2\text{O}_7$: C, 14.72; H, 1.17; N, 3.43%).

Aurivillius phase, $\text{Bi}_2\text{SrNb}_2\text{O}_9$ was obtained as white single-phase polycrystalline and exhibited excellent crystallinity as demonstrated in powder XRD pattern (Supporting information 1a). The XRD pattern of $\text{Bi}_2\text{SrNb}_2\text{O}_9$ can be indexed on the basis of an orthorhombic cell ($a = 0.5520$, $b = 0.5521$, and $c = 2.502$ nm), in agreement with the previous literature.¹² The acid leaching is analogous to ion exchange because it replaces the interlayer

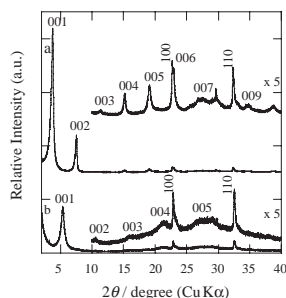


Figure 2. XRD patterns of (a) $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compound and (b) $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ intercalation compound.

(Bi_2O_2) $^{2+}$ cation with protons.¹³ The presence of a low-angle reflection at 9.02° 2θ ($d = 0.98$ nm) in the diffraction pattern of $\text{H}_2\text{SrTa}_2\text{O}_7$ (Supporting information 1b) indicates that the interlayer gallery is reduced by 0.27 nm relative to $\text{Bi}_2\text{SrNb}_2\text{O}_9$, which has a low-angle peak at 7.05° 2θ ($d = 1.25$ nm).

Figure 2 shows the XRD patterns of $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compounds. Upon intercalation, the characteristic peak of the (001) reflection shifted toward a lower-angle, indicating increased interlayer distance from 0.98 to 2.33 nm. The interlayer height of the $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compounds is larger than the chain length of the corresponding $n\text{-C}_6\text{H}_{13}\text{NH}_2$ (1.02 nm).¹⁴ This phenomenon can be explained by the formation of a bilayer of alkylammonium chains, which made the interlayer height larger than the chain length. Taking into account the perovskite layer thickness (ca. 0.78 nm),¹⁵ we can get the net interlayer height (1.55 nm). Therefore, the alkylammonium chains are supposed to be inclined at an angle $\alpha = 50^\circ$ with respect to the (SrTa_2O_7) $^{2-}$ layer surface. On the basis of elemental analysis (C, 9.88; H, 2.36; N, 1.94%), the calculated formula to the $\text{H}_2\text{SrTa}_2\text{O}_7$ matrix intercalated by n -hexylamine is $(n\text{-C}_6\text{H}_{13}\text{NH}_3^+)_{0.9}\text{-H}_{1.1}\text{SrTa}_2\text{O}_7$. The experimental C/N molar ratio was 5.94, which is in agreement with the expected value of 6.0. Figure 2b shows the XRD patterns of $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ intercalation compounds. Upon guest-guest ion exchange, the (001) reflections of the $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compounds disappear and new (001) reflections appear at higher angles, suggesting the formation of a layered structure with a smaller repeating distance. These shifts in the (001) reflections indicate a decrease of the interlayer distance from 2.33 to 1.63 nm. The (100) and (110) reflections of intercalation compounds should be observed in the same positions as shown in Figure 2. Scanning electron micrographs of (a) $\text{Bi}_2\text{SrTa}_2\text{O}_9$, (b) $\text{H}_2\text{SrTa}_2\text{O}_7$, (c) $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$, and (d) $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ (Supporting information 2) indicate that the sheet sizes are not changed. These results indicate an expansion along the c axis with no structural change as regards the a and b axes.¹⁶

The infrared spectrum of the $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ intercalation compound exhibited no absorption bands ascribable to C-H stretching vibration at 2960, 2930, and 2859 cm^{-1} for the n -hexylammonium ions, while characteristic absorption bands of $\text{Ru}(\text{bpy})_3^{2+}$ were observed at 1643, 1568, 1508, and 1461 cm^{-1} . The IR spectrum along with the elemental analysis indicate that $n\text{-C}_6\text{H}_{13}\text{NH}_3^+$ ions are completely replaced with $\text{Ru}(\text{bpy})_3^{2+}$ ions in the intercalation compound.

The $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ intercalation compound has an orange color. The absorption band, which is normally at 452 nm in aqueous solution is red-shifted to 464 nm for $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ as shown in Figure 3a. The λ_{max} in the hybrid environment is

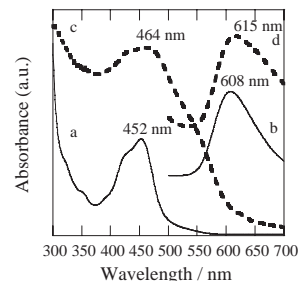


Figure 3. (a) UV-vis and (b) luminescence spectra of the $\text{Ru}(\text{bpy})_3^{2+}$ aqueous (solid line), (c) Diffuse reflectance and (d) luminescence spectra of $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ hybrids (broken line).

actually red-shifted even when compared with those in ethanol (451 nm) and acetonitrile (451 nm) and is rather close to those in tetrahydrofuran (474 nm) or 1,4-dioxane (471 nm) with rather small dielectric constant. The similar red shift have also been observed in most of other intercalation compounds of $\text{Ru}(\text{bpy})_3^{2+}$.¹⁷ The MLCT luminescence was observed in the emission spectrum as shown in Figure 3b. The luminescence maximum was observed at around 615 nm, which was also red-shifted from that of an aqueous solution of $\text{Ru}(\text{bpy})_3^{2+}$ (608 nm). The red shifts of both absorption and emission spectra of the hybrid compound strongly suggest that $\text{Ru}(\text{bpy})_3^{2+}$ is situated in less polar microenvironment than in water, ethanol, and acetonitril, but in rather nonpolar one such as in tetrahydrofuran and 1,4-dioxane. Since the film of the hybrid compound is free from solvent molecules and $\text{Ru}(\text{bpy})_3^{2+}$ ions are immobilized loosely in the interlayer spaces through electrostatic interaction, the results might be rationalized.

In conclusion, the $\text{Ru}(\text{bpy})_3^{2+}\text{-SrTa}_2\text{O}_7$ intercalation compound has been synthesized for the first time by a guest ion-exchange technique using an $n\text{-C}_6\text{H}_{13}\text{NH}_3^+\text{-SrTa}_2\text{O}_7$ intercalation compound as an intermediate. $\text{Ru}(\text{bpy})_3^{2+}$ are intercalated as a monomolecular coverage with their c axis perpendicular to the (SrTa_2O_7) $^{2-}$ sheet.

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