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A Rapid Flux-Assisted Synthetic Approach Towards the Bandgap Engineering of Layered Perovskites

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Metal-oxide solids have shown a remarkable ability for the efficient utilization of ultraviolet light in photocatalytic reactions over their surfaces, e.g., as for TiO_2 or $NaTaO_3$.[1] Previously, we have shown that molten-salt fluxes can dramatically shorten their synthesis times from weeks down to hours or minutes and, equally, yield a rich source of highly crystalline particles with nano- to micrometer sizes.[2,3] In $NaTaO_3$, for example, these methods result in double the photocatalytic rates for hydrogen production.[2] For optimizing their use with solar energy, general and rapid synthetic routes to metal-oxides with smaller visible-light bandgaps and suitable band-level potentials are of the highest importance. Described herein is an effective approach toward the prominent challenge of how to modify their visible-light absorption via rapid flux-assisted exchange reactions (≤1−2 h), which illustrates for the first time the utility of molten-salt flux syntheses in modifying the bandgaps of photocatalytic solids.

The Dion−Jacobson (DJ) layered perovskite family members,[4] $A[\acute{A}_{n-1}B_nO_{3n+1}]$ (A = alkali metal; $\acute{A}$ = alkaline earth metal or rare earth metal; B = transition metal; $n \geq 2$), have been intensely investigated for their photocatalytic properties.[5] The weakly bound alkali-metal ions between their perovskite layers also display a remarkable ability to undergo topotactic exchange.[6] Some of the several known examples include the $(ACl)LaNb_2O_7$ and $A_{0.5}LaNb_2O_7$ (A = V, Cr, Mn, Fe, Co, Cu) series,[7,8] which are obtained from 1:1 (ACl) and 1:2 (A) exchange reactions with the alkali metals, as shown in Figure 1. However, the reported synthesis procedures are time-consuming, usually requiring >1−2 weeks and avoidance of exposure to moisture or air. The insertion of late transition metals and halides stimulates a dramatic change in their colors, though their optical absorptions or electronic structures have not been reported. Thus, we report a more general and facile synthetic route to access this broad array of new metal oxides for investigation as a potentially new class of visible-light photocatalysts, and concomitantly, enables more detailed studies of their electronic structures and optical absorption as a function of the transition metals and halides.

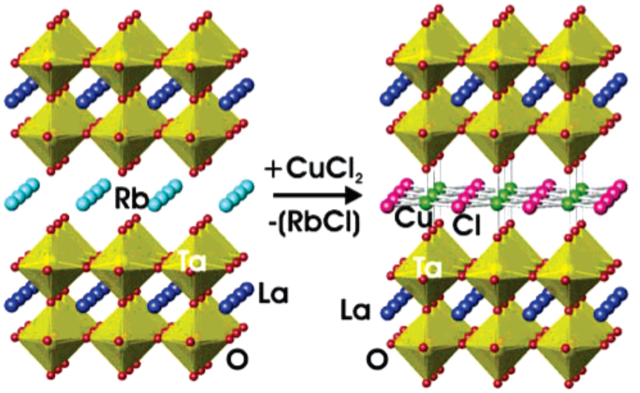

Figure 1. Structural pictures of the ion-exchange conversion of $RbLaTa_2O_7$ (left) to $(CuCl)LaTa_2O_7$ (right).

The parent solids belonging to the DJ series of layered perovskites, $RbLaM_2O_7$ and $RbCa_2M_3O_{10}$ (M = Nb, Ta),[9−11] were obtained by reported high-temperature solid-state reaction methods starting from Rb_2CO_3, $Ca(NO_3)_2{\cdot}9H_2O$, dried La_2O_3, Nb_2O_5, and Ta_2O_5, as obtained from Alfa with stated purities >99%. The products were washed thoroughly, dried overnight, and their purities were confirmed using powder X-ray diffraction (PXRD). The metal-halide exchanged $(CuCl)LaM_2O_7$ and $(CuCl)Ca_2M_3O_{10}$ (M = Nb, Ta) were prepared by low-temperature reactions in a $LiNO_3$ (mp 253 °C), $KHSO_4$ (214 °C), or KNO_3 (337 °C) salt flux with cupric chloride dihydrate using a 1:2:20 molar ratio of DJ-phase:cupric-chloride:flux. The reactant mixtures were heated at 300−400 °C for 1−2 h in either a $LiNO_3$ or KNO_3 flux, or at 300 °C for 1 h in the $KHSO_4$ flux. The samples were washed with distilled water to remove the flux and RbCl by-products, to give final products that were dark green to green colored. The chemical compositions were analyzed by energy-dispersive X-ray spectroscopy (EDS) using a Hitachi S-3200 SEM, and their structures were characterized by PXRD on an INEL powder diffractometer. Final unit-cell parameters, Table 1, were refined by a Le Bail fit using the Fullprof program.[12,13]

The layered $(CuCl)LaM_2O_7$ solids were obtained in pure form according to powder XRD at 300 °C using $LiNO_3$ as

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Table 1. Refined Unit-Cell Parameters For Parent DJ Compounds And the CuCl-Exchanged Products.

compd	A	*a* (Å)	*c* (Å)	*V* (Å^3)
$ALaNb_2O_7$	Rb	3.8827(3)	11.0137(9)	166.03(2)
	CuCl	3.8839(4)	11.706(2)	176.58(3)
$ALaTa_2O_7$	Rb	3.8788(3)	11.102(2)	167.03(3)
	CuCl	3.8791(4)	11.713(2)	176.26(4)
$ACa_2Nb_3O_{10}$	Rb	3.8662(3)	14.929(1)	223.16(3)
	CuCl	3.8545(4)	15.631(2)	232.23(5)
$ACa_2Ta_3O_{10}$	Rb	3.8572(2)	15.051(1)	223.92(3)
	CuCl	3.8517(3)	15.667(2)	232.43(4)

the flux for a reaction duration of 2 h (M = Nb) and 1 h (M = Ta). When the temperature (>300 °C), flux amount, or reaction time (>2 h) is increased, an impurity of CuO also appears in the products, but can be easily removed by treatment with dilute HCl. These reactions could also be similarly performed using anydrous $CuCl_2$ to obtain the products in high purity. Using the $KHSO_4$ flux, pure (CuCl)-$LaTa_2O_7$ is readily formed at 300 °C in 1 h. As is typical for metal-halide insertion reactions, the *c* axes (interlayer distance) of the perovskite hosts were found to expand significantly, as compared in Table 1. The PXRD data and EDS results (see the Supporting Information) show a high product purity, with only trace amounts of Rb and refined unit-cell parameters consistent with the reported parameters. The absence of inserted alkali-metal cations between the layers is due to a strong preference for the insertion of Cu^{2+} cations. Previous reported attempts to react or subsequently exchange the (CuCl)-inserted phases have demonstrated this,[7a,7b] which is likely driven by the stronger electrostatic forces and coordination of Cu^{2+} between the layers. The resulting products exhibited a feathery morphology, Figure 2, and were relatively similar in size to the well-defined platelets of the parent phases.

The new flux-assisted route for these metal-halide insertion reactions was further tested on another series of host DJ phases, $RbCa_2M_3O_{10}$ (M = Nb, Ta). With $LiNO_3$ as the flux, the $(CuCl)Ca_2Nb_3O_{10}$ solid was also obtained in pure form at 300 °C within a reaction duration of 2−3 h. The (CuCl)-$Ca_2Ta_3O_{10}$ solid was obtained with an impurity of host phase even after long reaction durations of 24h. However, using $KHSO_4$ as a flux at 300 °C, $(CuCl)Ca_2Ta_3O_{10}$ can be obtained in pure form in 1h. These results are similar to those for the $RbLaNb_2O_7$ system, and with similar product morphologies. The short reaction times of the flux method arise from the facile diffusion of the Rb^+ and $CuCl^+$ species in the molten flux. When KNO_3 is used as the flux, the reactions are complete in 1 h at 350 °C, but at 400 °C the insertion of K^+ becomes favored over $CuCl^+$. The KNO_3 flux products of $(CuCl)LaNb_2O_7$ were accompanied by a small amount of CuO impurity and DJ parent phase. Prolonged reaction durations of up to 2−3 h did not help in fully transforming the parent DJ phases.

To determine the effect of these exchange reactions on the bandgaps of the layered perovskites, their optical properties and electronic structures were investigated. The

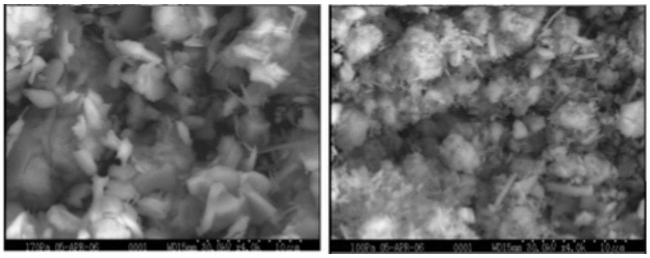

Figure 2. SEM images of metal-halide-exchanged $(CuCl)LaM_2O_7$, M = Nb (left) and Ta (right).

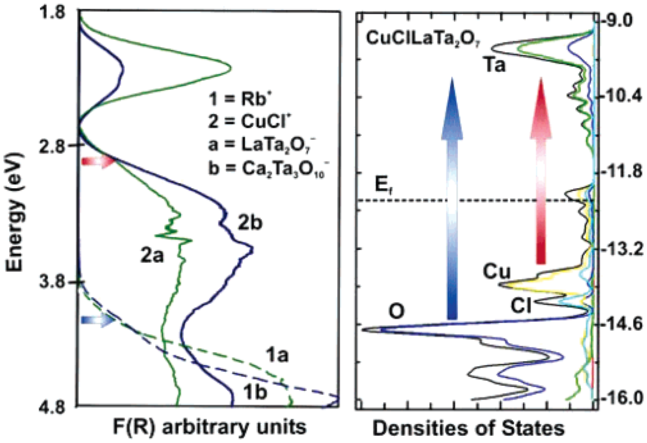

Figure 3. Left, UV−vis diffuse reflectances of the parent DJ and metal-halide-exchanged layered tantalates, and right, the calculated densities of states for $(CuCl)LaTa_2O_7$.

UV−vis diffuse reflectance spectra of the parent DJ phases, plotted as the dashed curves for M = Ta in Figure 3 (left), show that $RbLaM_2O_7$ and $RbCa_2M_3O_{10}$ exhibit optical band gap sizes, respectively, of 3.7 and 3.5 eV for M = Nb and 4.1 and 4.2 eV for M = Ta. The conduction band for layered tantalates is known to be ∼0.5−1.0 eV higher in energy than in niobates,[14] consistent with these results. Furthermore, upon insertion of the metal-halide layers into these solids, the optical band gaps decrease by ∼1 eV for M = Nb and by ∼1.4 eV for M = Ta, shown as the solid lines in Figure 3 for M = Ta. Thus, the onset of optical absorption has decreased significantly and occurs in the visible-light range. The smaller absorption peak at ∼2.2 eV is characteristic of d−d transition energies for Cu^{2+} ions.

Modifying the band gap sizes of metal oxides for the visible-light photocatalysis of water requires raising the valence band energy by ∼1.0−2.0 eV closer to the conduction band energy (and to the O_2/H_2O redox couple), as described before.[15] Therefore, it is also critical to determine the origin of the change in electronic structure that leads to the absorption of visible light. As an approximate model for the electronic structure, the total densities of states and projected atomic contributions were calculated using the tight-binding approach[16] and are shown for M = Ta in Figure 3 (right). Calculations have also been reported for the parent DJ phases[5a] and are similar with the exception of the absence of Cu and Cl orbital contributions. Although the insulating

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nature of these solids is not accurately reproduced, it does provide a rough electronic structure with a consistent depiction of the optical transitions. The higher-energy absorptions in the UV−vis of both parent and (CuCl)-inserted phases, at ∼3.8−4.2 eV, arise from the excitation of electrons between O- and Ta-derived bands, labeled with blue arrows in each. The lower-energy absorptions of ∼2.5−2.8 eV, highlighted by the red arrows, are due to excitations between the Ta conduction band and the newly added (CuCl)-derived valence band. The latter conclusion is confirmed by a comparison with the absorption edges for $CuCl_2$ and $CuCl_2 \cdot 2(H_2O)$ that are >3.0 eV (see the Supporting Information). Intermediate energy states near the Fermi level on Cu at ∼12 eV likely lead to the d−d transitions at ∼2.2 eV, but further interpretation requires a more precise band structure. Thus, a new higher-energy valence band derives from the inserted (CuCl) layers, as required to enable a visible-light photocatalytic reaction with water.

The present study demonstrates that rapid flux syntheses can be used to exchange copper-halide layers into a variety of DJ-type perovskite hosts. The inserted transition metal and halide layers add new higher-energy valence bands and decrease the band gap sizes. Preliminary photocatalysis tests show these compounds have a low activity, but further studies are necessary using different surface cocatalysts to optimize the reaction rates. Also, further promising synthetic results have been found, e.g., for $Cu_{0.5}LaNb_2O_7$, which show that flux methods can access a broader array of metal oxides that will ultimately be necessary in order to probe and understand the mechanisms of photocatalytic activity.

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Supporting Information Available: A typical synthetic procedure, results of UV−vis diffuse reflectance data, and electronic structure calculations for M = Nb, and complete EDAX and PXRD data for all flux products. This material is available free of charge at http://pubs.acs.org.

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