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Supporting Information

Tailoring the Photocatalytic Activity of Layered Perovskites by Opening the Interlayer Vacancy *via* Ion-exchange Reactions

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Synthesis of $K_2La_2Ti_3O_{10}$

Typically, $Ti(OC_4H_9)_4$ (6.81 g, 20 mmol) was first dissolved in the mixture of MeOH (51 g, 1.6 mol), ethylene glycol (EG) (50 g, 0.8 mol) and citric acid (CA) (38 g,0.2 mol) was subsequently added with continuous stirring. After complete dissolution was achieved, excessive KNO_3 was added. The amount of KNO_3 was twice excess (2.70 g, 26.7 mmol) in order to compensate for the loss of potassium by volatilization. The mixture was stirred at room temperature until it became transparent. $La(NO_3)_3{\cdot}6H_2O$ (5.77 g, 13.3 mmol) was added and the solution was stirred at 323 K for a few minutes. The obtained transparent solution was heated at 403 K with continuous stirring. There was no formation of visible precipitation during the polymerization. The mixture of K, La, and Ti cations was considered to remain as molecularly homogeneous. After heating, the brown resin was calcined in an electric furnace at 673 K for a few hours, it became a black powder. The black powder precursor was calcined at 1173K for 2h in air.

Ni-Loading of photocatalytic hydrogen evolution sample

Ni-loaded samples were used for photocatalytic hydrogen evolution test. Ni was loaded by impregnation powder samples with an aqueous $Ni(NO_3)_2$ solution (2 atom% of Ni) followed by heating in the air at 573 K for 20 min. The Ni-loaded catalysts were activated by H_2 reduction at 773K for 2 h and subsequent reoxidation by air at 473 K for 20 min.

Profile fitting and least-square refinement of PXRD patterns

The PXRD pattern index, profile fitting and least-square refinements were carried out using the computer program TOPAS 4.0. All of the reflections could be assigned to orthorhombic symmetry, compared to the tetragonal symmetry of $K_2La_2Ti_3O_{10}$. All peaks in the powder XRD pattern $BaLa_2Ti_3O_{10}$ and $SrLa_2Ti_3O_{10}$ can be well indexed to the space group *C*222, and $Ca_{1-x}K_{2x}La_2Ti_3O_{10}$ can be indexed to the space group *P*nnm. Cell parameters were listed in Table S2. Figure S1 show the cell volume as a function of ionic radius of *M* or the exchange ratio *x*.

Table S1 Selected Bond Lengths (Å) of $CaLa_2Ti_3O_{10}$ and $BaLa_2Ti_3O_{10}$

$CaLa_2Ti_3O_{10}$		$BaLa_2Ti_3O_{10}$	
Ti1-O1	2 × 1.919	Ti1-O5	2 × 1.814
Ti1-O2	2 × 1.920	Ti1-O6	2 × 1.917
Ti1-O3	2 × 2.046	Ti1-O1	2 × 1.932
Ti2-O4	1.725	Ti2-O3	1.642
Ti2-O6	1.732	Ti2-O4	2 × 1.918
Ti2-O5	2 × 1.959	Ti2-O2	2 × 1.957
Ti2-O3	2.156	Ti2-O5	2.143
Ti2-O4	2.271	La-O2	2 × 2.464
La-O5	2.367	La-O4	2 × 2.629
La-O4	2 × 2.442	La-O5	4 × 2.736
La-O3	2 × 2.557	La-O1	2 × 2.841
La-O5	2.785	La-O6	2 × 2.851
La-O1	2.834	Ba-O3	2 × 2.830
La-O2	2 ×2.857	Ba-O3	4 × 2.916
La-O1	2 × 2.881		
La-O3	2.887		
Ca-O6	2.227		
Ca-O6	2 × 2.390		
Ca-O5	2.810		
Ca-O5	2.887		
Ca-O4	2 × 3.035		
Ca-O5	2 × 3.090		

Table S2. Cell parameter of ion-exchanged product

	***a*/Å**	***b*/Å**	***c*/Å**	**V/Å^3**	***Space group***
$CaLa_2Ti_3O_{10}$	3.8989(3)	27.908(2)	3.7851(2)	411.9	*P*nnm
$SrLa_2Ti_3O_{10}$	3.8126(3)	28.123(4)	3.8724(4)	415.2	*C*222
$BaLa_2Ti_3O_{10}$	3.8753(1)	28.514(2)	3.8279(2)	423.0	*C*222
$Ca_{0.95}K_{0.10}La_2Ti_3O_{10}$	3.8438(4)	28.138(3)	3.8669(5)	418.2	*P*nnm
$Ca_{0.89}K_{0.22}La_2Ti_3O_{10}$	3.8763(5)	28.455(4)	3.8476(6)	424.4	*P*nnm
$Ca_{0.75}K_{0.50}La_2Ti_3O_{10}$	3.8357(6)	28.711(5)	3.8937(7)	428.8	*P*nnm

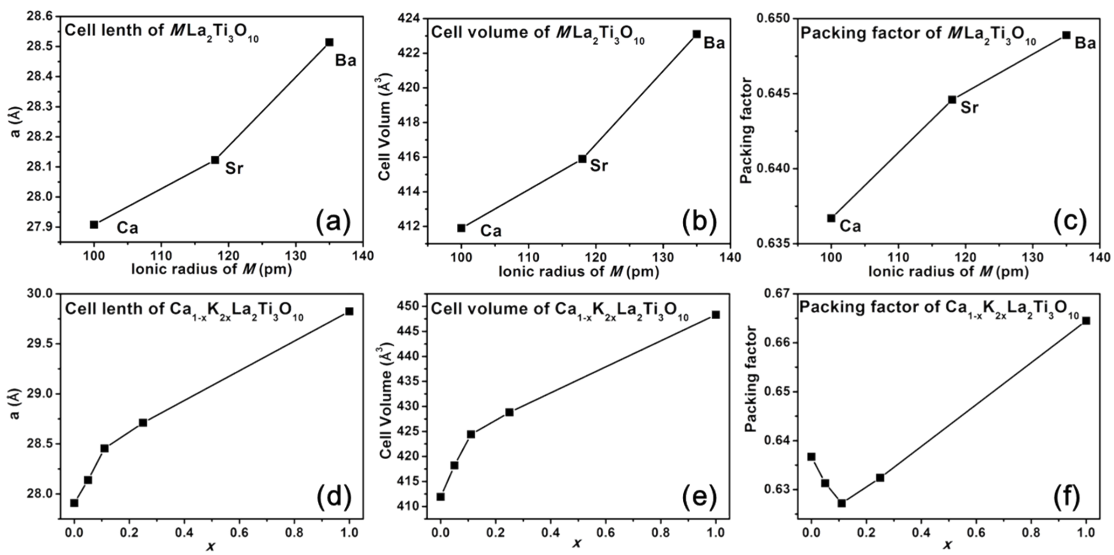

Figure S1. Longest cell parameter (in the direction perpendicular to the perovskite layer) of (a) $MLa_2Ti_3O_{10}$ and (d) $K_{2x}Ca_{1-x}La_2Ti_3O_{10}$. Cell volume of (b) $MLa_2Ti_3O_{10}$ and (e) $K_{2x}Ca_{1-x}La_2Ti_3O_{10}$. Packing factor of (c) $MLa_2Ti_3O_{10}$ and (f) $K_{2x}Ca_{1-x}La_2Ti_3O_{10}$.

Photoluminescence spectra

The PL spectra of $MLa_2Ti_3O_{10}$ (M = K_2, Ca, Sr, Ba) and $K_{2x}Ca_{1-x}La_2Ti_3O_{10}$ (x = 0, 0.05, 0.11, 0.25, 1) were recorded with an excitation wavelength of 205 nm. All the compounds show complex broad emission spectra (360-600nm) with the maximum around 380nm (Figure S2). This result indicates that the energy structures of photo-excitation and relaxation for these layered perovskite are similar. This broad band is assigned to charge transfer emission which directly related to the separation and recombination situation of photo-induced charge carriers. The sharp peak around 470nm was assigned to excitonic PL signal, which related to defects, surface state, etc. [1-3] The ion-exchanged product showed a lower photo luminescent intensity than the original $K_2La_2Ti_3O_{10}$. The result agreed well with the photocatalytic activity. The orderly deferent PL intensities indicate that the differences in photocatalytic activities of $K_{2x}M_{1-x}La_2Ti_3O_{10}$ series is related with the lifetime of photo-generated electrons and holes, further evidence the intrinsic relation between lower PF and higher photocatalytic activity.

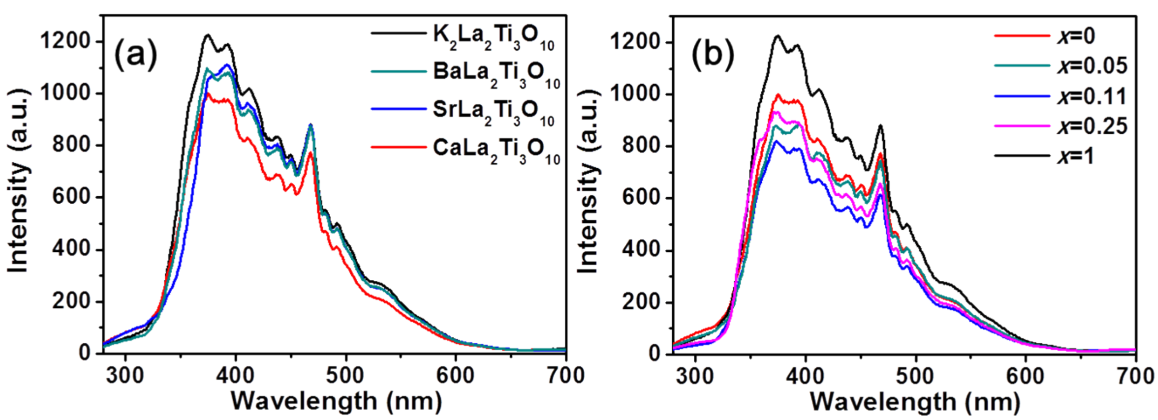

Figure S2. Photoluminescence spectra of (a) $MLa_2Ti_3O_{10}$ (M = K_2, Ca, Sr, Ba) and (b) $K_{2x}Ca_{1-x}La_2Ti_3O_{10}$ (x = 0, 0.05, 0.11, 0.25, 1) at room temperature (excitation at 205 nm)

Reference

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