Supporting Information

Li$_2$Na$_2$TiP$_2$O$_9$: an ordered Na$_4$TiP$_2$O$_9$-Type Crystal with Ion-Exchange Properties

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Single Crystal and Powder X-ray Diffraction

A colorless crystal with dimensions of 0.06×0.03×0.01 mm$^3$ was selected for single-crystal X-ray diffraction. The diffraction data were collected on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) at 153.15 K and a Saturn CCD detector. CrystalClear program was used to record the intensity data and to conduct cell refinement and data reduction. The crystal structure was solved by the direct method with program SHELXS-97$^1$ and refined by full matrix least squares on F2 by SHELXL-97 programs. The structure was verified using the ADDSYM algorithm from the program PLATON, and no higher symmetry was found. The diffraction data of powder samples was collected by powder X-ray diffraction measurement on a Bruker D8 ADVANCE X-ray diffractometer using Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å) at room temperature in the angular range of 2$\theta$ = 5-80$^\circ$ with a scan step width of 0.02$^\circ$ and a scan rate of 0.1.

UV-Vis diffuser reflectance

The reflection spectrum of LNTP crystal was performed with a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer in the range of 200–1100 nm.

Thermal Analysis

The differential scanning calorimetric (DSC) analysis (Fig.2) was performed on a NETZSCH STA–409CD apparatus using Al$_2$O$_3$ as reference material under N$_2$ flow with a sample heating rate of 10.0 k/min from 50$^\circ$C to 1050$^\circ$C. The crystal powders has melt at 850$^\circ$C, after the melting, the sample was checked by powder XRD.
**Ion exchange**

The crystals of Li$_2$Na$_2$TiP$_2$O$_9$ (≈10.0 mg) were added into 0.2 mol/L water solution (10 mL) of AgNO$_3$, BaCl$_2$, CdCl$_2$, Pb(NO$_3$)$_2$, SrCl$_2$, ZnCl$_2$ and CoCl$_2$, respectively. The mixture kept shaking for 24 h at RT and was then isolated by filtration and washed several times with water and acetone then dried in air. The ground powder of Li$_2$Na$_2$TiP$_2$O$_9$ (≈100 mg) were added in 0.2 mol/L water solution (20 mL) of CdCl$_2$, Pb(NO$_3$)$_2$, SrCl$_2$, ZnCl$_2$ and CoCl$_2$, respectively. The mixture was kept under magnetic stirring for 24 h at RT. The solution was filtered and washed as previously mentioned.
Figure S1. (a) DSC curve for LNTP; (b) PXRD pattern for residuals DSC and calculated PXRD pattern for LNTP.
Figure S2. EDS result for the ion-exchange experiment of Ag⁺ in LNTP.
Figure S3. EDS result for the ion-exchange experiment of Cd$^{2+}$ in LNTP.
Figure S4. EDS result for the ion-exchange experiment of Pb$^{2+}$ in LNTP.
Figure S5. EDS result for the ion-exchange experiment of Sr$^{2+}$ in LNTP.
**Figure S6.** EDS result for the ion-exchange experiment of Zn$^{2+}$ in LNTP.
Table S1. Crystal data and structure refinement for LNTP.

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</tr>
<tr>
<td>b (Å)</td>
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<td>β</td>
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<td>γ</td>
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*R(F) = Σ | | Fₒ | - | F_c | | / ∑ | Fₒ | for Fₒ² > 2σ(Fₒ²).*

*Rₒ(Fo²) = (| Σ [w(Fₒ²-F_c²)]² / Σ wFₒ⁴ |)¹/² for all data.*

*w⁻¹ = σ²(Fₒ²) + (zP)², where P = (Max(Fₒ², 0) + 2 F_c²)/3.*
Table S2. Atomic coordinates and equivalent isotropic displacement parameters for LNTP.

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<th>y/b</th>
<th>z/c</th>
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### Table S3. Anisotropic displacement parameters, in Å²

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O4—Ti1—O4\textsuperscript{v} 38.573(170) O3—Na2—O4 53.977(167)
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O1\textsuperscript{xiii}—Ti1—O5\textsuperscript{v} 39.083(31) O3\textsuperscript{v}—Na2—O1\textsuperscript{xiii} 38.389(41)
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O1\textsuperscript{vii}—Ti1—O1\textsuperscript{i} 163.499(49) O3\textsuperscript{v}—Na2—Li1\textsuperscript{xii} 43.739(306)
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O1xi—Na1—O1  139.440(133)  O4viii—Li1—O5xvii  12.035(37)
O1xi—Na1—Li1xii  41.241(104)

(i) -x, 1-y, 1-z; (ii) -x, 1-y, -0.5+z; (iii) 1+x, y, z; (iv) x, -0.5-y, -z;
(v) x, y, 1.5-z; (vi) x, 1.5-y, 0.5+z; (vii) x, 0.5-y, -z; (viii) -x, 1.5+y, 1.5-z;
(ix) -x, 2.5+y, z; (x) 1+x, -0.5-y, -z; (xi) -x, 0.5+y, 1.5-z; (xii) x, 0.5-y, 0.5+z;
(xiii) 1+x, 1.5-y, 0.5+z; (xiv) 1+x, 0.5-y, -z; (xv) 1-x, 1-y, -0.5+z; (xvi) 1-x, 1-y, 1-z;
(xvii) -x, 2.5+y, 1+z.

REFERENCES
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