Supplemental Material for

(NaLa₂)NaPtO₆: The First 2H-Perovskite Related Oxide with a Rare Earth Cation on the A-Site.

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X-ray Structure Determination, (NaLa₂)NaPtO₆

Crystals of (NaLa₂)NaPtO₆ formed as small yellow parallelepipeds. Diffraction patterns from several crystals were examined, and all reflections from each could be indexed to a primitive trigonal / hexagonal lattice with $a \sim 9.5$, $c \sim 11.5$ Å, contrary to the expected rhombohedral K₄CdCl₆-type oxide. A highly redundant data set was collected on one such crystal and processed according to a primitive lattice. Examination of the reflection data showed conspicuously few reflections violating an obverse R-centered lattice (reflection condition $-h+k+l=3n$), with a slightly higher proportion violating the reverse R-centered lattice (reflection condition $h-k+l=3n$). This information suggested the true symmetry was rhombohedral and that the crystal was an obverse-reverse twin. The rhombohedral symmetry was eventually confirmed by inspection of the completed twinned structure.

Strategies for the refinement of obverse-reverse twins are well known.¹ The reflection data were processed as follows:

An obverse rhombohedral unit cell was indexed with the aid of the GEMINI program.² The raw data frames were re-integrated on this cell with the obverse rhombohedral integration condition, thus discarding all reflections belonging solely to the reverse domain. Final unit cell parameters were determined after integration by least-squares refinement of 2708 reflections from the data set. Two classes of reflections were produced:

- (a) those belonging only to the obverse domain (i.e. $-h+k+l=3n$ but $h-k+l \neq 3n$)
- (b) those belonging to both the obverse and reverse domains (i.e., reflections with both $-h+k+l=3n$ and $h-k+l=3n$ simultaneously).

The data were merged according to Laue group $\bar{3}m1$ to yield 390 unique data. The resulting reflection file was modified in preparation for refinement with the HKLF 5 option in SHELX, as outlined.¹ Individual reflections in class (b) involve contributions from both domains. These were duplicated in the reflection file and each assigned a separate scale factor for refinement: batch 1 for the obverse domain and batch -2 for the reverse. Reflections from class (a) were assigned the batch 1 scale factor.

Atomic coordinates from the K₄CdCl₆-type oxide Sr₃MgPtO₆ (space group $R\bar{3}c$)³ were used as a starting model for refinement, with La on the Sr site and Na on the Mg site. Refinement of La site as fully occupied led to an unreasonably large La displacement parameter, high R-factors, and a violation of electroneutrality. Allowing for mixed Na/La occupancy led to a precipitous drop in the R-factors and reasonable displacement parameters for all atoms. Refinement of the occupancy for Pt showed no

significant deviation from unity. Refinement of the occupancies of Na and O are less reliable due to the low X-ray scattering power of these atoms compared to La and Pt. While the Na occupancy remained at unity, refinement of the oxygen occupancy was unstable and would not converge. The Na/La occupancy refined to 0.677(4)/0.323(4), giving a composition of “(NaLa₂)NaPtO₆”. These values were then fixed to allow for refinement of the thermal parameters. After full anisotropic refinement of all atoms, the residuals were R1 = 0.0234, wR2 = 0.0457 for all 390 data and 22 parameters. The twin fraction refined to 0.091(5), indicating the data crystal was composed of 91% of the obverse domain.

Refinement without accounting for twinning resulted in acceptable R-factors of R1 = 0.0307 and wR2 = 0.0648, but included several large electron density maxima, the largest being +7.8 e⁻/Å³, in the polyhedral chains. With refinement as an obverse-reverse twin, the residual electron density extremes were +2.17 / -2.39 e⁻/Å³. Intensity data were collected on a second twinned crystal, and the obverse domain twin fraction refined to 0.450(4) with the identical composition as the first crystal.

Evaluation of crystal quality and intensity data collection were performed with a Bruker SMART APEX ccd-based diffractometer (Mo K α radiation, λ = 0.71073 Å). The data collection covered reciprocal space to θ_{max} = 33.21°. Raw data frame integration and Lp corrections were performed with SAINT+. An empirical absorption correction was applied with SADABS.⁴ Full-matrix least-squares refinement on F² was performed with SHELXTL.⁵

References:

- (1) Sheldrick, G. M. and Herbst-Irmer, R. *Acta Crystallogr. Sect. B.* **2002**, B58, 477.
- (2) *GEMINI, Version 1.02. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1999.*
- (3) Smith, M. D. and zur Loye, H.-C. *Acta Crystallogr. Sect. E.* **2003**, E59, i75.
- (4) SMART Version 5.625, SAINT+ Version 6.22 and SADABS Version 2.03. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2001.
- (5) Sheldrick, G. M. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Figure S1. ORTEP drawing of $(\text{NaLa}_2)\text{NaPtO}_6$ with 80% thermal ellipsoids. Grey: lanthanum/sodium cations; blue: platinum cations; red: sodium cations; yellow: oxygen anions.