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($NaLa_2$)$NaPtO_6$: The First 2H-Perovskite Related Oxide with a Rare Earth Cation on the A-Site

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Crystals of ($NaLa_2$)$NaPtO_6$ were grown in an acidic ("wet") NaOH flux. ($NaLa_2$)$NaPtO_6$ forms in a 2H-perovskite related structure type and contains mixed cation (Na/La) occupancy on the A-site. The crystal was a rhombohedral obverse-reverse twin, and it crystallizes in the space group $R\bar{3}c$ (hexagonal setting) with lattice parameters of $a = 9.5031(2)$ Å and $c = 11.4625(5)$ Å. ($NaLa_2$)$NaPtO_6$ is the first example of an $m = 0$, $n = 1$ ($A_3A'BO_6$) member of the $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ family of oxides where either a lanthanide or a sodium cation occupies the A-site.

($NaLa_2$)$NaPtO_6$ is a novel and unusual $m = 0$, $n = 1$ (or $A_3A'BO_6$) member of the $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ family of 2H-perovskite related oxides by virtue of being the first example of an oxide in this family containing a rare earth cation on the A-site. Motivated by the interesting magnetic properties observed in some members of this family, and intrigued by the compositional diversity,[1,2] numerous research groups have targeted the synthesis of new compositions belonging to this family. This has resulted in a multitude of oxides of the $m = 0$, $n = 1$ structure type ($A_3A'BO_6$) containing metals in oxidation states ranging from A'^{+}/B^{5+} to A'^{4+}/B^{2+}. Up to now, the A-site cations have always been Ca, Sr, or Ba with representative examples of A'^{+}/B^{5+}, Sr_3LiRhO_6[3] and Sr_3NaSbO_6;[4] A'^{2+}/B^{4+}, Ca_3MgIrO_6[5] and Sr_4PtO_6;[6] A'^{3+}/B^{3+}, Sr_3SmRhO_6[7] and Sr_3InNiO_6;[8] and A'^{4+}/B^{2+}, Sr_3PbNiO_6.[9] During our exploration of the La−Na−Pt−O phase space, we synthesized ($NaLa_2$)$NaPtO_6$, a novel $m = 0$, $n = 1$ oxide and the first example of one containing La^{3+} (or any lanthanide, for that matter) on the A-site. Furthermore, ($NaLa_2$)$NaPtO_6$ is the first example of an oxide with this structure type having two types of elements in the A-site.

The idealized ABO_3 perovskite structure results from the stacking of close-packed [AO_3] layers and the filling of the thus generated octahedral sites with B cations, where an ABCABC stacking results in the cubic and the ABAB stacking results in the hexagonal perovskite structure. In addition, the triple and quadruple perovskite structures are generated by mixed cubic (ABC) and hexagonal (AB) stacking sequences. Further structural variety is obtained if one allows for the use of a close-packed layer other than [AO_3]. For example, the inclusion of an [$A_3A'O_6$] layer leads to a family of 2H-related perovskites with general formula $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ that was first described by Darriet and Subramanian.[10,11] The simplest member of this family, the $m = 0$, $n = 1$ or $A_3A'BO_6$ structure, results from the hexagonal stacking of all [$A_3A'O_6$] layers and the filling of the generated octahedral sites by the B-cations. This gives rise to a structure that contains infinite chains of alternating face-sharing octahedra and trigonal prisms; these chains are in turn separated from each other by chains composed of the A-cation.

A major breakthrough in the synthesis and structural characterization of oxides belonging to this family was realized by the ability to grow single crystals[1] from molten salts or fluxes.[12] Interestingly, while carbonates and halides have been the most successful fluxes for the growth of high quality single crystals of this family, they have failed to yield crystals containing any lanthanides. Fortunately, it is known that hydroxide melts are an excellent medium for synthesizing lanthanide containing oxides[13,14] and that the acid−base

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chemistry of hydroxide fluxes is well described by the Lux−Flood acid−base definition.[15,16] Moreover, the application of the Lux−Flood description dictates the necessity of controlling the water content of the flux in order to control its acid−base properties and hence the solubility of the rare earths within it;[15−17] specifically, it has been established that rare earth oxides (RE_2O_3's) are soluble in acidic ("wet") hydroxide solutions.[13] Our group has recently begun a concerted effort to use hydroxide fluxes to grow single crystals of perovskite and perovskite related oxides containing both platinum group metals and lanthanide elements. One result, the growth of crystals of the unusual $(NaLa_2)NaPtO_6$, is communicated herein.

Crystals of $(NaLa_2)NaPtO_6$[18] were grown from a high temperature "wet" hydroxide melt. La_2O_3 (Alfa, 99.9%, 0.5 mmol) and $(NH_4)_2PtCl_6$ (prepared according to Kaufman,[19] 1 mmol) were mixed thoroughly and placed in a silver crucible and topped with 10 g of NaOH (Fisher, ACS reagent) and 2 g of H_2O. The crucible was covered with a silver lid and heated in air at a rate of 5 °C/min to 700 °C, and held at that temperature for 12 h, at which point the furnace was shut off and allowed to cool to room temperature. Small yellow crystals of $(NaLa_2)NaPtO_6$ were isolated from the flux by washing with water, aided by the use of sonication. All of the several crystals examined were obverse-reverse twins, and typical crystals measured approximately 40 μm × 60 μm.

Scanning electron micrographs of several crystals were obtained using an FEI Quanta 200 ESEM instrument utilized in the low vacuum mode. A representative image of a $(NaLa_2)NaPtO_6$ crystal emphasizing crystal morphology is shown in Figure 1. Energy dispersive spectroscopy verified the presence of La, Na, Pt, and O, and also within the detection limits of the instrument, the absence of extraneous elements.

An approximate [110] view of the structure of $(NaLa_2)NaPtO_6$ is shown in Figure 2. $(NaLa_2)NaPtO_6$ is an $m = 0$, $n = 1$ member of the $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ family, whose structure consists of infinite chains of alternating face-shared $[NaO_6]$ trigonal prisms and $[PtO_6]$ octahedra. The structure is derived from the hexagonal stacking of close packed $[(La_2Na)NaO_6]$ layers with the subsequent filling of the generated octahedral sites by the Pt atoms. The polyhedral chains run along [001] and are separated from each other by six spiral chains of distorted $[(La/Na)O_8]$ square antiprisms.

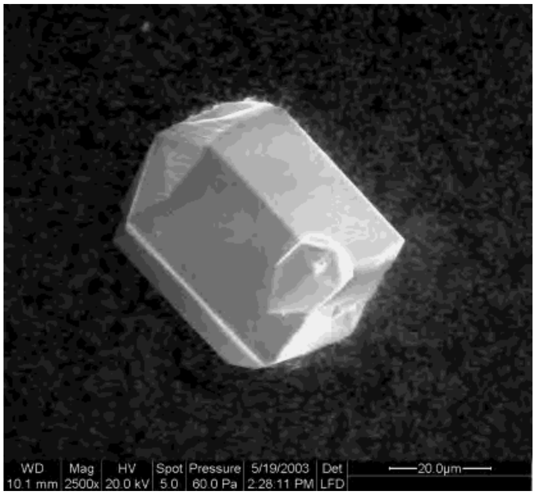

Figure 1. SEM micrograph of a $(NaLa_2)NaPtO_6$ crystal.

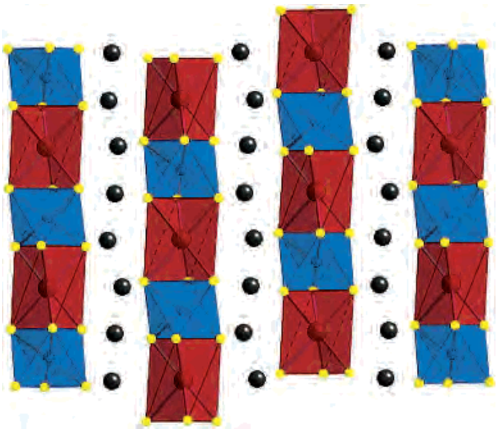

Figure 2. Structure of $(NaLa_2)NaPtO_6$ viewed along [110] consisting of chains of alternating face-sharing PtO_6 octahedra (blue) and NaO_6 trigonal prisms (red) separated by chains of Na/La atoms. Lanthanum/sodium atoms are shown as black spheres; oxygen atoms are shown in yellow.

$(NaLa_2)NaPtO_6$ is the first example of an oxide having this structure type in which a lanthanide cation (La^{3+}) occupies the A-site. All previous examples have contained divalent alkaline earth cations, such as Ca^{2+}, Sr^{2+}, and Ba^{2+}. It is not, however, unprecedented for lanthanide elements to exist in the $A_3A'BO_6$ structure; however, they have previously only occupied the trigonal prismatic A′-site.[7,8,20−23] From a size standpoint, it is not surprising that La would occupy the A-site, as La^{3+} (1.18 Å) and Ca^{2+} (1.12 Å) in an 8-fold coordination environment are quite similar.[24] Furthermore, the A-site in this structure type appears to be very receptive to cations of variable size, accommodating lanthanum and alkaline earth cations into this structure.

Another interesting feature of $(NaLa_2)NaPtO_6$ is the fact that the A-site is shared between one sodium and two

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(18) Crystal data for $(NaLa_2)NaPtO_6$: formula $La_2Na_2PtO_6$, MM = 614.89 g/mol, trigonal, space group $R\bar{3}c$, $a = b = 9.5031(2)$ Å, $c = 11.4625(5)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 896.48(5)$ Å^3, $Z = 6$, $T = 293$ K, $\lambda = 0.71073$ Å, $D_c = 6.834$ g/cm^3, crystal size 0.06 × 0.04 × 0.02 mm^3, $\mu = 37.498$ mm^{-1}, $\theta_{max} = 33.21°$, independent reflections 390 ($R_{int} = 0.0339$), data/restraint/parameters 390/0/22, final $R(F) = 0.0234$, $R_w(F^2) = 0.0457$ (all data). Atomic coordinates (x, y, z) and equivalent isotropic displacement parameters: Pt (0, 0, 0) 0.00501(12) Å^2; La (0, 0.3612(4), $^1/_4$) 0.00970(16) Å^2; Na1 (0, 0.3612(4), $^1/_4$) 0.00970(16) Å^2; Na2 (0, 0, $^1/_4$) 0.0113(9) Å^2; O (0.1863(5), 0.0255(5), 0.1025(3)) 0.0125(3) Å^2. The La site occupancy is 0.677(4), and the Na1 site occupancy is 0.323(4). The crystal was an obverse-reverse twin; see Supporting Information for complete details of refinement.
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lanthanum cations. Sodium and lanthanum are of course known to substitute for one another and are very close in size ($Na^+ = 1.16$ Å, $La^{3+} = 1.18$ Å).[24] When A = alkaline earth, charge neutrality requires the A′ and B site charges to sum to +6. A corresponding A = lanthanide analogue would only allow a sum of +3 for the A′ and B sites.[25] Since the B and A′ site cations, platinum (+4) and sodium (+1), sum to a previously unheard of +5, charge neutrality prevents the A-site from being fully occupied by a trivalent lanthanide cation. However, charge balance can be achieved by mixed ($NaLa_2$) occupancy, as is observed for this compound. Refinement of the X-ray data supports this argument. Refinement of the A-site as a mixed La/Na position (with the total occupancy constrained to sum to unity) resulted in La/Na occupancies of 0.677(4)/0.323(4), very close to satisfying charge balance as well as giving excellent refinement statistics.

The oxidation states of platinum and sodium were assigned on the basis of their known chemistry in oxides (sodium is always +1 and platinum is either +2 or +4) and the correlation between oxidation state and metal oxygen bond lengths. The Pt−O bond distance in $(NaLa_2)NaPtO_6$ is 2.035(4) Å and thus in good agreement with other Pt^{4+} containing oxides of both this structure type and others (Pt^{4+}−O bond 2.01−2.04 Å).[26−28] Likewise, while the trigonal prismatic coordination about the sodium atoms is unusual outside this structure type, the Na−O distance of 2.371(4) Å is comparable to previous examples (Na^+−O bond 2.33−2.40 Å).[4,29] Accepting, therefore, that $(NaLa_2)NaPtO_6$ contains La^{3+}, Na^+, and Pt^{4+}, a charge balance is achieved between the A-site (+7), the A′-site(+1), the B-site (+4), and the oxygens (−12).

In summary, $(NaLa_2)NaPtO_6$, a novel 2H-related perovskite, is the first example of a member of the $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ family containing La^{3+} in the A-site as well as having mixed A-site occupancy. This study further establishes the utility of molten hydroxides for the crystal growth of oxides containing both a platinum group and a lanthanide row element. Finally, since the A-site appears to adapt to elements of a wide size range, work toward the crystal growth of analogous compounds containing additional lanthanide elements is currently underway.

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Supporting Information Available: X-ray crystallographic information for $(NaLa_2)NaPtO_6$ in CIF format. Detailed information regarding the strategy used in the refinement of the obverse-reverse twinned $(NaLa_2)NaPtO_6$ crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) This in not unheard of in the halide analogues, where K_4CdCl_6 is such an example. In fact, the $m = 0$, $n = 1$ structure is referred to as the K_4CdCl_6 structure type.

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