**Crystal growth of Incommensurate Members of 2H-Hexagonal
Perovskite Related Oxides: $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ (M = Co, Ni, Cu, Zn, Mg, Pt)**

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Abstract

Millimeter sized crystals of six oxides of approximate composition $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Mg}, \text{Pt}$) were grown from molten K_2CO_3 fluxes and found to crystallize in a 2H hexagonal perovskite-related structure type. The compositions of these incommensurate structures, which belong to the $\text{A}_{3n+3m}\text{A}'_n\text{B}_{3m+n}\text{O}_{9m+6n}$ family of 2H hexagonal perovskite related oxides, were characterized by X-ray diffraction, energy dispersive spectroscopy, and magnetic susceptibility measurements. The specific synthetic considerations, crystal growth conditions, and magnetic susceptibility measurements are discussed.

Keywords: Crystal growth, flux growth, oxides, incommensurate, magnetism

1. Introduction

Perovskites are perhaps the most versatile structure type when it comes to composition, structural variations and observed physical properties [1-5]. For this reason, interest in the synthesis of new perovskite compositions and, in particular, the growth of single crystals, continues to this day [6-8]. The ideal cubic perovskite is best described as having the general composition ABO_3 consisting of a cube of 8 corner shared BO_6 octahedra, the center of which is occupied by a 12-coordinate A-site cation. An alternate structural description for the simple cubic perovskite structure is based on the ABC stacking of AO_3 layers and the filling of the created octahedral sites by the B-cation. Several structural variants exist in the general perovskite family based on the stacking sequence of AO_3 layers, including the cubic, the hexagonal, mixed cubic/hexagonal and 2H-perovskite related structures. The hexagonal (2H), rather than the cubic structure, is obtained if the AO_3 layers stack in an ABAB fashion and the octahedral sites are filled by the B cation. This results in chains of face-sharing BO_6 octahedra that are separated by the A-cation. This variant is observed when the A-cation is too large for the cavity created by the 8 BO_6 corner-sharing octahedra [9].

Although less widely studied, there also exists a family of low dimensional oxides related to the 2H-hexagonal perovskite structure with general formula $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ that contains trigonal prisms within the infinite chains of face-sharing octahedra [10-12]. Whereas the cubic and hexagonal perovskite structures are composed of close packed $[AO_3]$ layers, the 2H hexagonal perovskite related oxides contain a tripled $[AO_3]$ layer, $[A_3O_9]$, typically designated as m , shown in Fig. 1, that stacks with a second type of layer, $[A_3A'O_6]$, typically designated as n , shown in Fig. 2,

as described by Darriet and Subramanian [12]. This $[A_3A'O_6]$ layer is unique to this family of oxides, and consists of an $[A_3O_9]$ layer in which three oxygen atoms have been replaced by one A' cation. Introduction of this second type of layer results in the A' cation occupying the trigonal prismatic sites and the B cation occupying the octahedral sites in the infinite chains of face-sharing polyhedra. As there is no limit to the combination of m and n layer stacking, essentially an infinite number of different compositions and structural variations can be generated, with an example of the different stacking motifs possible shown in Figure 3. Within this large number of structural variations, incommensurate structures are often observed, a rarity in the traditional perovskites [11].

To account for the appearance of incommensurate structures, it is necessary to accommodate non-integer values for m and n [13]. For this reason, an alternate structural description based on a composite structure model containing two unique sub-cells, each comprised of infinite chains, has been developed [13]. The first sub-cell, representing the infinite chains of face-sharing octahedra and trigonal prisms, consists of $[(A',B)O_3]_\infty$ with the second sub-cell representing the A cation, $[A]_\infty$. This results in a general formula of $A_{1+x}(A'_xB_{1-x})O_3$ in which the value of x , corresponding to the relationship between trigonal prismatic sites and octahedral sites, lies between 0 and 0.5, where only rational values of x result in a commensurate structure, and where the ratio of trigonal prismatic to octahedral sites is given by: $N_{\text{prisms}} / N_{\text{octahedra}} = x / (1-x)$. The lattice parameters of each sub-cell are directly related to the overall structure and sequence of trigonal prisms and octahedra by the relationship of $c_1 / c_2 = (1+x) / 2$. [13] In the ideal structure, the height of a trigonal prism should be twice that of an octahedron and the ratio of c_1/c_2 is a rational

number. When the quotient c_1/c_2 is not a rational number, then the structure is incommensurate. A more detailed explanation of this family of oxides as modulated composite structures using the superspacegroup formalism can be found in the following references [13-17].

Single crystals of 2H hexagonal perovskite-related oxides have been grown using a variety of fluxes, including chlorides [11], hydroxides [18,19], and carbonates [20], giving rise to vast compositional diversity [11]. A large number of platinum group metal (PGM) containing oxides belonging to this family have been synthesized, such as $\text{Sr}_3\text{NiPtO}_6$ [21], $\text{Ba}_{1.14}\text{RhO}_3$ [22], $\text{Ba}_9\text{Rh}_8\text{O}_{24}$ [23,24], $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ [25], and $\text{Ca}_3\text{NaRuO}_6$ [26]. The flux growth of single crystals of PGMs in these complex oxides necessitates the use of an oxidizing flux that can readily dissolve platinum group metals and that can be removed via dissolution at the conclusion of the crystal growth process in order to isolate the crystals from the solidified flux matrix. Both carbonates and hydroxides meet these conditions, with hydroxides being used in primarily the 400-800°C temperature range while carbonate fluxes are used in the 800-1200°C temperature region [27]. Empirically, larger crystals are obtained from carbonate fluxes than from hydroxide fluxes and to explore the crystal growth of new 2H-hexagonal perovskite related oxides we focused on the growth of platinum containing structures out of carbonate fluxes. Herein we present the crystal growth, synthetic rationale, characterization, and magnetic susceptibility measurements of several new oxides belonging to the family of 2H-hexagonal related oxide with the approximate composition of $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Mg}, \text{Pt}$).

2. Experimental Procedure

2.1 Crystal Growth

All crystals described in this paper were grown by high temperature flux synthesis. K_2CO_3 (99.99%) was purchased from BDH. Transition metal carbonates, MnCO_3 (99.985%), CoCO_3 (99.5%) were purchased from Alfa Aesar. Transition metal oxides, NiO (99.999%), CuO (99+%), ZnO (99.99%), and MgO (99.99%) were purchased from Sigma Aldrich, while Pt (99.9995%) and Rh (99.9995%) were purchased from Engelhard.

To grow crystals of these phases, all reagents were placed into an alumina crucible with a loose fitting alumina lid to prevent evaporation of the flux. The millimol ratio of alkaline earth : dopant metal : PGM reagents found to yield the highest quality single crystals was 6:1:1. The K_2CO_3 flux was always placed on top of all reagents in an amount equaling 10x the total mass of the reagents. These crucibles were placed into a programmable tube furnace with 3 inch diameter mullite process tubes. These samples were heated in air at a rate of $600\text{ }^\circ\text{C} / \text{hour}$ to the target temperature of $1150\text{ }^\circ\text{C}$. The samples were maintained at that temperature for 10 hours before cooling at a rate of $5\text{ }^\circ\text{C} / \text{hour}$ to $800\text{ }^\circ\text{C}$, at which point the furnace was turned off and the sample was allowed to cool to room temperature.

Collection of the single crystals was accomplished by dissolving the flux in water, aided by sonication. The single crystal product was collected by vacuum filtration followed by additional washing with water before the crystals were finally dried using acetone. A summary of the reaction conditions, crystal morphology, crystal size, composition and yield is given in Table 1.

2.2 Characterization

Crystals of the parent composition, $\text{Ba}_4\text{Pt}_3\text{O}_9$, and all other compositional variants formed as well faceted hexagonal rods and plates. Representative optical and SEM images for each morphology are shown in Fig. 4-6. All single crystals were determined to be incommensurate. For powder diffraction analysis, the crystals were ground into a fine powder and characterized using a Rigaku D/Max-2100 powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation. The step scans covered the angular range $10\text{-}70^\circ 2\theta$ in steps of 0.02° .

Elemental analysis was performed on single crystals of the reported series using a Thermo EDS instrument equipped Tescan Vega-3 SEM instrument utilized in the low vacuum mode. The crystals were mounted on carbon tape and analyzed using a 30 kV accelerating voltage and an accumulation time of 20 s. As a qualitative measure, Energy Dispersive Spectroscopy (EDS) verified the presence of the platinum, respective transition metals, and barium in the reported compounds. The absence of extraneous elements, such as potassium, was confirmed within the detection limits of the instrument.

Magnetic susceptibility was measured on ground samples of $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ ($\text{M} = \text{Co, Ni, Cu}$). The susceptibility was measured under zero-field-cooled conditions at an applied field, H , of 1000 Oe using a Quantum Design Magnetic Properties Measurement System (QD MPMS3 Squid Magnetometer). The raw moment was corrected for sample shape and radial offset effects using a combination of DC and VSM scan data collected at 2 K [28].

3. Discussion

3.1 Synthetic Considerations

The use of K_2CO_3 to grow crystals of platinum group metal containing oxides, in particular the 2H-perovskite related oxides, has several advantages over the use of chloride and hydroxide fluxes. Specifically, chloride fluxes have been used to grow crystals of members of this family of oxides, such as $\text{Sr}_3\text{PbNiO}_6$ [29]; however, because of the redox neutral nature of chloride fluxes, there has been limited success using these fluxes to grow PGM containing oxides when starting with the platinum group metals in the metallic state. Although hydroxide melts are sufficiently oxidizing to dissolve PGMs, some alkaline earth hydroxides have limited solubility in water, making separation of the resulting single crystals from the flux matrix more difficult. Additionally, the very oxidizing nature of the flux can take the oxidation process too far and result in very high, unstable oxidation states, thus producing hydrolytically sensitive compositions [18]. By contrast, alkali metal carbonates possess an intermediate level of oxidative strength, thereby typically avoiding the formation of unstable oxidation states, while affording high solubility in water in addition to the ability to dissolve most reagents easily, including PGMs.

The crystal growth of this unique family of oxides is very sensitive to small changes in growth conditions, requiring a careful tailoring of all aspects, including heating rates, temperatures, time, oxygen partial pressure and flux choice [11]. The largest, best faceted crystals resulted from a slow cooling rate of 5°C/h . Increasing the cooling rate slightly resulted in smaller crystals, however, using significantly faster cooling rates such as 10°C/min or quenching the reaction from 1150°C to RT resulted in no crystal formation. Utilizing cooling rates slower than 5°C/h did not result in improved crystal quality.

The use of high temperature carbonate fluxes has been shown to effectively dissolve precious metals in the temperature range of 1050 °C to 1150 °C [9], even when starting with the PGMs in the metallic state. Within this temperature range, higher temperatures were found to promote the growth of larger single crystals and it is possible that the higher temperatures, especially when coupled with slow cooling rates, simply created longer growth times, which increased the crystal size.

The dwell time of 10 hours at 1150°C was empirically determined to result in superior crystal quality than longer dwell times, such as 24 hours, for this specific system. Although K_2CO_3 does not exhibit a very high vapor pressure at 1150 °C, longer dwell times resulted in significant evaporative losses, causing a loss of crystal quality. For this reason the alumina crucibles were covered with loose fitting lids to minimize flux loss during the 10 hour dwell.

The decision to use K_2CO_3 vs. Na_2CO_3 as the flux is expected to make a significant difference as the potassium cation is much larger than the sodium cation and cannot substitute for the B-site metals in the perovskite and perovskite related structures. For example, the use of Na_2CO_3 has lead to the crystal growth of Ca_3NaIrO_6 [20] where the sodium cation occupies the trigonal prismatic A' position, making it a reactive flux. In contrast, the use of the larger alkali metals, such as potassium, rubidium or cesium, ensures that the alkali metal will not substitute on the A' or B site of the 2H-perovskite related structure, thus rendering this an inert flux. This conveniently removes one variable from the crystal growth process and is thus preferred.

The ratio of flux to the total mass of the reagents was varied and empirically determined to yield higher quality, better faceted crystals when an at least 10 fold excess

of flux to reagents was used. The use of ratios lower than a 10 fold excess of flux to reagents yielded smaller crystals, and higher ratios yielded comparable results. This observation is consistent with what has been reported in the literature for the crystal growth of other compositions of this structure type, including $\text{Ca}_3\text{NaRuO}_6$ [20], $\text{Ba}_{1.06}(\text{Cu}_{0.33}\text{Ir}_{0.67})\text{O}_3$ [20], $\text{Ba}_8\text{CoRh}_6\text{O}_{21}$ [30], $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ [25], and $\text{Ba}_{12}\text{Rh}_{9.25}\text{Ir}_{1.75}\text{O}_{33}$ [23].

3.2 Structure Analysis

The parent structure of the title compounds, $\text{Ba}_4\text{Pt}_3\text{O}_9$, crystallizes in an incommensurate structure that was first solved using the Rietveld method by Darriet et al. [31], who determined that it is an $n = 3$, $m = 1$ member of the 2H-perovskite related oxide family ($\text{A}_{3n+3m}\text{A}'_n\text{B}_{3m+n}\text{O}_{9m+6n}$), shown in Fig. 7.

The idealized $n = 3$, $m = 1$ structure of $\text{Ba}_4\text{Pt(II)Pt(IV)}_2\text{O}_9$, as shown in Fig 4, contains infinite chains of face shared octahedra and trigonal prisms, with an average repeat unit of two octahedra for every one trigonal prism. The larger Pt(II) ($0.80 \text{ \AA}$) cations are located in the trigonal prismatic sites whereas the smaller Pt(IV) ($0.625 \text{ \AA}$) cations occupy the octahedral sites. The a lattice parameter can be understood as the distance between the chains, and the c lattice parameter as the length of the chain per unit cell. However, the actual modulated structure is better described as having two independent c parameters for the $[(\text{A}'\text{B})\text{O}_3]_\infty$ and $[\text{A}]_\infty$ subcells, respectively. The ratio of these c parameters provides a good approximation of the stacking sequence of trigonal prisms to octahedra, which is useful for determining the overall repeat sequence in the structure.

For incommensurate structures belonging to this family, it is often easier to conceptualize this structure using the general formula $A_{1+x}(A'_xB_{1-x})O_3$, where, for the average $Ba_4Pt(II)Pt(IV)_2O_9$ structure, $x = 1/3$. Based on the aforementioned $c_1 / c_2 = (1+x) / 2$ relationship, the ratio of the c lattice parameters for each sub-cell should be 0.667, which is in excellent agreement with the value of $2.85 \text{ \AA} (c_1) / 4.31 \text{ \AA} (c_2) = 0.661$, determined by powder diffraction data that was analyzed using the superspacegroup formalism [13,31]. The ratio of trigonal prisms to octahedra along the c_1 sub-cell, which was experimentally determined to be 1:2, agrees well with the equation $N_{\text{prisms}} / N_{\text{octahedra}} = x / (1-x)$, providing a close value of 0.48.

As previously discussed, small changes in reaction conditions can result in large structural changes in this family of oxides, sometimes making the difference between a commensurate and incommensurate phase. While the complete process by which incommensurate structures form is unclear, it has been suggested that oxygen uptake during the heating or cooling cycle of a synthesis can lead to oxygen incorporation into the face-sharing polyhedral $[(A',B)O_3]_{\infty}$ chains [11]. This oxygen uptake causes trigonal prismatic sites, which are on average 1.7 times the height of a regular octahedron, to split into two octahedra, thus changing the length of the c_1 axis of the $[(A',B)O_3]_{\infty}$ subcell without concomitantly changing the length of the c_2 axis of the $[A]_{\infty}$ subcell. It is empirically uncertain if the slow cool times required for crystal formation caused increased susceptibility to oxygen uptake, but this is a reasonable possibility that may explain the incommensurate nature of the parent compound and of all subsequent substitutional variants.

Synthetically, the goal was to incorporate divalent cations into the trigonal prismatic sites by selecting cations having ionic radii that are larger than that of Pt(IV) and close to that of Pt(II). Hence, the assumption for the crystal growth of the series $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Mg}$) was that the M(II) cation would replace Pt(II) in the trigonal prismatic site. Pt(IV) typically occupies the octahedral site in this family of structures and metals larger than the Pt(IV) cation are expected to occupy the trigonal prismatic M site in this formula and only if additional M(II) is incorporated, substitute for the Pt(IV) in the octahedral site. A table of ionic radii as a function of oxidation state and crystal field splitting for the substituted cations can be found in Table 2 [32].

The evaluation of the EDS data combined with an analysis and comparison of the powder X-ray diffraction data of the parent $\text{Ba}_4\text{Pt}_3\text{O}_9$, shown in Fig. 8, with the diffraction data of the divalent metal substituted species, permits us to propose that in all cases at least a partial replacement of the Pt(II) with the respective metal has occurred and that the $\text{Ba}_4\text{Pt}_3\text{O}_9$ structure was substantially maintained.

To determine the octahedral and trigonal prismatic repeat sequence in the infinite chains, the c_1 and c_2 sub-cell lattice parameters were determined from powder diffraction data analyzed using the JADE software. Although it is expected that substituting for Pt(II) would change the c lattice parameter, the distances between the infinite chains, reflected by the a lattice parameter, should change only minimally. Using the a lattice parameter of 10.098 Å of $\text{Ba}_4\text{Pt}_3\text{O}_9$, both the c_1 and c_2 lattice parameters were determined for each substitutional variant. The quotient of c_1/c_2 can be used with the aforementioned equations to determine an x value, thus obtaining a reasonable description of the overall structure according to the general formula $\text{A}_{1+x}(\text{A}'_x\text{B}_{1-x})\text{O}_3$. It is important to note that

although the x value can determine the layer stacking and, hence, an overall structure, it does not dictate which elements fill these crystallographic sites. A summary of lattice parameters, x values, ratios of trigonal prisms to octahedra, and approximate stoichiometries for all title compounds can be found in Table 3. A more detailed analysis of c parameter determination is included in the Supplemental Information.

It is known that trigonal prismatic sites can convert to two octahedral sites under oxidizing conditions, thereby changing the modulation vector q of the structure. Hence, while we believe that the structure is substantially maintained, the specific modulation vector may well have changed slightly, thereby resulting in a very similar incommensurate structure with, a slightly different repeat sequence of octahedra and trigonal prisms in the chains. The “average” structure, however, is thought to remain substantially the same, which is consistent with the determined x values reported in Table 3, suggesting an approximate 1 : 2 ratio of trigonal prisms to octahedra.

In addition to determining the overall structure from the diffraction patterns, suggested stoichiometries were obtained from EDS data, found in Table 4. As a qualitative technique, these ratios are rough estimations of the overall elemental composition; nonetheless, this data indicates a ratio of dopant to platinum ranging from 1 : 1.5 to 1 : 2.5, bracketing the expected value of 1 : 2.

To improve on the EDS data, magnetic susceptibility data were collected for the compositions containing one of the magnetic cations, Co, Ni, and Cu, shown in Figures 9, 10 and 11. For all compounds, the formula weight per magnetic M ion was determined such that the observed moment agreed with the expected moment for the respective cation. The M ion concentration was then determined by finding the value z such that the

formula weight of $\text{Ba}_{y/z}\text{M}_1\text{Pt}_{(3-z)/z}\text{O}_{9/z}$ equaled the determined formula weight, where y is equal to the Ba stoichiometry determined from the lattice parameter analysis, see Table 3. Of course, using the observed moment to determine the magnetic cation content is complicated by the wide range of published values of μ_{eff} for most first row transition metals and thus, intrinsically, this approach involves substantial uncertainty. We therefore calculated a range of formulas for each analogue with the high M concentration of the range being the spin only case and the low M concentration of the range being the maximum typically observed moment due to spin orbit coupling [33]. A detailed description of the magnetic data analysis for $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ (M = Co, Ni, Cu) is provided in the Supplemental Information.

The magnetic susceptibility of $\text{Ba}_4\text{Cu}_z\text{Pt}_{3-z}\text{O}_9$ is shown in Figure 9. The susceptibility follows a modified Curie-Weiss behavior, $\chi = \chi_0 + C/(T - \theta)$, where χ_0 is a temperature independent diamagnetic contribution. As χ_0 will vary based on the formula, the diamagnetic contribution was subtracted from the raw moment data instead of the susceptibility data. Using the calculated spin only moment for Cu(II) of $1.73 \mu_{\text{B}}/\text{Cu}$, the formula weight of $\text{Ba}_4(\text{Cu}_y\text{Pt}_{z-y})_z\text{Pt}_{3-z}\text{O}_9$ was found to be 818.2 g/mol Cu. The formula weight corresponds to the formula $\text{Ba}_4\text{Cu}_{1.35}\text{Pt}_{1.65}\text{O}_9$. Based on the stoichiometry $\text{Ba}_4\text{Cu}'\text{Pt}_2\text{O}_9$ determined from the lattice parameter analysis, the formula $\text{Ba}_4\text{Cu}_{1.35}\text{Pt}_{1.65}\text{O}_9$ would require Cu(II) to dope onto the octahedral site which is typically occupied by Pt(IV). This is not expected due to the large size difference between Pt(IV) and Cu(II). For this reason, the actual composition for the high M content end of the range is believed to be $\text{Ba}_4\text{CuPt}_2\text{O}_9$. Based on this formula, the effective moment is $2.05 \mu_{\text{B}}/\text{Cu}$, which falls within the range of $1.7 - 2.2 \mu_{\text{B}}/\text{Cu}$ typically observed for Cu(II) [33]

and suggests that some spin-orbit coupling occurs, i.e. that the spin only approximation is not accurate in this case. If the high end of the observed moment range is used, a formula weight of 1320.1 g/mol Cu is obtained which corresponds to a composition of $\text{Ba}_4(\text{Cu}_{0.88}\text{Pt}_{0.12})\text{Pt}_2\text{O}_9$. The magnetic data coupled with the lattice parameter analysis therefore provides a range for the Cu concentration of 0.88 – 1.00/F.U.

The magnetic susceptibility and $2.827(\chi_m T)^{1/2}$ of $\text{Ba}_{3.98}(\text{Ni}_y\text{Pt}_{z-y})_z\text{Pt}_{3-z}\text{O}_9$ are shown in Figure 10. The susceptibility does not follow Curie-Weiss behavior. Since a χ_0 could not be calculated from the data, we subtracted a diamagnetic contribution that was determined based on the Cu data, as it is reasonable to expect the diamagnetic moment per unit mass to be similar for the Ni and Cu analogues, given the similarity between the two compounds. Due to the non-Curie Weiss behavior, the observed moment is approximated as the value of $2.827(\chi_m T)^{1/2}$ at 300K. Based on the calculated spin only moment for Ni(II) of $2.83 \mu_B/\text{Ni}$, the formula weight of $\text{Ba}_{3.98}(\text{Ni}_y\text{Pt}_{z-y})_z\text{Pt}_{3-z}\text{O}_9$ was found to be 1271.4 g/mol Ni. This formula weight corresponds to a stoichiometry of $\text{Ba}_{3.98}\text{Ni}_{1.00}\text{Pt}_{2.00}\text{O}_9$. Considering the formula $\text{A}_{3.98}\text{A}'_{0.98}\text{B}_{2.02}\text{O}_9$ determined from the lattice parameter analysis, the stoichiometry $\text{Ba}_{3.98}\text{Ni}_{1.00}\text{Pt}_{2.00}\text{O}_9$ would require Ni(II) to dope onto the octahedral site, which is not expected due to the large size difference. Therefore, the formula for the maximum Ni concentration is believed to be $\text{Ba}_{3.98}\text{Ni}_{0.98}\text{Pt}_{2.02}\text{O}_9$. The range of typically observed moments for Ni(II) is 2.8-4.0 μ_B/Ni [33]. The high end of this range would provide a formula weight of 2743.6 g/mol Ni corresponding to a composition of $\text{Ba}_{3.98}(\text{Ni}_{0.44}\text{Pt}_{0.54})\text{Pt}_{2.02}\text{O}_9$. The magnetic data coupled with the lattice parameter analysis therefore provides a range for the Ni concentration of 0.44 – 0.98/F.U.

The magnetic susceptibility of $\text{Ba}_{4.05}(\text{Co}_y\text{Pt}_{z-y})_z\text{Pt}_{3-x}\text{O}_9$ is shown in Figure 11 and follows Curie-Weiss behavior with no indication of an appreciable diamagnetic contribution, which is not unexpected given the much larger moment of Co compared to Cu. The analysis of the magnetism is considerably more difficult for the Co analogue as Co is known to be able to adopt multiple oxidation states, namely Co(II), Co(III) and Co(IV), and has been found to mix onto the octahedral site in related compounds [34]. Two cases which will be considered here are Co(II) substituting onto the trigonal prisms, similar to the other M cations, and equal amounts of Co(III) doping onto the trigonal prism and octahedral sites, such that charge balance is maintained. In the first case, Co(II) substituting onto the trigonal prisms, the Co must be high spin based on the observed moment and provides a range of compositions from $\text{Ba}_{4.05}(\text{Co}_{0.82}\text{Pt}_{0.23})\text{Pt}_{1.95}\text{O}_9$ (spin only) to $\text{Ba}_{4.05}(\text{Co}_{0.47}\text{Pt}_{0.58})\text{Pt}_{1.95}\text{O}_9$ (maximum typically observed spin-orbit coupling, $5.2 \mu_B/\text{Co(II)}$) [33]. In the second case, Co(III) doping onto both sites, one or both of the Co(III) sites can be high spin, as low spin Co(III) is diamagnetic. If one site is high spin, a range of compositions from $\text{Ba}_{4.05}(\text{Co}_{0.5}\text{Pt}_{0.55})(\text{Co}_{0.5}\text{Pt}_{1.45})\text{O}_9$ (spin only) to $\text{Ba}_{4.05}(\text{Co}_{0.45}\text{Pt}_{0.6})(\text{Co}_{0.45}\text{Pt}_{1.5})\text{O}_9$ (maximum typically observed spin-orbit coupling, $5.4 \mu_B/\text{Co(III)}$) is obtained [33]. If both sites are high spin, a range of compositions from $\text{Ba}_{4.05}(\text{Co}_{0.26}\text{Pt}_{0.79})(\text{Co}_{0.26}\text{Pt}_{1.69})\text{O}_9$ (spin only) to $\text{Ba}_{4.05}(\text{Co}_{0.24}\text{Pt}_{0.81})(\text{Co}_{0.24}\text{Pt}_{1.71})\text{O}_9$ (spin orbit coupling). Therefore, considering only the two cases described above, the magnetic data coupled with the lattice parameter analysis therefore provides a range for the Co concentration of 0.47 – 1.00/F.U.

Table 5 summarizes the possible compositions based on magnetic susceptibility data, and Figure 12 graphically shows this information including the EDS data. This data,

coupled with lattice parameter analysis, indicates we were successful in the substitution of M(II) cations for Pt(II) in trigonal prismatic sites, resulting in an approximate composition of $\text{Ba}_4\text{MPt}_2\text{O}_9$. The targeted substitution of divalent cations (Mn, Co, Ni, Cu, Zn, Mg) into the trigonal prisms, otherwise occupied by Pt(II), served two purposes. The first was to incorporate magnetic ions into the structure. In the trigonal prismatic site, Pt(II), d^8 , possesses two unpaired electrons; however, Pt(II) has shifted into the faces of the trigonal prism to take on a pseudo square-planar coordination environment, as has been observed for Cu(II). In that coordination environment Pt(II) has no unpaired electrons and is expected to be diamagnetic. This was confirmed by running a magnetic susceptibility measurement on the parent structure $\text{Ba}_4\text{Pt}_3\text{O}_9$, which was diamagnetic at 300 K. Therefore, the addition of first row transition metals with unpaired electrons to this structure has the potential of leading to interesting magnetism, as is observed in the case of nickel. The second purpose for substituting divalent cations into the trigonal prismatic sites was the expectation that cations such as zinc or magnesium would have no preference for a square planar coordination environment and, therefore, would be expected to occupy the center of the trigonal prism, thus perhaps favoring a commensurate structure. This, however, was not observed.

4. Conclusion

The series $\text{Ba}_4\text{M}_z\text{Pt}_{3-z}\text{O}_9$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Mg}, \text{Pt}$) was grown as large, well faceted single crystals that crystallize in the 2H hexagonal perovskite related structure type. The known structure of $\text{Ba}_4\text{Pt}_3\text{O}_9$ was used to identify the structure type of the grown crystals, which consisted of substitutional variants in which divalent cations substituted for the platinum in the trigonal prismatic site, with apparently some Co(III) or

Co(IV) substituting into the octahedral sites. The structures of all compositional substitutions were determined to be incommensurate by X-ray diffraction. Powder X-ray diffraction, energy dispersive spectroscopy, and magnetic susceptibility measurements were used to characterize the compositional substitutions made to the parent structure and identify their structural similarity.

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TABLES

Table 1: Summary of reaction conditions

Composition	Temperature (°C)	Dwell (h)	Cool Rate (°C/h)	Flux	Dopant	Crystal Morphology	Crystal Size (mm)	Yield (%)
Ba ₄ Pt ₃ O ₉	1150	10	5	K ₂ CO ₃	N/A	Rods and plates	1.3 x 0.5	99
Ba ₄ Pt _{3-z} Co _z O ₉	1150	10	5	K ₂ CO ₃	CoCO ₃	Rods and plates	1.0 x 0.4	92
Ba ₄ Pt _{3-z} Ni _z O ₉	1150	10	5	K ₂ CO ₃	NiO	Rods and plates	1.1 x 0.5	91
Ba ₄ Pt _{3-z} Cu _z O ₉	1150	10	5	K ₂ CO ₃	CuO	Rods and plates	1.4 x 0.5	93
Ba ₄ Pt _{3-z} Zn _z O ₉	1150	10	5	K ₂ CO ₃	ZnO	Rods and plates	1.3 x 0.6	95
Ba ₄ Pt _{3-z} Mg _z O ₉	1150	10	5	K ₂ CO ₃	MgO	Rods and plates	1.0 x 0.3	94

Table 2: Summary of ionic radii as a function of oxidation state [32]

Element	Oxidation State	Ionic Radii (Å)
Pt	II	0.80
	IV	0.625
Co	II	0.745 (H.S.) 0.65 (L.S.)
	III	0.61 (H.S.) 0.545 (L.S.)
	IV	0.53 (H.S.)
Ni	II	0.69
	III	0.60 (H.S.) 0.56 (L.S.)
Cu	II	0.73
Zn	II	0.74
Mg	II	0.72

Table 3: Summary of lattice parameters, stacking sequence and estimated stoichiometry

Dopant	C ₁	C ₂	Prism / Octahedra	X value*	Approx. Stoichiometry
Platinum	2.85	4.31	0.476	0.325	A ₄ A'B ₂ O ₉
Cobalt	2.77(1)	4.10(1)	0.514	0.351(1)	A _{4.05} A' _{1.05} B _{1.95}
Nickel	2.78(1)	4.20(2)	0.479	0.324(2)	A _{3.98} A' _{0.98} B _{2.02} O ₉
Copper	2.79(1)	4.19(2)	0.496	0.332(2)	A ₄ A'B ₂ O ₉
Magnesium	2.80(1)	4.19(2)	0.507	0.337(2)	A _{4.01} A' _{1.01} B _{1.99} O ₉
Zinc	2.81(1)	4.21(1)	0.504	0.335(1)	A ₄ A'B ₂ O ₉

* Based on the general formula A_{1+x}(A'_xB_{1-x})O₃

Table 4: Stoichiometries determined from EDS data

Dopant	Stoichiometry
Platinum	Ba _{3.4(2)} Pt _{3.0(2)} O _x
Cobalt	Ba _{3.0(2)} Co _{0.6(4)} Pt _{2.4(2)} O _x
Nickel	Ba _{3.2(2)} Ni _{0.9(4)} Pt _{2.1(3)} O _x
Copper	Ba _{3.3(3)} Cu _{0.9(2)} Pt _{2.1(3)} O _x
Magnesium	Ba _{2.6(3)} Mg _{1.1(3)} Pt _{1.9(1)} O _x
Zinc	Ba _{2.6(2)} Zn _{1.2(2)} Pt _{1.8(2)} O _x

Table 5: Magnetic moments of end member compositions of the potential M dopant range for $\text{Ba}_{3+z}(\text{M}_y\text{Pt}_{z-y})_z\text{Pt}_{3-z}\text{O}_9$ determined from the magnetic data and lattice parameter analysis.

Dopant	Stoichiometry	μ_{eff} (μ_B/M)	μ_{obs} (μ_B/M) [33]
Cobalt(II)	$\text{Ba}_{4.05}(\text{Co}_{0.82}\text{Pt}_{0.23})\text{Pt}_{1.95}\text{O}_9$	3.87	4.1-5.2 (H.S.)
	$\text{Ba}_{4.05}(\text{Co}_{0.47}\text{Pt}_{0.58})\text{Pt}_{1.95}\text{O}_9$	5.2	
Cobalt(III) 1 site magnetic	$\text{Ba}_{4.05}(\text{Co}_{0.5}\text{Pt}_{0.55})(\text{Co}_{0.5}\text{Pt}_{1.45})\text{O}_9$	4.90	4.9-5.4 (H.S.)
	$\text{Ba}_{4.05}(\text{Co}_{0.45}\text{Pt}_{0.6})(\text{Co}_{0.45}\text{Pt}_{1.5})\text{O}_9$	5.40	
Cobalt(III) 2 sites magnetic	$\text{Ba}_{4.05}(\text{Co}_{0.26}\text{Pt}_{0.79})(\text{Co}_{0.26}\text{Pt}_{1.69})\text{O}_9$	4.90	4.9-5.4 (H.S.)
	$\text{Ba}_{4.05}(\text{Co}_{0.24}\text{Pt}_{0.81})(\text{Co}_{0.24}\text{Pt}_{1.71})\text{O}_9$	5.40	
Nickel	$\text{Ba}_{3.98}\text{Ni}_{0.98}\text{Pt}_{2.02}\text{O}_9$	2.84	2.8-4.0
	$\text{Ba}_{3.98}(\text{Ni}_{0.44}\text{Pt}_{0.54})\text{Pt}_{2.02}\text{O}_9$	4.40	
Copper	$\text{Ba}_4\text{CuPt}_2\text{O}_9$	2.05	1.7-2.2
	$\text{Ba}_4(\text{Cu}_{0.88}\text{Pt}_{0.12})\text{Pt}_2\text{O}_9$	2.20	

Figures

Figure 1. $[A_3O_9]$ layer, known as m , with blue spheres as A site atom and white spheres as oxygen. ABC or AB stacking of these layers results in the traditional cubic or hexagonal perovskite, respectively.

Figure 2. $[A_3A'O_6]$ layer, known as n , with blue spheres as A site atom, green spheres as A' atom, and white spheres as oxygen. This layer is unique to 2-H perovskite related oxides, resulting in the formation of trigonal prismatic sites.

Figure 3. Possible stacking motifs, with $BaNiO_3$ resulting from ABAB stacking of $[A_3O_9]$ m layers with the B site cation occupying the resulting octahedra, Sr_4PtO_6 resulting from ABAB stacking of $[A_3A'O_6]$ n layers with the B cation occupying both octahedra and trigonal prismatic sites, and $Ba_4Pt_3O_9$ as one of many possible examples of mixed stacking of both n and m layers.

Figure 4: Representative optical image of $\text{Ba}_4\text{A}'\text{Pt}_2\text{O}_9$

Figure 5. SEM photograph of $\text{Ba}_4\text{Pt}_3\text{O}_9$, approximately 1.3 mm in length.

Figure 6. SEM photograph of $\text{Ba}_4\text{Cu}_z\text{Pt}_{3-z}\text{O}_9$, approximately 1.4 mm in length.

Figure 7. Average commensurate unit cell of $\text{Ba}_4\text{Pt}_3\text{O}_9$ with Pt^{4+} shown as grey octahedra, Pt^{2+} shown as green trigonal prisms, and Ba as blue spheres.

Figure 8. Powder X-ray diffraction patterns of parent structure $\text{Ba}_4\text{Pt}_3\text{O}_9$, shown in red, and $\text{Ba}_4\text{Ni}_z\text{Pt}_{3-z}\text{O}_9$, shown in blue.

Figure 9: Temperature dependent susceptibility and inverse susceptibility for $\text{Ba}_4(\text{Cu}_y\text{Pt}_{3-y})\text{Pt}_2\text{O}_9$ based on the two end member compositions of the potential Cu range determined from the magnetic data and lattice parameter analysis.

Figure 10: Temperature dependent susceptibility and $2.827((\chi-\chi_0)T)^{1/2}$ for $\text{Ba}_{3.98}(\text{Ni}_y\text{Pt}_{3-y})_2\text{Pt}_{2.02}\text{O}_9$ based on the two end member compositions of the potential Ni range determined from the magnetic data and lattice parameter analysis.

Figure 11: Temperature dependent susceptibility and inverse susceptibility for $\text{Ba}_{4.05}(\text{Co}_y\text{Pt}_{3-y})\text{Pt}_3\text{O}_9$ based on the two end member compositions of the potential Co range determined from the magnetic data and lattice parameter analysis. The susceptibility is plotted per mole magnetic Co in the case of $\text{Ba}_{4.05}(\text{Co}_{0.5}\text{Pt}_{0.55})(\text{Co}_{0.5}\text{Pt}_{1.45})\text{O}_9$ where only one Co site is magnetic.

Figure 12: Dopant concentration in $\text{Ba}_{3+z}(\text{M}_y\text{Pt}_{z-y})_z\text{Pt}_{3-z}\text{O}_9$ based on EDS and magnetic data.

Graphical Abstract

SEM image and average commensurate unit cell of $\text{Ba}_4\text{Pt}_3\text{O}_9$.