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Structure Determination of the One-Dimensional Compound Sr_3ZnPtO_6, Containing Zinc in a Highly Unusual Trigonal Prismatic Coordination Environment

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We report the synthesis and structure of a new zinc-containing strontium platinum oxide, Sr_3ZnPtO_6, in which zinc is present in a highly unusual trigonal prismatic coordination environment. The common coordination environment for zinc in oxides, as well as in most other materials, is tetrahedral.[1] Zinc(II), with its filled d shell, exhibits few of the characteristic properties of the transition metals. Since the d^{10} configuration affords no crystal field stabilization energy, the stereochemistry around the zinc cation is often found in the literature as a function of the size and polarizability of the zinc, as well as of the steric requirements of the ligand. Consequently, zinc usually prefers a 4-coordinate, tetrahedral environment. This is the case in ZnO and ZnS, as well as in numerous zinc-containing ferrites.[2] There are some examples of zinc in 6-fold, octahedral coordination, such as in $[Zn(NH_3)_6]^{2+}$,[3] and even in higher coordination for bidentate oxygen donor ligands, such as NO_3^- or NO_2^-.[1] However, there are few, if any, examples of zinc in trigonal prismatic coordination in the literature. In this paper we present the synthesis and structural characterization of Sr_3ZnPtO_6, containing zinc in a trigonal prismatic coordination.

Experimental Section

The Sr_3ZnPtO_6 powder sample was prepared via a solid state reaction using $SrCO_3$ (Alfa, 99.99%), ZnO (Alfa, 99.99%), and Pt metal grains (Engelhard, 99.95%) in a platinum crucible. Stoichiometric quantities were ground and initially calcined in air at 1073 K for 10 h followed by three heat treatments at 1273 K for 3 days each, with intermittent grindings. Intermediate phase-analysis by powder X-ray diffraction showed strontium-containing impurity phases due to small losses of zinc. Therefore, excess of ZnO was added to the sample before the final heat treatment at 1273 K for 2 days. The brownish yellow powder sample used for this structure determination contained two phases, Sr_3ZnPtO_6, described below, and a small amount of unreacted ZnO.[4] Powder X-ray diffraction was performed at 295 K using a Siemens D5000 diffractometer using Cu Kα radiation (graphite monochromator). The step scan covered the range 2.00−118.01° in steps of 0.03° in 2θ. Three step scans were collected and summed.

Structure refinements of Sr_3ZnPtO_6 were carried out in the space group $R\bar{3}c$ (No. 167), using the structure of Sr_4PtO_6[5] as the starting model. On the basis of our experience with the structurally related compound Sr_3NiPtO_6,[6] zinc was assigned to the trigonal prismatic site 6a and strontium to the 18e site. Structure refinements were performed using the Rietveld method[7] implemented in the computer program GSAS.[8] The wurtzite structure of ZnO is known,[9] and the ZnO phase was included as such in the refinement. The profiles of the diffraction peaks of Sr_3ZnPtO_6 were described by a pseudo-Voigt function[10] varying two Gaussian half-width parameters, U and W, and one variable accounting for the Lorentzian isotropic strain, X. Refinement of peak asymmetry was allowed. The background was described by a shifted Chebyshev polynomial function with six refinable coefficients. One parameter was used for the refinement of the zero-point offset and one for the histogram scale factor. Cell parameters for Sr_3ZnPtO_6 were refined to $a = 9.6192(1)$ Å and $c = 11.2174(2)$ Å. The atomic positions and displacement parameters are listed in Table 1, and bond distances are listed in Table 2. The final agreement factors were $R_p = 7.15\%$, $R_{wp} = 9.59\%$, and $\chi^2 = 2.49$. The observed intensities, the calculated pattern, and their differences are shown in Figure 1. Since a trigonal prismatic coordination for zinc is rather unusual, attempts were made to refine mixed occupancies in the structure by placing platinum atoms on the zinc positions and vice versa to confirm the accuracy of the model. Similarly, random-site substitution between zinc and strontium was tested. No significant (<1%) site mixing was found for either case. It was previously reported[2] that certain reaction conditions of zinc-containing oxides can lead to the formation of stacking faults and even the formation of different polytypes. Consequently, stacking faults within the one-dimensional chains are possible and were detected as some peak broadening; therefore, one stacking fault anisotropy parameter was included in the refinement.

Table 1. Results from the Rietveld Refinement of the Sr_3ZnPtO_6 Crystal Structure

atom	site	x	y	z	B (Å^2)
Sr	18e	0.3648(1)	0	$^1/_4$	0.0126(3)
Zn	6a	0	0	$^1/_4$	0.0162(7)
Pt	6b	0	0	0	0.0090(3)
O	36f	0.1747(5)	0.0230(6)	0.1137(4)	0.0010(1)

Table 2. Selected Bond Distances (Å) for Sr_3ZnPtO_6

Zn−Sr	3.5095(10), 3.5911(4)	Zn−O	2.199(4)
Zn−Pt	2.80436(5)	Pt−O	2.032(4)
Sr−Pt	3.2054(4)	Sr−O	2.477(4), 2.622(5) 2.664(4), 2.733(5)

Results and Discussion

The rhombohedral structure of Sr_3ZnPtO_6 consists of one-dimensional infinite chains of alternating face-sharing PtO_6 octahedra and ZnO_6 trigonal prisms. The trigonal prismatic coordination environment of the zinc is shown in greater detail in Figure 2. The collinearity of the metals in the one-dimensional chain can be seen clearly, as well as the slight distortion of the trigonal prism described by the oxygen atoms. These chains are surrounded by a strontium oxygen chainlike network (Figure 3) as has been seen in Sr_4PtO_6,[5] Sr_3NiPtO_6,[6] Ba_3NaNbO_6,[11] and Sr_3NaBiO_6.[12]

In the three isostructural platinates Sr_3ZnPtO_6, Sr_3NiPtO_6, and Sr_4PtO_6, the atomic distances of the trigonal prismatic site are similar.[13] The relative size of the metal(II) cation, $r(Zn^{2+}) = 0.74$ Å, $r(Sr^{2+}) = 1.18$ Å, and $r(Ni^{2+}) = 0.69$ Å,[14] in the trigonal prismatic site, does not appear to affect significantly either the structure or the metal−oxygen distances. Consequently, the

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(13) Bond lengths: Zn−O = 2.199(4) Å, Zn−Pt = 2.80436(5) Å, Ni−O = 2.212(5) Å, Ni−Pt = 2.80686(7) Å (C. Lampe-Önnerud, unpublished work), Sr−O = 2.33 Å, Sr−Pt = 2.97 Å (based on the crystallographic data of Ben-Dor[5]).

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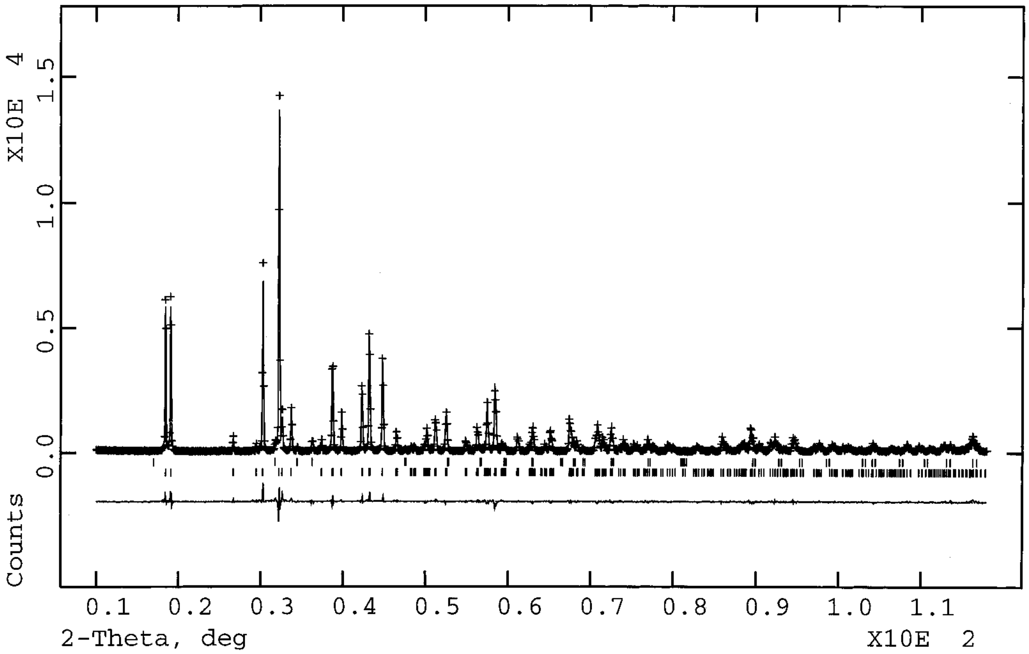

Figure 1. Observed (dotted) and calculated (solid line) X-ray profiles. Tic marks below the diffractogram represent Sr_3ZnPtO_6 (bottom) and ZnO (top), respectively. The difference line, observed minus calculated, is located at the bottom of the figure.

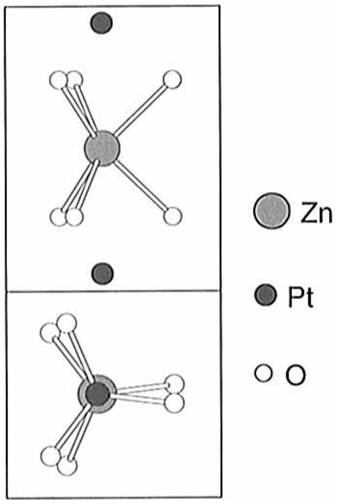

Figure 2. Close-up of the trigonal prismatic site in Sr_3ZnPtO_6. The top portion emphasizes the collinearity between zinc and platinum along the chain. The slight distortion of the trigonal prism viewed down the *c* axis is revealed in the bottom portion of the figure. Atomic sizes are scaled according to thermal parameters.

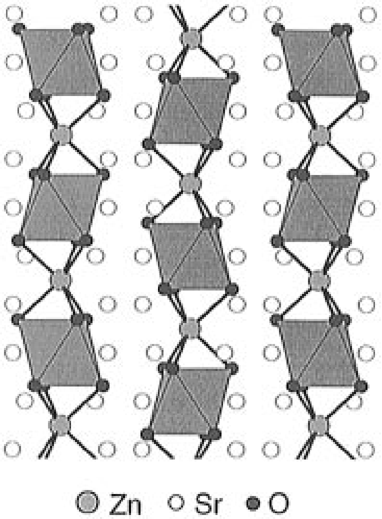

Figure 3. One-dimensional chain structure of Sr_3ZnPtO_6 viewed along the *b*-axis, showing polyhedral representations of the PtO_6 octahedra and ball and stick representations for all other atoms. Atomic sizes are scaled according to thermal parameters.

trigonal prismatic site could be viewed as resulting from two sterically rigid tridentate PtO_6 ligands held in place by the strontium cations. It is likely that the geometry of this site can also be influenced by crystal field stabilization effects. This may explain why Cu^{2+} (r = 0.73 Å),[14] which also can be substituted for the divalent metal cation in the strontium–platinum–oxygen system, changes the structure from rhombohedral to monoclinic.[15] With the exception of the copper ion, which is located in a distorted square planar coordination, the atomic arrangement is similar to that found in the Sr_4PtO_6 parent and related structures.[5,16,17] In the absence of crystal field stabilization energies, it appears that the presence of the octahedral PtO_6 units influences the geometry of this one-dimensional chain structure.

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Supporting Information Available: The Rietveld refinement output including refined parameters and atomic bond distances and angles (26 pages). Ordering information is given on any current masthead page.

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