# **Inorganic Chemistry**

# PbMn(IV)TeO<sub>6</sub>: A New Noncentrosymmetric Layered Honeycomb Magnetic Oxide

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# **S** Supporting Information

**ABSTRACT:** PbMnTeO<sub>6</sub>, a new noncentrosymmetric layered magnetic oxide was synthesized and characterized. The crystal structure is hexagonal, with space group  $P\overline{6}2m$  (No. 189), and consists of edge-sharing  $(Mn^{4+}/Te^{6+})O_6$  trigonal prisms that form honeycomb-like two-dimensional layers with  $Pb^{2+}$  ions between the layers. The structural difference between PbMnTeO<sub>6</sub>, with disordered/trigonal prisms of  $Mn^{4+}/Te^{6+}$ , versus the similar chiral SrGeTeO<sub>6</sub> (space group P312), with long-range order of Ge<sup>4+</sup> and Te<sup>6+</sup> in octahedral coordination, is attributed to a difference in the electronic



effects of Ge<sup>4+</sup> and Mn<sup>4+</sup>. Temperature-dependent second harmonic generation by PbMnTeO<sub>6</sub> confirmed the noncentrosymmetric character between 12 and 873 K. Magnetic measurements indicated antiferromagnetic order at  $T_N \approx 20$  K and a frustration parameter ( $|\theta|/T_N$ ) of ~2.16.

# INTRODUCTION

Noncentrosymmetric (NCS) oxide materials have been studied for decades because of their interesting physical properties, including ferroelectricity, piezoelectricity, pyroelectricity, multi-ferroicity, magnetoelectricity, and second harmonic generation (SHG).<sup>1–5</sup> Recently, much experimental research focused on finding new multiferroic and magnetoelectric transition metal oxides along with theoretical calculations to understand the origin of multiferroic/magnetoelectric behavior and to predict new structural chemical properties for the design of new materials with optimal characteristics.<sup>6–11</sup>

The crystal structure of PbSb<sub>2</sub>O<sub>6</sub>-type materials (general formula ABB'O<sub>6</sub>) basically exhibit a layered structure (centrosymmetric space group  $P\overline{3}1m$ , No. 162) consisting of edge-shared B/B'O<sub>6</sub> octahedra that form honeycomb-like layers separated by A cations (AO<sub>6</sub> octahedra).<sup>12</sup> PbSb<sub>2</sub>O<sub>6</sub>-type compounds containing 3d or 4d transition metals show interesting magnetic behavior. For example, divalent 3d transition metal arsenates AAs<sub>2</sub>O<sub>6</sub> (A = Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>) exhibit long-range antiferromagnetic ordering at around 30 K,<sup>13,14</sup> and the 4d transition metal arsenate Pd(II)As<sub>2</sub>O<sub>6</sub> shows a relatively high Néel temperature ( $T_N$ ) of 140 K.<sup>15,16</sup> More interestingly, SrRu<sub>2</sub>O<sub>6</sub> (Ru<sup>5+</sup>, S = 3/2) shows an extraordinarily high antiferromagnetic transition temperature ( $T_N$ ) of 565 K.<sup>17,18</sup>

If the B and B' cations order crystallographically, the crystal structure adopts the lower-symmetry chiral space group P312 (No. 149).<sup>12</sup> To date, only one compound, SrGeTeO<sub>6</sub>, has been reported with the chiral PbSb<sub>2</sub>O<sub>6</sub>-type structure.<sup>19,20</sup> The

crystal structure of BaGeTeO<sub>6</sub> (P312) was also reported, but it is not isostructural with SrGeTeO<sub>6</sub>.<sup>20</sup> If the substitution of magnetic cations (3d–5d transition metals) into the chiral PbSb<sub>2</sub>O<sub>6</sub> structure is possible, such new phases should be good candidates for the design of new NCS magnetic oxides.

Interestingly, the crystal structure of SrMnTeO<sub>6</sub> was reported with a similar layered structure (NCS space group  $P\bar{6}2m$ , No. 189) as that of SrGeTeO<sub>6</sub>, but it consists of edge-sharing disordered (Mn<sup>4+</sup>/Te<sup>6+</sup>)O<sub>6</sub> trigonal prisms, which also form honeycomb-like layers separated by Sr<sup>2+</sup> cations (SrO<sub>6</sub> trigonal prisms).<sup>21,22</sup> This result suggests that two similar layered structures may be observed in A(II)B(IV)Te(VI)O<sub>6</sub>: the chiral space group P312 or the NCS space group  $P\bar{6}2m$  depending on the B-site cation arrangement.

On the basis of these observations, the exploratory synthesis of  $A(II)M(IV)TeO_6$  (A(II) = Sr, Ba, Pb; M(IV) = V, Mn, Ru, Re, Os, Ir) phases was undertaken to find new multifunctional materials. Here, we report the successful synthesis and characterization of the new NCS compound PbMnTeO<sub>6</sub>.

#### EXPERIMENTAL SECTION

**Reagents.** PbO (Alfa Aesar, 99.99%),  $MnO_2$  (Strem Chemical, 99.995%), and  $H_2TeO_4$ ·2 $H_2O$  (Alfa Aesar, 99+%) were used without any further purification.

**Synthesis.** Polycrystalline PbMnTeO<sub>6</sub> was prepared by a conventional solid-state reaction. Stoichiometric amounts of PbO (0.3348 g,

Received: November 22, 2015

1.5 mmol), MnO<sub>2</sub> (0.1304 g, 1.5 mmol), and TeO<sub>3</sub> (0.2634 g, 1.5 mmol; amorphous TeO<sub>3</sub> was prepared by heating H<sub>2</sub>TeO<sub>4</sub>·2H<sub>2</sub>O at 400 °C for 12 h in air<sup>23</sup>) were thoroughly ground and pressed into a pellet. The pellet wrapped in Pt foil was placed in a quartz tube that was evacuated and flame-sealed. The sealed ampule was heated to 700 °C for 12 h and then cooled to room temperature (the heating and cooling rates were 200 °C/h). After that, the resulting product was washed with dilute HNO<sub>3</sub> solution several times to remove Pb<sub>2</sub>MnTeO<sub>6</sub> impurities<sup>24</sup> (see Figure S1). The final product obtained was dark-brown-black polycrystalline PbMnTeO<sub>6</sub>. Energy-dispersive X-ray spectroscopy (EDX) analysis of the final product PbMnTeO<sub>6</sub> indicated a chemical composition of Pb<sub>0.99(8)</sub>Mn<sub>1.04(7)</sub>Te<sub>0.98(1)</sub>O<sub>x</sub>; thus, the compound is stoichiometric within the standard deviation range of error (see Figure S2).

**Powder X-ray Diffraction.** The final product was characterized by powder X-ray diffraction (PXRD) (Bruker AXS D8 Advance diffractometer, Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å), 40 kV, 30 mA, step scan 10–120°/0.02°/10.5s) for purity and phase identification. Diffraction data analysis and Rietveld refinement were performed with the TOPAS<sup>25</sup> and GSAS-EXPGUI<sup>26</sup> software packages.

**Second Harmonic Generation.** The temperature dependence of the optical SHG by PbMnTeO<sub>6</sub> was measured for a pellet between 12 and 873 K in normal-incidence reflection geometry using an 800  $\pm$  20 nm fundamental input generated by a Ti:sapphire laser (Coherent Libra, 2 mW, 80 fs, 2 kHz). The SHG signal was detected with a photomultiplier tube (Hamamatsu H7926). The sample was cooled and heated at a rate of 6.0 °C/min between 12 and 320 K in a cryostat and 7.0 °C/min between 300 and 873 K on a heating stage.

**Magnetic Measurements.** The magnetic measurements for PbMnTeO<sub>6</sub> were performed with a commercial Quantum Design SQUID magnetometer. The dc magnetic susceptibility data were collected at 2 K  $\leq$  *T*  $\leq$  300 K under applied magnetic fields of 1000 and 10 000 Oe. Isothermal magnetization curves were obtained for magnetic fields –5 T  $\leq$  *H*  $\leq$  5 T at *T* = 2 and 300 K.

# RESULTS AND DISCUSSION

**Synthesis.** Previously, Woodward et al.<sup>20</sup> reported the synthesis and crystal structures of AGeTeO<sub>6</sub> (A = Sr<sup>2+</sup>, Ba<sup>2+</sup>), which were prepared at ~900 °C in air. Because the ionic radii of Mn<sup>4+</sup> and Ge<sup>4+</sup> in a sixfold coordination environment are identical (0.53 Å),<sup>27</sup> the AMn(IV)TeO<sub>6</sub> (A = Sr<sup>2+</sup>, Ba<sup>2+</sup>) phase should also form. Interestingly, Wulff and Müller-Buschbaum<sup>22</sup> reported the crystal structure of SrMnTeO<sub>6</sub> from a single-crystal sample obtained from the reaction of Sr(OH)<sub>2</sub>·8H<sub>2</sub>O, MnCO<sub>3</sub>·xH<sub>2</sub>O, and TeO<sub>2</sub> at 800 °C for 8 days in air, which also produced crystals of Sr<sub>2</sub>MnTeO<sub>6</sub> as a byproduct.<sup>22</sup> However, our attempts to prepare phase-pure AMnTeO<sub>6</sub> (A = Sr<sup>2+</sup>, Ba<sup>2+</sup>) with synthetic methods similar to those used for PbMnTeO<sub>6</sub> have not been successful to date (see Figures S3 and S4).

Structure. Initially, the structural refinements were performed on PXRD data based on the two possible structural models (space group P312, No. 149, for SrGeTeO<sub>6</sub> and space group  $P\overline{6}2m$ , No. 189, for SrMnTeO<sub>6</sub>). The two models gave comparable results by the Le Bail fit ( $R_p = 5.07\%$ ,  $R_{wp} = 6.84\%$ , and  $\chi^2 = 1.43$  for SrGeTeO<sub>6</sub> and  $R_p = 5.09\%$ ,  $R_{wp} = 6.86\%$ , and  $\chi^2 = 1.43$  for SrMnTeO<sub>6</sub>). From Rietveld refinement with the SrGeTeO<sub>6</sub> structure model (space group P312), when the Mn<sup>4+</sup> and Te<sup>6+</sup> ions were fixed as ordered, the thermal parameters of both atoms were negative, and thus, the refinement was unreliable. When the Mn4+ and Te6+ ions were randomly distributed, the refinement was stable with  $R_p$  = 5.39%,  $R_{\rm wp}$  = 7.15%, and  $\chi^2$  = 1.56, but because of the symmetry constraints, this structure had to adopt the highersymmetry centrosymmetric space group  $P\overline{3}1m$  rather than the chiral space group P312.<sup>12</sup> Moreover, the SHG measurements clearly established the NCS character of PbMnTeO<sub>6</sub> (vide

infra). Finally, Rietveld refinement of PbMnTeO<sub>6</sub> with the SrMnTeO<sub>6</sub> structural model (space group  $P\overline{6}2m$ ) yielded  $R_p = 5.18\%$ ,  $R_{wp} = 6.92\%$ , and  $\chi^2 = 1.46$  with lattice parameters of a = b = 5.10143(5) Å, c = 5.39643(6) Å, V = 121.62(4) Å<sup>3</sup>, and Z = 1. The Pb atoms are located at the 1*a* (0, 0, 0) positions, Mn/ Te atoms at the 2*d*  $\binom{2}{3}$ ,  $\binom{1}{3}$ ,  $\binom{1}{2}$  positions, and O atoms at the 6*i* (*x*, 0, *z*) positions in space group  $P\overline{6}2m$ . The Rietveld refinement plot of the PXRD data is shown in Figure 1; atomic coordinates and atomic displacement parameters are summarized in Table 1.



Figure 1. Rietveld refinement plot of the PXRD data for PbMnTeO<sub>6</sub>.

PbMnTeO<sub>6</sub> exhibits a two-dimensional crystal structure consisting of edge-sharing  $Mn(1)/Te(1)O_6$  trigonal prisms that form honeycomb-like layers in the *ab* plane with Pb<sup>2+</sup> cations (PbO<sub>6</sub> trigonal prisms) located between the layers (see Figure 2). The crystal structures of SrGeTeO<sub>6</sub> (chiral space group *P*312) and PbMnTeO<sub>6</sub> (as well as SrMnTeO<sub>6</sub>, NCS space group *P*62*m*) are similar (see Figure 3), but two major differences come from the order/disorder character of the cations and the arrangement of oxygens: ordered/octahedra in SrGeTeO<sub>6</sub> versus disordered/trigonal prisms in PbMnTeO<sub>6</sub> (and SrMnTeO<sub>6</sub>). The origin of these differences is likely due to electronic differences between Mn<sup>4+</sup> and Ge<sup>4+</sup>. Interestingly, these differences affect the long-range ordering of M<sup>4+</sup> cations (M = Mn, Ge) in the layer (Ge<sup>4+</sup>-O-Te<sup>6+</sup>-O-Ge<sup>4+</sup> vs (Mn<sup>4+</sup>/Te<sup>6+</sup>)-O-(Mn<sup>4+</sup>/Te<sup>6+</sup>)).<sup>20</sup>

The Mn(1)/Te(1)–O(1) bond distances in PbMnTeO<sub>6</sub> range between 1.9091(2) and 1.9095(1) Å, and the Mn(1)/Te(1)–O(1)–Mn(1)/Te(1) bond angle is 100.94(4)°. It is noteworthy that the Pb(1)–O(1) bonds in the PbO<sub>6</sub> trigonal prisms are equivalent with lengths of 2.5572(1) Å, which indicates that the 6s<sup>2</sup> lone pair on the Pb<sup>2+</sup> cation is non-stereoactive, as also observed in other Pb<sup>2+</sup> containing layered oxides.<sup>12,28</sup> Selected bond distances and bond angle for PbMnTeO<sub>6</sub> are summarized in Table 2. The local coordination environments are shown in Figure S5. Bond valence sum (BVS) calculations<sup>29,30</sup> resulted in values of 1.80, 3.93, and 6.13 for Pb<sup>2+</sup>, Mn<sup>4+</sup>, and Te<sup>6+</sup>, respectively (see Table 2).

**Second Harmonic Generation.** The SHG intensity for PbMnTeO<sub>6</sub> as a function of temperature is shown in Figure 4. Finite SHG signals were observed over the whole temperature measurement range, confirming that PbMnTeO<sub>6</sub> is NCS. Overall, the SHG intensity gradually decreases in the temperature range up to 873 K. A noncentrosymmetric-to-

Tabl	e 1	. Atomic	Coordinates	and Atomic	Displacement	Parameters	for	PbMnTeC	) <sub>6</sub> "
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	O(1)	6 <i>i</i>	0.6139(1)	0	0.3022(1)	0.0260(2)	1
	Mn(1)/Te(1)	2 <i>d</i>	<sup>2</sup> / <sub>3</sub>	<sup>1</sup> / <sub>3</sub>	<sup>1</sup> / <sub>2</sub>	0.0064(8)	0.5/0.5
	Pb(1)	1 <i>a</i>	0	0	0	0.0063(6)	1
	atom	Wyckoff position	x	у	z	$U_{ m eq}~({ m \AA}^2)^b$	SOF

<sup>*a*</sup>From PXRD Rietveld refinement using space group  $P\overline{6}2m$  (No. 189):  $R_p = 5.18\%$ ,  $R_{wp} = 6.92\%$ , and  $\chi^2 = 1.46$ . Unit cell parameters: a = b = 5.10143(5) Å, c = 5.39643(6) Å, V = 121.6240(30) Å<sup>3</sup>, Z = 1. <sup>*b*</sup> $U_{eq}$  is defined as one-third of the trace of the orthogonal  $U_{ij}$  tensor.



**Figure 2.** Ball-and-stick diagram of the PbMnTeO<sub>6</sub> structure in the (a) bc and (b) ab planes.

centrosymmetric phase transition was observed to be above 873 K, likely ~900 K. The sample was not heated above 873 K in the SHG experiment because a thermogravimetric analysis (TGA) measurement for PbMnTeO<sub>6</sub> at 1023 K in air indicated the decomposition of the compound (see Figures S6 and S7).

Table 2. Selected Bond Distances, Bond Angle, and BVS for PbMnTeO $_6$ 

cation	anion	bond length (Å)	BVS	
Pb(1)	O(1)	$2.5572(1) \times 6$	1.80	
Mn(1)/Te(1)	O(1)	$1.9091(1) \times 2$	3.93/6.13	
	O(1)	$1.9092(5) \times 2$		
	O(1)	$1.9095(1) \times 2$		
	bond a	bond angle (deg)		
Mn(1)/Te(1)-0	D(1) - Mn(1) /	Te(1) 10	0.94(4)	

A pseudosymmetry analysis was performed in order to gain insight into the origin of the noncentrosymmetry in PbMnTeO<sub>6</sub>. The optical SHG intensity gradually decreases with increasing temperature, although it does not reach zero up to 873 K, indicating a second-order phase transition from a noncentrosymmetric phase to a centrosymmetric phase. Assuming that the phase transition is second order, the centrosymmetric phase should belong to supergroups of the noncentrosymmetric  $P\overline{6}2m$  (No. 189) structure shown in Figure 5a. The possible supergroup structures were searched within atomic displacements of 2 Å using the PSEUDO program.<sup>31</sup> We found one possible structure with P6/mmm symmetry. Figure 5b shows the P6/mmm (No. 191) structure along with arrows representing a distortion that leads to the  $P\overline{6}2m$  structure. The distortion corresponds to rotations of oxygen prisms enclosing the Mn/Te sites, which break the



**Figure 3.** Comparison of ball-and-stick diagrams for the three similar crystal structures: (a)  $PbSb_2O_6$  in the *bc* plane,<sup>12</sup> (b) SrGeTeO<sub>6</sub> in the *ab* plane,<sup>20</sup> and (c)  $PbMnTeO_6$  in the *ab* plane (this work).



**Figure 4.** Temperature dependence of the optical SHG intensity for a PbMnTeO<sub>6</sub> pellet between 12 and 873 K. The inset shows the schematic of the SHG experiment, where the sample pellet is irradiated with an 800 nm laser and the 400 nm SHG is scattered off the sample.



**Figure 5.** (a) Noncentrosymmetric  $P\overline{6}2m$  (No. 189) structure of PbMnTeO<sub>6</sub> and (b) possible parent centrosymmetric structure with space group P6/mmm (No. 191). The black arrows in (b) represent a distortion that leads to the  $P\overline{6}2m$  structure.

inversion symmetry. This is likely the origin of the noncentrosymmetry in  $PbMnTeO_6$ .

**Magnetic Behavior.** The dc magnetic susceptibility of PbMnTeO<sub>6</sub> was measured at 1000 and 10 000 Oe over the temperature range 2–300 K, and the results are shown as plots of  $\chi$  and  $1/\chi$  versus T in Figures 6 and 7, respectively. PbMnTeO<sub>6</sub> exhibits antiferromagnetic behavior with a broad



**Figure 6.** Temperature dependence of the magnetic susceptibility of PbMnTeO<sub>6</sub> measured at 1000 and 10 000 Oe. The inset shows a close-up of the low-temperature region revealing the Néel temperature of  $\sim$ 20 K.



**Figure 7.** Inverse magnetic susceptibility of PbMnTeO<sub>6</sub> with a Curie–Weiss fit (solid line).

Néel transition temperature  $(T_N)$  at ~20 K, consistent with low-dimensional magnetic behavior.<sup>32,33</sup> No significant divergence between the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves was observed. From the plot of  $1/\gamma$ versus T shown in Figure 7, the susceptibility data were fit to the Curie–Weiss (CW) law,  $\chi = C/(T - \theta)$  for T > 150 K, where C is the Curie constant and  $\theta$  is the Weiss constant; the values C = 1.81 emu K mol<sup>-1</sup> and  $\theta = -43.22$  K were extracted from the CW fit of the data. On the basis of the CW fit, the effective magnetic moment,  $\mu_{\text{eff}} = 3.81 \mu_{\text{B}}$  per Mn, is in good agreement with the theoretical spin-only value of  $3.87\mu_{\rm B}$  for  $Mn^{4+}$  (S =  $3/_2$ ). The negative Weiss constant indicates antiferromagnetic interactions, which could arise from superexchange interactions of nearest-neighbor Mn4+-O2--Mn<sup>4+,34-36</sup> It is noteworthy that the frustration parameter  $(|\theta|/T_{\rm N})^{37}$  of ~2.16 in PbMnTeO<sub>6</sub> indicates that some degree of magnetic frustration is present in this quasi-two-dimensional honeycomb lattice. The origin of magnetic frustration in PbMnTeO<sub>6</sub> is likely due to the competition between nearestneighbor and next-nearest-neighbor antiferromagnetic interactions, but the degree of magnetic frustration is relatively lower because magnetic interactions are diluted by nonmagnetic Te<sup>6+</sup> cations compared with an only Mn<sup>4+</sup>-containing honeycomb lattice antiferromagnet, Bi<sub>3</sub>Mn<sub>4</sub>O<sub>12</sub>(NO<sub>3</sub>).<sup>33,38</sup>

As shown in Figure 8, the isothermal magnetization of PbMnTeO<sub>6</sub> measured at 2 and 300 K as a function of the applied field H is linear, which indicates that no ferromagnetic interactions are involved. The magnetic interactions of  $Mn^{4+}$  and  $Mn^{4+}$  between layers are negligible because the layers are well-separated by the Pb<sup>2+</sup> ions with distances longer than 5.0 Å.

## CONCLUSION

A new noncentrosymmetric layered honeycomb magnetic oxide, PbMnTeO<sub>6</sub>, was successfully synthesized by a conventional solid-state reaction. The crystal structure of PbMnTeO<sub>6</sub> exhibits a two-dimensional structure (space group  $P\overline{6}2m$ ) consisting of edge-sharing (disordered Mn<sup>4+</sup>/Te<sup>6+</sup>)O<sub>6</sub> trigonal prisms, which form honeycomb-like layers. In contrast, the similar layered SrGeTeO<sub>6</sub> presents long-rage order of Ge<sup>4+</sup> and Te<sup>6+</sup> ions in octahedral coordination, forming a chiral PbSb<sub>2</sub>O<sub>6</sub>-type structure (space group P312). The origin of these differences is likely due to electronic differences between

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**Figure 8.** Isothermal magnetization of PbMnTeO<sub>6</sub> measured at 2 and 300 K as a function of applied field H.

Mn<sup>4+</sup> and Ge<sup>4+</sup>. Second harmonic generation for PbMnTeO<sub>6</sub> confirmed the noncentrosymmetric character. PbMnTeO<sub>6</sub> exhibits low-dimensional antiferromagnetic behavior with  $T_{\rm N} \approx 20$  K, and some degree of magnetic frustration ( $|\theta|/T_{\rm N} \approx 2.16$ ) is observed, which is attributable to competition between nearest-neighbor and next-nearest-neighbor antiferromagnetic interactions in this quasi-two-dimensional honeycomb lattice; no interlayer interaction is observed, because of the large separation of the Mn<sup>4+</sup> ions by the Pb<sup>2+</sup> ions. Further synthetic studies of single-phase AMnTeO<sub>6</sub> (A = Sr<sup>2+</sup>, Ba<sup>2+</sup>) are underway.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02677.

Experimental PXRD patterns, EDX analysis data, ORTEP diagrams, and TGA data (PDF) Crystallographic data (CIF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors.

# Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

S.W.K., Z.D., M.R.L., and M.G. gratefully acknowledge support from the ARO-434603 grant (DOD-VV911NF-12-1-0172). A.S.G., H.A., and V.G. gratefully acknowledge support from the National Science Foundation MRSEC Center for Nanoscale Science at Penn State through Grant DMR-1420620. S.W.K. thanks Prof. Mark Croft for fruitful discussions and Graeme Gardner for EDX measurements.

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