

**ON A LEAD NICKEL MANGANESE TELLURIUM OXIDE $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$
CONTAINING Mn^{2+} IN TRIGONAL PRISMATIC OXYGEN COORDINATION****B. Wedel^{1*}, K. Sugiyama², K. Hiraga², and K. Itagaki¹**¹Tohoku University, Institute for Advanced Materials Processing (IAMP), Katahira 2-1-1,
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(Refereed)

(Received February 5, 1999; Accepted March 8, 1999)

ABSTRACT

A new lead manganese nickel tellurium oxide $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ is light green in color and crystallizes in hexagonal symmetry, space group $C_{6h}^2 P6_3/m$ (no. 176), with cell parameters $a = 9.294(1)$, $c = 8.823(1)$ Å, and $Z = 2$. The structure was determined from a single crystal X-ray study and refined to the conventional values $R = 0.026$ and $wR(F^2) = 0.046$. Ni^{2+} and Te^{6+} show octahedral and Mn^{2+} shows trigonal prismatic coordination by O^{2-} . The crystal structure is featured by a ${}_{\infty}^2[\text{Ni}_6\text{Te}_3\text{O}_{18}]^{6-}$ network together with two kinds of channels along [001] with trigonal and hexagonal shape. Isolated face shared $[\text{Mn}_2\text{O}_9]^{14-}$ trigonal prismatic polyhedra doubles are located in the trigonal channels, while one-dimensional infinite chains of $[\text{PbO}_{6+6}]^{22-}$ oxygen cube dodecahedra are incorporated in the hexagonal channels. © 2000

*Elsevier Science Ltd***KEYWORDS:** A. inorganic compounds, A. oxides, C. X-ray diffraction, D. crystal structure**INTRODUCTION**

We have recently characterized the quaternary lead(II) nickel tellurium oxide $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$ [1] with a stereo active lone pair located at Pb^{2+} and $\text{Pb}(\text{Mn},\text{Te})\text{O}_3$ [2]. The

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lead manganese tellurium oxide shows a spherical symmetry of the lone pair, which indicates a s^2 character, and this compound crystallizes in the cubic perovskite type.

Reported quaternary nickel tellurium oxides are rare; only a few compounds have been reported. $\text{BaMn}_2\text{NiO}_6$ [3], $\text{Ba}_2\text{NiTeO}_6$ [4], and $\text{Sr}_2\text{NiTeO}_6$ [5] should be mentioned. $\text{Sr}_2\text{MnTeO}_6$ [6], $\text{Ba}_2\text{MnTeO}_6$ [2], and $(\text{Mn}_{2.4}\text{Cu}_{0.6})\text{TeO}_6$ [2] have to be named in the case of manganese(II) compounds.

The earth alkaline metal compounds crystallize in a small number of perovskite variants.

It was our aim to study the character of the lone pair in a lead tellurium oxo-compound containing manganese(II) and nickel(II) and to compare the character of the stereo active lone pair in $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$ with the character of the spherical lone pair in $\text{Pb}(\text{Mn},\text{Te})\text{O}_3$.

EXPERIMENTAL

The hitherto unknown compound $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ was synthesized as a polycrystalline powder and as single crystals in a solid-state reaction in air. Yellow PbO (Kanto Chemical Co. Inc.), basic NiCO_3 (Kanto Chemical Co. Inc.), basic MnCO_3 , and TeO_2 (prepared by oxidation of tellurium metal (Kanto Chemical Co. Inc.) by concentrated HNO_3 in air at 473 K for 6 h [7]) were intimately mixed in the ratio 1:5:3:5 and ground thoroughly before being placed in a platinum crucible. This crucible was placed in a furnace and heated in air to 1073 K for 336 h. The furnace was allowed to cool to room temperature and the samples were then removed from the furnace. The high ratio of TeO_2 was necessary because of evaporation losses.

After cooling, many single crystals with different shapes and colors were found in the inhomogeneous reaction product. Besides a few light-green single crystals, there were various yellow, dark-red, and dark-green crystals. By energy-dispersive X-ray spectroscopy (Hitachi X650S, EDX system KEVEX 7000Q) and X-ray diffraction (XRD; Rigaku X-ray diffractometer RINT 2000), these crystals were identified as PbTeO_3 [8], Mn_3TeO_6 [9], and $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$ [1]. The light-green crystals were stable in air and suitable for single crystal X-ray diffraction analysis. They were selected for use under a polarized light microscope; one of them, with trigonal shape ($0.10 \times 0.09 \times 0.06$ mm), was selected for this study. By energy-dispersive X-ray spectroscopy, a ratio $\text{Pb}:\text{Ni}:\text{Mn}:\text{Te} = 1.1:6.3:2.0:3.1$ was determined.

The symmetry and the lattice parameter were determined with oscillation and Weissenberg photographs, and imaging plate measurements (Rigaku Imaging plate CS, modified for the Institute of Material Research (IMR)). The crystal used for the final intensity measurement was mounted on the top of a glass fiber. Diffraction measurements at 293 K were made on a Rigaku AFC6S four-circle diffractometer using $\text{Mo K}\alpha$ radiation. The unit cell was determined by the least-squares procedure, applied to 25 randomly selected reflections (range $27.22^\circ < 2\theta < 34.84^\circ$) obtained by using the AFC6 automatic search. Crystal data, data collection parameters, and the results of the analysis of $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ are listed in Table 1.

The compound $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ crystallizes in the hexagonal crystal system. The patterns observed in the data were consistent with the space groups $P6_3$, $P6_3/m$, or $P6_322$. The centric space group $P6_3/m$ was assumed and confirmed by the successful solution and refinement of the structure.

The structure was solved by a combination of direct methods and difference Fourier syntheses (SHELX package [10,11]). All atoms were refined with anisotropic thermal parameters. The positional parameters in $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ are listed in Table 2 and the

TABLE 1
Crystallographic Data for $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ [23]

Formula	$\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$
Crystal size (mm)	$0.10 \times 0.09 \times 0.06$
Formula weight	1340.13
Crystal system	hexagonal
Lattice parameters	
<i>a</i> (Å)	9.294(1)
<i>c</i> (Å)	8.823(1)
<i>V</i> (Å ³)	659.95(1)
Space group	$P6_3/m$ (no. 176)
Z value	2
Index ranges	$0 < h < 14; -14 < k < 12; 0 < l < 14$
ρ_{calc} (g/cm ³)	6.744
λ (Mo $K\alpha$) (mm ⁻¹)	29.525
Temperature (K)	293
2 θ max. (°)	70
Number of observations ($I > 4\sigma$)	817
Number of variables	52
Goodness of fit	1.043
Residuals: R; R_w	0.026; 0.046
Absorption correction	Ψ -scan [24]
Min/max absorption	0.6481/0.9843
Largest final peak and hole (e/Å ³)	1.185 and 1.116

selected interatomic bond distances and angles can be found in Table 3. The anisotropic thermal parameters are summarized in Table 4. The space group was determined by using the ABSEN program [12]; all structure plots appearing in this paper were performed by an ORTEP program [13] and STRUPOL [14].

DESCRIPTION OF THE STRUCTURE

The $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ crystal structure is a ${}^3_{\infty}[\text{Ni}_6\text{Te}_3\text{O}_{18}]^{6-}$ network consisting of edge and corner connected octahedra. Figure 1 shows a typical plane of the network composed by the

TABLE 2
Positional Parameter and $U(\text{eq})$ for $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Pb	2b	0	0	0	23(1)
Te	6h	0.3375(1)	0.3622(1)	3/4	4(1)
Ni	12i	0.9880(1)	0.3482(1)	0.9110(1)	6(1)
Mn	4f	1/3	2/3	0.0602(1)	7(1)
O(1)	12i	0.1011(3)	0.3060(4)	0.0915(2)	8(1)
O(2)	12i	0.1296(3)	0.6074(3)	0.9120	7(1)
O(3)	6h	0.5810(5)	0.4485(5)	3/4	6(1)
O(4)	6h	0.1073(5)	0.2923(5)	3/4	7(1)

TABLE 3
Interatomic Distances (Å) for $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$

Pb–O(1) 6×	2.636(3)	Mn–O(2) 3×	2.138(2)
Pb–O(4) 6×	3.250(3)	Mn–O(3) 3×	2.335(2)
Te–O(4)	1.904(3)	Ni–O(4)	2.017(3)
Te–O(1) 2×	1.936(2)	Ni–O(1)	2.046(3)
Te–O(2) 2×	1.938(2)	Ni–O(2)	2.067(3)
Te–O(3)	1.987(3)	Ni–O(2)	2.094(3)
		Ni–O(1)	2.102(3)
		Ni–O(3)	2.117(3)

Esd's given in parentheses.

edge and corner connection of the NiO_6^{10-} and TeO_6^{6-} . Along the c axis these oxygen octahedra are connected so as to make double chains by showing their edges. The sequence of the metals in one chain is $\text{Ni}^{2+}\text{--Ni}^{2+}\text{--Te}^{6+}\text{--Ni}^{2+}\text{--Ni}^{2+}\text{--Te}^{6+}$; the second chain is connected over edges with the first and shifted by one octahedron. Figure 2a shows a double chain of the $(\text{Ni}^{2+}, \text{Te}^{6+})$ octahedra.

In the plane, the double chains are connected by corners and edges. Three oxygen octahedra of Ni^{2+} and three oxygen octahedra of Te^{6+} form a ring with trigonal shape. These rings build up channels parallel to [001] in which the Mn^{2+} ions are located. Three oxygens of NiO_6^{10-} and three oxygens of TeO_6^{6-} are connected by corners to form hexagonal rings. The Pb^{2+} ions are incorporated into the hexagonal channels formed by the double chains of NiO_6^{10-} and TeO_6^{6-} octahedra rings, which gives Pb^{2+} a 6 + 6 coordination by oxygen, consisting of six inner and six outer O^{2-} ions, forming a stretched cube octahedron. The high thermal parameter of Pb^{2+} found in the channel structure of $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ is not unusual for channel structures.

The manganese ions obtain a trigonal prismatic oxygen coordination in the channels, which is unusual for common Mn^{2+} coordination. Only a few examples of this trigonal prismatic coordination of Mn^{2+} are known so far, e.g., $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}\text{OH}_{0.1}$ [15], Mn_2GeO_4 [16], and $(\text{Cu}, \text{Mn})_{3.66}\text{Mo}_3\text{O}_{12}$ [17]. Nevertheless, the coordination prisms are connected by their edges in these compounds. In $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$, the prisms share a

TABLE 4
Anisotropic Displacement Factor [$\text{Å}^2 \times 10^3$] for $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	13(1)	13(1)	45(1)	0	0	6(1)
Te	4(1)	4(1)	3(1)	0	0	2(1)
Ni	6(1)	6(1)	5(1)	1(1)	0(1)	3(1)
Mn	7(1)	7(1)	7(1)	0	0	3(1)
O1	7(1)	12(1)	6(1)	–1(1)	0(1)	6(1)
O2	7(1)	6(1)	6(1)	–1(1)	–2(1)	2(1)
O3	3(2)	6(2)	8(2)	0	0	3(1)
O4	4(2)	10(2)	5(2)	0	0	2(1)

Esd's given in parentheses.

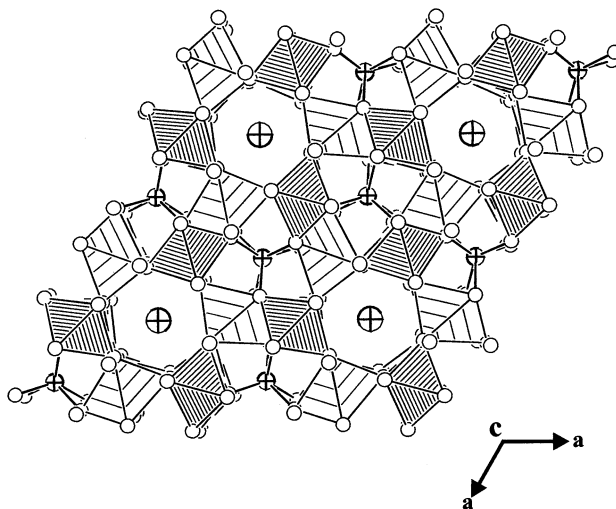


FIG. 1

Perspective view along [001] in $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$. Light octahedra = NiO_6^{10-} ; dark octahedra = TeO_6^{6-} ; big sphere with cross = Pb^{2+} ; small sphere with cross Mn^{2+} ; open sphere = O^{2-} .

common triangular face to form Mn_2O_6 dimers, a feature not previously observed in any compound. The Mn_2O_6 double prisms are connected by two empty prisms on each side, to form a ${}^1_{\infty}[\text{Mn}_2\text{O}_6 \text{ [empty]}]^{8-}$ chain. This sequence along [001] is demonstrated in Figure 2b.

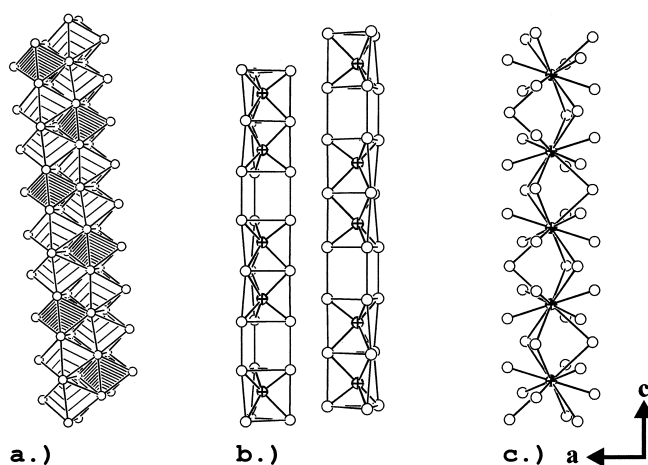


FIG. 2

Chains in $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$. (a) ${}^1_{\infty}[\text{Ni}_6\text{Te}_3\text{O}_{18}]^{6-}$ chain; (b) ${}^1_{\infty}[\text{Mn}_2\text{O}_6 \text{ [empty]}]^{8-}$ chain; (c) ${}^1_{\infty}[\text{PbO}_9]^{16-}$ chain along [001]. The symbols correspond to the symbols of Figure 1.

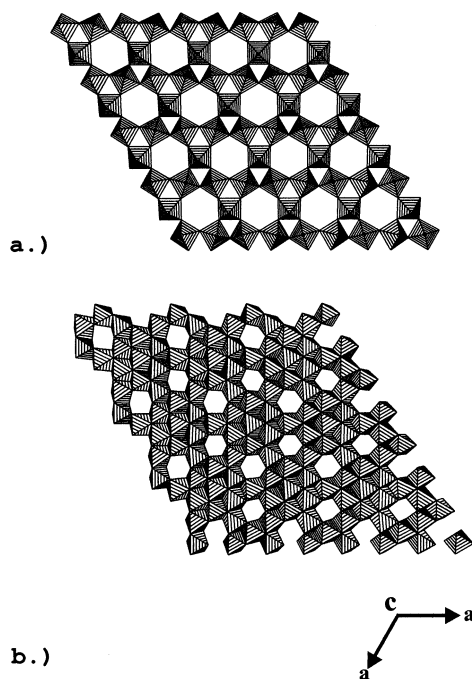


FIG. 3

(a) [001] plane of edge- and corner-connected octahedra of hexagonal tungsten bronze type structure; (b) of $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$.

According to a calculation of ECoN [18] values, the Pb^{2+} ions are coordinated by 12 oxygen ions. Six of them form an inner coordination sphere, the other six an outer sphere, resulting in [6 + 6] coordination. These PbO_{6+6} polyhedra share trigonal faces with two neighbors forming a ${}^1_{\infty}[\text{PbO}_9]^{16-}$ chain along [001] (Fig. 2c). Because of the symmetric shape of the oxygen coordination of Pb^{2+} , it is not possible to find a reasonable position of the lone pair in the coordination polyhedron with geometric or MAPLE [19,20] methods. Therefore we assume that the lone pair has a spherical s-orbital shape.

Finally, a similarity is noted between the present $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ structure, the well-known hexagonal tungsten bronze type structure [21,22], and the $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$ structure [1]. All of these three structures crystallize in hexagonal space groups, which are related to each other as subgroups and supergroups. The systematic absence conditions of them are the same. In $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$, there are only hexagonal channels along [001], while the tungsten bronze type structure contains hexagonal and trigonal channels like those in the $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ structure, except, in this case, the rings are built up by three polyhedra only and the atoms in these smaller rings do not have a trigonal prismatic oxygen coordination. Figure 3 shows the comparison of these structure types.

ACKNOWLEDGMENTS

The generous support given by the Japanese Ministry of Education is gratefully acknowledged. Special thanks is given to Mr. Y. Sato for the EPMA analysis and Dr. L. Wulff for

helping to calculate the Coulomb part of the lattice energy and helpful discussions to prepare this paper.

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