Lei Geng*

The crystal structure of $\text{Ba}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$ containing ${}^1_\infty[\text{Mn}(\text{SeO}_3)_2\text{Cl}_2]^{4-}$ chains

Table 1: Data collection and handling.

Crystal:	Colorless needle
Size:	0.20 × 0.12 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	17.7 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 QUEST,
θ_{max} , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6943, 604, 0.047
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 584
$N(\text{param})_{\text{refined}}$:	39
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

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Abstract

$\text{Ba}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$, orthorhombic, $Pnmm$ (no. 58), $a = 6.7685(5)$ Å, $b = 12.8618(10)$ Å, $c = 5.4685(4)$ Å, $V = 476.06(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0191$, $wR_{\text{ref}}(F^2) = 0.0854$, $T = 298(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents used in this synthesis were purchased without further purification. The initial materials of 4 mmol BaCO_3 (0.789 g), 2 mmol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.396 g), and 4 mmol SeO_2 (0.444 g) were weighted and loaded in a 23 ml Teflon lining. Two milliliter H_2O was then added into the lining and stirred before sealed in an autoclave. The mixture was

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba1	0.30482 (6)	0.26921 (3)	0.0000	0.0119 (2)
Mn1	0.0000	0.0000	0.0000	0.0108 (3)
Se1	0.76363 (10)	0.42182 (4)	0.0000	0.0102 (3)
O1	0.6103 (5)	0.3885 (2)	0.2359 (5)	0.0140 (6)
O2	0.9208 (8)	0.3220 (4)	0.0000	0.0211 (10)
Cl1	0.6736 (2)	0.10477 (14)	0.0000	0.0183 (4)

heated to 463 K in an oven within 2 h, held for four days, and then slowly cooled to room temperature at the rate of 4 K/h. Colorless needle crystals of $\text{Ba}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$ were gathered with more than 76% yield after rinse with purified water.

Experimental details

The structure was solved by Direct Methods with SHELXS-97 and further refined with the SHELXL program. All atoms were refined anisotropically without any constraints or restraints.

Comment

Low-dimensional transition metal oxides have attracted great interest in recent years owing to their fundamental

*Corresponding author: Lei Geng, College of Physics and Physical Engineering, Qufu Normal University, Qufu, 273165, China, E-mail: lgeng.cn@gmail.com. <https://orcid.org/0000-0002-2160-3762>

and fascinating physical phenomena such as superconductivity, magnetic spin frustration or their use as spin glass [4–7]. It has been reported that the structural unit SeO_3 pyramids with lone-pair electrons can usually be utilized as chemical scissors to terminate further bonding with near units and thus reduce the dimensionality of a structural motif [8–10]. In addition, partial substitution of oxide with chloride ions on transition metal polyhedron can also prevent the extension of functional units. Thus introducing chlorine into transition metal oxides can serve as an effective strategy to design new low-dimensional structures [11, 12].

Based on the above assumption, our group synthesized two new compounds in the Ba–Zn selenite chloride system: $\text{Ba}_2\text{Zn}(\text{SeO}_3)_2\text{Cl}_2$ with one-dimensional and 2D $\text{BaZn}_2(\text{SeO}_3)_2\text{Cl}_2$ with two-dimensional structures [13]. In this research, we attempted to extend the exploration of the Mn isomorph and obtained a new compound: $\text{Ba}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$. Similar isomorphous structure can also be found in the corresponding Co compound [14].

The one-dimensional $[\text{Mn}(\text{SeO}_3)_2\text{Cl}_2]^{4-}$ anionic chains with electron balanced Ba^{2+} cations compose the crystal structures of $\text{Ba}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$. MnO_4Cl_2 octahedra are linked with four SeO_3 pyramids through bridging oxygen atoms on MnO_4Cl_2 (see the figure). Two chloride ions on MnO_4Cl_2 units protrude from both sides of the MnO_4 square with Mn–O and Mn–Cl distances of 2.170 and 2.588 Å, respectively. The Ba cations are surrounded by seven oxygen atoms with an average Ba–O distance of 2.891 Å and three chloride ions with an average Ba–Cl distance of 3.290 Å. Bond valence sums (BVS) were calculated for central cations with the results of $\text{BVS}(\text{Ba}) = 2.04$, $\text{BVS}(\text{Mn}) = 2.02$, and $\text{BVS}(\text{Se}) = 4.12$, which is consistent with the expected valences of 2, 2, and 4 for Ba, Mn, and Se, respectively [15, 16].

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