

## THE CRYSTAL STRUCTURE OF TUSIONITE, $Mn^{2+}Sn^{4+}(BO_3)_2$ , A DOLOMITE-STRUCTURE BORATE

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### ABSTRACT

Tusionite,  $Mn^{2+}Sn^{4+}(BO_3)_2$ , has been found at two new localities: Thomas Mountain, Riverside County, California, and Řečice, Moravia, Czech Republic. At both localities, tusionite occurs in granitic pegmatites of the elbaite subtype, together with tourmaline, hambergite, danburite, hellandite and boromuscovite. Tusionite occurs as small tabular crystals in mirolitic cavities, and as thin flakes and rosettes in massive pegmatite; in the latter occurrence, it is commonly replaced by fine-grained cassiterite. The crystal structure,  $a$  4.781(1),  $c$  15.381(7) Å,  $V$  304.5(2) Å<sup>3</sup>,  $R\bar{3}$ ,  $Z = 3$ , has been refined to an  $R$  index of 2.4% for 204 observed reflections measured with  $MoK\alpha$  X-radiation. Tusionite is isostructural with dolomite,  $CaMg(CO_3)_2$ . Electroneutrality constraints show Sn to be tetravalent and Mn to be divalent, and the observed mean bond-lengths are in accord with this:  $\langle Sn-O \rangle = 2.055$ ,  $\langle Mn-O \rangle = 2.224$  Å. The variation in  $\langle M-O \rangle$  as a function of cation radius is significantly nonlinear for the calcite-type structures, the values for  $M = Zn, Fe^{2+}, Mn^{2+}$  being  $\sim 0.01$  Å less than predicted by linear interpolation between magnesite and calcite. For the dolomite-type structures, variations in  $\langle A-O \rangle$  ( $A$  representing Ca, Mn) and  $\langle B-O \rangle$  ( $B$  representing Mg,  $Fe^{2+}$ , Mn) as a function of cation radius are linear, but the two octahedra show very different behavior. The  $\langle B-O \rangle$  distance shows a response similar to that of the calcite-type structures, except that it is  $\sim 0.025$  Å shorter for a given cation-radius; the  $\langle A-O \rangle$  distance is  $\sim 0.025$  Å longer than the corresponding distance in calcite, but decreases in size with decreasing cation-radius more rapidly than in the calcite-type structures.

**Keywords:** tusionite, crystal structure, dolomite, granitic pegmatite, Thomas Mountain, California, Řečice, Czech Republic.

### SOMMAIRE

Nous avons trouvé la tusionite,  $Mn^{2+}Sn^{4+}(BO_3)_2$ , au mont Thomas, comté de Riverside, en Californie, et à Řečice, en Moravie, République Tchèque, localités nouvelles pour cette espèce. Aux deux endroits, la tusionite se trouve dans une pegmatite granitique du sous-type dit "à elbaïte", avec tourmaline, hambergite, danburite, hellandite et boromuscovite. La tusionite se présente en plaquettes dans les miaroles, et en mince cristaux ou en rosettes dans la pegmatite massive. Dans cette dernière, la tusionite se voit remplacée par une cassitérite massive. La structure cristalline de la tusionite,  $a$  4.781(1),  $c$  15.381(7) Å,  $V$  304.5(2) Å<sup>3</sup>,  $R\bar{3}$ ,  $Z = 3$ , a été affinée jusqu'à un résidu  $R$  de 2.4% pour 204 réflexions observées et mesurées avec rayonnement  $MoK\alpha$ . La tusionite est isostructurale avec la dolomite,  $CaMg(CO_3)_2$ . D'après les contraintes d'électroneutralité, le Sn est tétravalent, et le Mn, bivalent; les longueurs moyennes des liaisons concordent avec cette assertion:  $\langle Sn-O \rangle = 2.055$ ,  $\langle Mn-O \rangle = 2.224$  Å. La variation dans la longueur  $\langle M-O \rangle$  en fonction du rayon du cation est fortement non linéaire pour les structures de type calcite, les valeurs pour  $M = Zn, Fe^{2+}, Mn^{2+}$  étant inférieures de  $\sim 0.01$  Å à ce que prédit une interpolation linéaire entre magnésite et calcite. Dans les structures de type dolomite, les variations dans les longueurs  $\langle A-O \rangle$  ( $A$  représentant Ca, Mn) et  $\langle B-O \rangle$  ( $B$  représentant Mg,  $Fe^{2+}$ , Mn) en fonction de rayon cationique sont linéaires, mais les deux octaèdres se comportent très différemment. La distance  $\langle B-O \rangle$  montre une réponse semblable à celle des structures de type calcite, sauf qu'elle est environ 0.025 Å plus courte pour un rayon cationique donné. Par contre, la distance  $\langle A-O \rangle$  est environ 0.025 Å plus longue que la distance correspondante dans la calcite, mais diminue à mesure que diminue le rayon cationique plus rapidement que dans les structures de type calcite.

(Traduit par la Rédaction)

**Mots-clés:** tusionite, structure cristalline, dolomite, pegmatite granitique, mont Thomas, Californie, Řečice, République Tchèque.

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## INTRODUCTION

Tusionite is a borate mineral,  $(\text{Mn,Fe})\text{Sn}(\text{BO}_3)_2$ , that was first reported by Konovalenko *et al.* (1983) from the southwestern Pamirs, Tajikistan. It occurs in a granitic pegmatite that cuts Precambrian garnet-biotite gneiss, both as lamellar intergrowths with tetrawickmanite and as small tabular crystals associated with tourmaline, danburite, hambergite, quartz, orthoclase and albite in miarolitic cavities. Konovalenko *et al.* (1983) showed from powder data that tusionite is isostructural with dolomite and wrote the ideal end-member formula as  $\text{MnSn}(\text{BO}_3)_2$ ; electroneutrality requires that Mn be divalent and Sn be tetravalent.

New localities of tusionite were recently found in the granitic pegmatites Belo Horizonte No. 1 and New Columbia No. 1, Thomas Mountain, Riverside County, southern California, and at Rečice, Moravia, Czech Republic. All occurrences are in B-rich complex pegmatites of the elbaitite subtype (Novák & Povondra 1994) characterized by the presence of common tourmaline and other B-rich minerals, such as hambergite, danburite, hellandite and boromuscovite. Tusionite occurs as thin blades and fan-like rosettes up to 3 cm across enclosed in massive pegmatite, or as small tabular crystals in miarolitic pockets. It is associated with K-feldspar, albite, quartz and tourmaline. Tusionite aggregates from massive pegmatite are commonly replaced by fine-grained cassiterite.

## EXPERIMENTAL

A tabular fragment of a single crystal from Belo Horizonte No. 1, Thomas Mountain, Riverside County, California, was mounted on a Nicolet R3m automated four-circle diffractometer equipped with a Mo X-ray tube. Twenty-five reflections were measured on a random-orientation photograph and aligned automatically on the diffractometer. From the resulting setting angles, least-squares refinement gave the cell dimensions listed in Table 1, together with the orientation matrix. Intensity data were measured according to the procedure of Hawthorne & Groat (1985). A total of 1052 reflections was measured to a maximum  $2\theta$  angle of  $60^\circ$ . Ten strong reflections uni-

TABLE 1. MISCELLANEOUS INFORMATION FOR TUSIONITE

<i>a</i> (Å)	4.781(1)	Crystal size (mm)	0.23 × 0.19 × 0.06
<i>c</i>	15.381(7)	Radiation	MoK $\alpha$ /Graphite
<i>V</i> (Å <sup>3</sup> )	304.5(2)	No. of Intensities	1052
Space group	R $\bar{3}$	No. of $ F_o  > 5\sigma( F )$	204
		<i>R</i> (azimuthal) %	6.2 → 3.4
		<i>R</i> (obs) %	2.4
		<i>wR</i> (obs) %	2.8
Cell contents	3[Mn <sup>2+</sup> Sn <sup>4+</sup> (BO <sub>3</sub> ) <sub>2</sub> ]		

formly distributed with regard to  $2\theta$  were measured at  $10^\circ$  intervals of  $\psi$  (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, modeling the crystal as a plate; this reduced the azimuthal *R* index from 6.2 to 3.4%. This correction was then applied to the  $\theta$ - $2\theta$  intensity data. The data were then corrected for Lorentz and polarization effects, averaged, and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of 5 standard deviations on the basis of counting statistics. Miscellaneous information pertinent to data measurement and structure refinement is given in Table 1.

Electron-microprobe analysis was done in the wavelength-dispersion mode on a Cameca Camebax SX50 instrument, with a beam diameter of 1–2  $\mu\text{m}$  and an accelerating potential of 15 kV. A sample current of 20 nA measured on a Faraday cup and a counting time of 20 seconds were used for Mn, Fe, Ca, Sn, Nb, and Ti. For Mg, Sb, As, Y, Sc, Zr, and W, 40 nA and 40 seconds were used. The standards MnNb<sub>2</sub>O<sub>6</sub> (MnK $\alpha$ , NbL $\alpha$ ), FeNb<sub>2</sub>O<sub>6</sub> (FeK $\alpha$ ), CaNb<sub>2</sub>O<sub>6</sub> (CaK $\alpha$ ), SnO<sub>2</sub> (SnL $\alpha$ ), rutile (TiK $\alpha$ ), MgNb<sub>2</sub>O<sub>6</sub> (MgK $\alpha$ ), stibiotantalite (SbL $\alpha$ ), mimetite (AsL $\alpha$ ), YAG (YL $\alpha$ ), NaScSi<sub>2</sub>O<sub>6</sub> (ScK $\alpha$ ), ZrO<sub>2</sub> (ZrL $\alpha$ ) and W metal (WM $\beta$ ) were used. The data were reduced using the PAP

TABLE 2. ELECTRON-MICROPROBE DATA\* AND UNIT FORMULAE FOR TUSIONITE

	1	2	3	4
WO <sub>3</sub>	0.45	0.10	0.40	–
SnO <sub>2</sub>	51.62	51.87	52.84	52.45
ZrO <sub>2</sub>	0.10	0.08	0.00	–
Sc <sub>2</sub> O <sub>3</sub>	0.06	0.07	0.07	–
MgO	0.00	0.00	0.86	–
CaO	1.71	1.67	0.14	0.39
FeO	2.31	2.27	0.77	3.57
MnO	18.72	18.78	20.87	20.46
B <sub>2</sub> O <sub>3</sub> **	23.72	23.70	24.08	24.16
Total	98.69	98.54	100.03	101.03
W <sup>6+</sup>	0.006	0.001	0.005	0.000
Sn <sup>4+</sup>	1.005	1.011	1.014	1.003
Zr <sup>4+</sup>	0.002	0.002	0.000	0.000
Sc <sup>3+</sup>	0.003	0.003	0.003	0.000
Mg <sup>2+</sup>	0.000	0.000	0.062	0.000
Ca <sup>2+</sup>	0.090	0.087	0.007	0.020
Fe <sup>2+</sup>	0.094	0.093	0.031	0.143
Mn <sup>2+</sup>	0.775	0.778	0.851	0.831
SUM	2.000	2.000	2.000	2.000

\* Nb, Ti, As, Y, Sb not detected

\*\* B<sub>2</sub>O<sub>3</sub> calculated by stoichiometry

– = not determined

1 - Belo Horizonte No. 1, Thomas Mountain, Riverside County, California

2 - New Columbia No. 1, Thomas Mountain, Riverside County, California

3 - Rečice, Moravia, Czech Republic

4 - southwestern Pamirs, Tajikistan (Konovalenko *et al.* 1983)

TABLE 3. FINAL ATOMIC PARAMETERS FOR TUSIONITE

Site	x	y	z	*U <sub>eq</sub>	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Mn	0	0	0	91(3)	72(4)	72(4)	128(5)	0	0	36(2)
Sn	0	0	1/2	62(2)	36(2)	36(2)	114(3)	0	0	18(1)
B	0	0	0.2444(3)	82(12)	62(15)	62(15)	124(21)	0	0	31(8)
O	0.2800(3)	-0.0155(4)	0.2453(1)	105(6)	64(7)	80(7)	183(9)	-17(6)	-10(5)	46(6)

$$* U_i = U_j \times 10^4$$

routine (Pouchou & Pichoir 1985). Ten or more points were analyzed for each sample; compositions and unit formulae are given in Table 2.

### STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from Ibers & Hamilton (1974). The *R* and *wR* (unit weights) indices are of the standard form and are given as percentages. The SHELXTL PLUS (PC version) system of programs was used in this work.

The starting parameters were those of the dolomite structure (Beran & Zemann 1977). The structure refinement converged rapidly to an *R* index of 2.4% for an anisotropic displacement model. Final positional and displacement parameters are given in Table 3, and selected interatomic distances and angles are given in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

### DISCUSSION

The structure refinement results given here confirm that tusionite has the dolomite-type structure and is isostructural with nordenskiöldine, CaSn<sup>4+</sup>(BO<sub>3</sub>)<sub>2</sub> (Effenberger & Zemann 1986).

There have been many studies of the stereochemical variations in carbonate minerals. Zemann (1981) has shown that most carbonate groups are planar or nearly planar, but also showed that small deviations from planar geometry do occur. Zemann *et al.* (1982) and Effenberger & Zemann (1986) noted that (BO<sub>3</sub>) groups can show significant pyramidal distortion, particularly in nordenskiöldine. Other work on calcite- and dolomite-group carbonates has focused primarily on distortions in octahedra (Effenberger *et al.* 1981, Peacor *et al.* 1987, Paquette & Reeder 1990, Reeder & Dollase 1989). There has been some examination of variation in mean bond-length in octahedra as a function of composition (Paquette & Reeder 1990, Reeder & Dollase 1989), but this has been within chemical subsystems of the calcite- and dolomite-group minerals. Thus a general examination of mean bond-length of octahedra as a function of cation radius seems desirable.

The variations in mean bond-length in octahedra as a function of cation radius for the calcite- and dolomite-type structures are shown in Figures 1 and 2; we use selected data from Althoff (1977), Beran & Zemann (1977), Effenberger *et al.* (1981, 1983), Markgraf & Reeder (1985), Oh *et al.* (1973), Paquette & Reeder (1990), Peacor *et al.* (1987), Reeder & Dollase (1989), and Reeder & Wenk (1983). For the calcite-type structures, a line through calcite, high-Mg calcite and magnesite (Fig. 1) has a slope of ~0.93; smithsonite, siderite, and rhodochrosite lie ~0.01 Å below this line. A line through calcite, high-Mg calcite, rhodochrosite, siderite and smithsonite has a slope of ~0.98, and magnesite lies ~0.01 Å above this line. We note that the value for magnesite, <M-O> = 2.102 Å, is confirmed by three determinations (Oh *et al.* 1973, Effenberger *et al.* 1981, Markgraf & Reeder 1985), and we suggest that the deviations from linearity in these structures are real.

The behavior of the dolomite-type structures is distinctly different (Fig. 2). Following Reeder & Dollase (1989), we label the large octahedron and its central site "A", and the smaller octahedron and its central site "B". For the A site, there is a linear relationship between <A-O> and cation radius (Fig. 2), with a slope of ~1.22. The <A-O> distance is ~0.02 Å longer in pure dolomite than in pure calcite, but the

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN TUSIONITE

B-O	x3	1.377(2)	O-B-Oa	x3	120.0(1)
Sn-O	x6	2.055(1)	Ob-Sn-Oc	x6	88.9(1)
			Ob-Sn-Od	x6	91.1(1)
			<O-Sn-O>		90.0
Mn-O	x6	2.225(1)	Oe-Mn-Of		86.8(1)
			Oe-Mn-Og		93.2(1)
			<O-Mn-O>		90.0

a: -y, x-y, z; b: ½-x, -½+y, -½-z; c: ½-y, -½+x-y, -½+z;  
d: -½+y, ½-x+y, ½-z; e: -½+x, ½+y, ½+z; f: -½-y,  
-½+x-y, ½+z; g: ½+y, ½-x+y, ½-z.

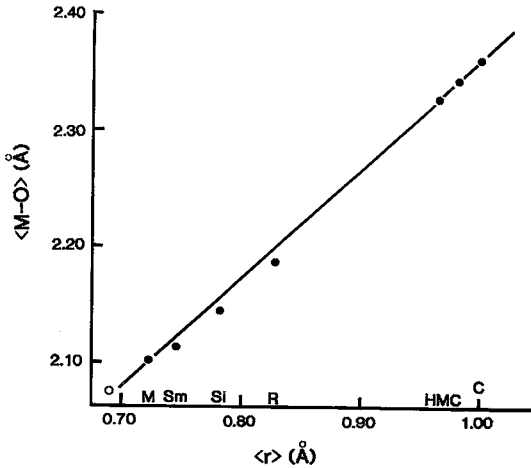


FIG. 1. Variation in  $\langle M-O \rangle$  as a function of cation radius in the calcite-type structures. Symbols: M: magnesite, Sm: smithsonite, Si: siderite, R: rhodochrosite, HMC: high-Mg calcite, C: calcite, O:  $\text{NiCO}_3$ . Note that  $\text{CoCO}_3$  overlaps smithsonite.

sizes of the octahedra in the two structure types converge with decreasing cation radius to become equal at a cation radius of  $\sim 0.93$  Å. There is a linear relationship between  $\langle B-O \rangle$  and cation radius (Fig. 2), with a slope of  $\sim 0.95$ . The  $\langle B-O \rangle$  distance is  $\sim 0.025$  Å shorter in pure dolomite than in pure magnesite, and unlike the  $\langle A-O \rangle$  distance, it does not linearly converge significantly with the calcite-type structures as  $r$  increases. It is possible that at intermediate values of cation radius, 0.85–0.95 Å, the  $A$  and  $B$  curves join in a smooth fashion, but many more data are needed on disordered dolomite-type structures before it is clear whether or not this is the case.

The  $\langle A-O \rangle$  distance in tusionite (Fig. 2) lies  $\sim 0.03$  Å above the trend for the other dolomite-type structures. In this region of cation radius, the  $\langle A-O \rangle$  and  $\langle B-O \rangle$  curves are defined by disordered kutnahorite (Peacor *et al.* 1987); whether or not this difference in stereochemistry is the result of differences in the degree of order will only be resolved by further work on this structure type.

The nonlinear variations in mean bond-lengths as a function of cation radius in both the calcite- and the dolomite-type structures seem to be significant (*i.e.*, not due to random experimental error), and a more extensive experimental examination of these structures seems warranted.

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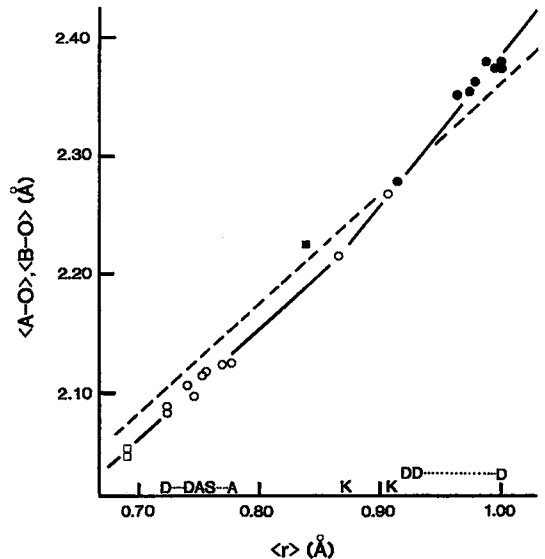


FIG. 2. Variation in  $\langle A-O \rangle$  (●) and  $\langle B-O \rangle$  (○) as a function of cation radius in the dolomite-type structures. Symbols: D: dolomite, DAS: dolomite-ankerite solid-solution, A: ankerite, K: kutnahorite, DD: disordered dolomite. The borate structures (tusionite and nordenskiöldine) are shown as ■ and □, and the broken line denotes the line through calcite and magnesite for the calcite-type structures. The value for the  $A$  site in nordenskiöldine overlaps that for dolomite ( $r \sim 1.0$  Å,  $\langle A-O \rangle = 2.377$  Å); several values for  $\langle A-O \rangle$  also overlap.

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#### REFERENCES

- ALTHOFF, P.L. (1977): Structural refinements of dolomite and a magnesian calcite and implications for dolomite formation in the marine environment. *Am. Mineral.* **62**, 772-783.
- BERAN, A. & ZEMANN, J. (1977): Refinement and comparison of the crystal structures of a dolomite and of an Fe-rich ankerite. *Tschermaks Mineral. Petrogr. Mitt.* **24**, 279-286.
- EFFENBERGER, H., KIRFEL, A. & WILL, G. (1983): Untersuchungen zur Elektronendichteverteilung im Dolomit  $\text{CaMg}(\text{CO}_3)_2$ . *Tschermaks Mineral. Petrogr. Mitt.* **31**, 151-164.
- \_\_\_\_\_, MEREITER, K. & ZEMANN, J. (1981): Crystal structure refinements of magnesite, calcite, rhodochrosite, siderite, smithsonite, and dolomite, with discussion of some aspects of the stereochemistry of calcite type carbonates. *Z. Kristallogr.* **156**, 233-243.

- \_\_\_\_\_. & ZEMANN, J. (1986): The detailed crystal structure of nordenskiöldine,  $\text{CaSn}(\text{BO}_3)_2$ . *Neues Jahrb. Mineral. Monatsh.*, 111-114.
- HAWTHORNE, F.C. & GROAT, L.A. (1985): The crystal structure of wroewolfeite, a mineral with  $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6(\text{H}_2\text{O})]$  sheets. *Am. Mineral.* **70**, 1050-1055.
- IBERS, J.A. & HAMILTON, W.C. (1974): *International Tables for X-ray Crystallography III*. Kynoch Press, Birmingham, England.
- KONOVALENKO, S.I., VOLOSHIN, A.V., PAKHOMOVSKII, YA.A., ANAN'EV, S.A., PERLINA, G.A., ROGACHEV, D.L. & KUZNETSOV, V.YA. (1983): Tusionite  $\text{MnSn}(\text{BO}_3)_2$  – a new borate from granitic pegmatites of the southwest Pamirs. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **272**, 1449-1453.
- MARKGRAF, S.A. & REEDER, R.J. (1985): High-temperature structure refinements of calcite and magnesite. *Am. Mineral.* **70**, 590-600.
- NOVÁK, M. & POVONDRA, P. (1994): Elbaite pegmatites in the Moldanubicum; a new subtype of the rare-element class. *Mineral. Petrol.* (in press).
- OH, K.D., MORIKAWA, H., IWAI, S. & AOKI, H. (1973): The crystal structure of magnesite. *Am. Mineral.* **58**, 1029-1033.
- PAQUETTE, J. & REEDER, R.J. (1990): Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals. *Am. Mineral.* **75**, 1151-1158.
- PEACOR, D.R., ESSENE, E.J. & GAINES, A.M. (1987): Petrologic and crystal-chemical implications of cation order-disorder in kutnahorite  $[\text{CaMn}(\text{CO}_3)_2]$ . *Am. Mineral.* **72**, 319-328.
- POUCHOU, J.L. & PICOIR, F. (1985): "PAP" procedure for improved quantitative microanalysis. *Microbeam Anal.* **20**, 104-105.
- REEDER, R.J. & DOLLASE, W.A. (1989): Structural variation in the dolomite – ankerite solid-solution series: an X-ray, Mössbauer, and TEM study. *Am. Mineral.* **74**, 1159-1167.
- \_\_\_\_\_. & WENK, H.-R. (1983): Structure refinements of some thermally disordered dolomites. *Am. Mineral.* **68**, 769-776.
- ZEMANN, J. (1981): Zur Stereochemie der Karbonate. *Fortschr. Mineral.* **59**, 95-116.
- \_\_\_\_\_, EFFENBERGER, H. & PERTLIK, F. (1982): Verfeinerung der Kristallstruktur des Kotoits,  $\text{Mg}_3(\text{BO}_3)_2$ : ein Beitrag zur Aplanarität von  $\text{BO}_3$ -Gruppen. *Österr. Akad. Wiss., Math. naturwiss. Kl., Anzeiger* **1982**, 61-62.

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