Crystal Structure of Silver Chromate Silicate, $Ag_6(CrO_4)(SiO_4)$

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The new silver chromate silicate $Ag_6(CrO_4)(SiO_4)$ has been obtained from Ag_2O and SiO_2 by solid-state reaction at elevated temperature and oxygen pressure in stainless-steel autoclaves. It crystallizes in space group $I4_1/amd$ (no. 141) with a = 7.256(2), c = 17.584(6) Å, V = 925.9(5) Å^3, Z = 4; the structure refinement was based on 314 independent reflections and resulted in $R1$ = 0.0488, $wR2$ = 0.0987 ($I \geq 2\sigma(I)$). The crystal structure consists of isolated CrO_4 and SiO_4 tetrahedra which are linked by Ag cations. The two different types of Ag atoms are in a square-planar fourfold, and linear twofold coordination by oxygen atoms, respectively. The linearly coordinated Ag atoms combined with the SiO_4 tetrahedra form a three-dimensional $^3_\infty[Ag_4SiO_4]$ framework, accommodating the CrO_4 tetrahedra and the remaining Ag atoms in the voids. The CrO_4 tetrahedron shows slightly enlarged displacement parameters indicating somewhat enhanced librational motion of the rigid body.

Key words: Silver, Chromium, Silver Chromate Silicate, High Oxygen Pressure, Crystal Structure

Introduction

Silver silicates have been studied intensively in the past, due to some of their special physical properties [1, 2] as well as to structural features in the context with possible attractive d^{10}-d^{10} interactions between silver cations [3, 4]. The syntheses of such ternary silver oxides with high silver contents are commonly complicated because of the limited thermal stability of Ag_2O, and the number of accessible and well-characterized ternary compounds has grown distinctly after techniques for syntheses at elevated oxygen pressures had become available [5 – 11]. Today, a number of silver silicates with Ag/Si ratios varying between 2 and 5 is known, with some of them showing unusual features, as there are the first tetrasilicate, $Ag_{10}Si_4O_{13}$ [8], and Ag_5SiO_4, a subvalent compound with respect to silver [9]. Surprisingly, only recently the supposedly simplest compound, Ag_4SiO_4, was obtained as a pure phase and structurally characterized [10]. The "Ag_4SiO_4", reported first in 1958 [12, 13], turned out to be the mixed silicate nitrate $Ag_9(SiO_4)_2(NO_3)$ [14], a composition that well complies with the method of synthesis, where melts of $AgNO_3$ were applied. Although the genuine silver orthosilicate had remained unknown until recently, isolated SiO_4 tetrahedra are frequently encountered in crystal structures of silver-containing silicates *e. g.* in the above mentioned Ag_5SiO_4 and $Ag_9(SiO_4)_2(NO_3)$, or in $Ag_{18}(SiO_4)_2(Si_4O_{13})$ [11], $Ag_6(SO_4)(SiO_4)$ [15], and Ag_5SiO_4Cl [16]. Apparently the formation of pure Ag_4SiO_4 is not favored over these competing compounds, and in a formal sense other species like AgCl, $AgNO_3$, Ag_2SO_4, $Ag_{10}Si_4O_{13}$, and even elemental Ag are easily incorporated in Ag_4SiO_4.

Here we report on $Ag_6(CrO_4)(SiO_4)$ which is representing another example of stuffed Ag_4SiO_4.

Experimental Section

$Ag_6(CrO_4)(SiO_4)$ was obtained as a by-product during experiments at elevated oxygen pressures and temperatures in stainless-steel autoclaves [17]. Ag_2O and SiO_2 were used as the reaction mixture in molar ratios around 2 : 1, water was added as a mineralizer, while chromium was dissolved from the autoclave wall under the reaction conditions. Crystals for structure determination were found after an experiment performed at 300 °C and 20 MPa oxygen pressure for 84 h.

EDX analyses were carried out on crystals of different samples with a Philips XL 30 TMP, equipped with an energy dispersive unit for microanalysis (Phoenix, EDAX). The Ag/Cr/Si ratios of the dark-red crystals were found to be close to 6 : 1 : 1.

Table 1. Crystallographic data and details of the structure determination of $Ag_6(CrO_4)(SiO_4)$.

Formula	$Ag_6(CrO_4)(SiO_4)$
M_r	855.31
Crystal size, mm^3	$0.15\times 0.1\times 0.05$
Crystal system	tetragonal
Space group	$I4_1/amd$ (no. 141)
a, Å	7.2563(18)
c, Å	17.584(6)
V, $Å^3$	925.9(5)
Z	4
D_{calcd}, $g\,cm^{-3}$	6.14
$\mu(MoK_\alpha)$, mm^{-1}	13.7
$F(000)$, e	1536
hkl range	$-9 \le h \le 9$ $-9 \le k \le 9$ $-19 \le l \le 22$
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.651
Refl. measured	6424
Refl. unique	314
R_{int}	0.1496
Param. refined	27
$R1(F)$ ($I \ge 2\sigma(I)$ / all data)	0.0488 / 0.0687
$wR2(F^2)$[a] ($I \ge 2\sigma(I)$ / all data)	0.0987 / 0.1052
GoF (F^2)	1.192
$\Delta\rho_{fin}$ (max / min), $e\,Å^{-3}$	2.05 / −1.77

[a] Weighting scheme: $1/[\sigma^2({F_o}^2) + (0.0324P)^2 + 54.5123P]$, where $P = ({F_o}^2 + 2{F_c}^2)/3$.

Table 2. Atomic coordinates and isotropic displacement parameters[a] (in $Å^2$) for $Ag_6(CrO_4)(SiO_4)$.

Atom	W.-site	x	y	z	U_{eq}
Ag(1)	16*f*	0.29505(17)	0	0	0.0216(5)
Ag(2)	8*e*	0	1/4	0.12199(14)	0.0372(7)
Cr	4*a*	0	3/4	1/8	0.0395(17)
Si	4*b*	1/2	1/4	1/8	0.0113(16)
O(1)	16*h*	0.3116(16)	1/4	0.0722(7)	0.021(3)
O(2)	16*h*	0	0.562(3)	0.077(2)	0.130(13)

[a] U_{eq} is defined as $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$.

A single crystal suitable for X-ray diffraction was selected and glued onto the tip of a glass capillary. Single crystal data were collected on an IPDS-II diffractometer (Stoe & Cie, Darmstadt, MoK_α, graphite monochromator, absorption correction by the integration method). The structure was solved by Direct Methods [18a], and all metal atoms were found at this stage, while the oxygen atoms were localized by Fourier analyses, refinement by full-matrix, and least-squares calculations based on F^2 [18b]. A summary of the data collection and processing, the crystallographic parameters, as well as details on structure solution and refinement are given in Table 1. The atomic coordinates and displacement parameters are shown in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420804.

Results and Discussion

Dark-red crystals of $Ag_6(CrO_4)(SiO_4)$ were obtained as a by-product of preparations originally aiming at silver silicates [10, 16], when elevated oxygen pressures with water added as mineralizer were applied in stainless-steel autoclaves [17]. While silver(I) oxide and silicon dioxide were given as the reaction mixture, the chromium is part of the autoclave steel and was dissolved from the autoclave wall under the reaction conditions. This is in accordance with former observations [19–21]: the presence of water is crucial for the formation of chromates in such experiments, and the release of chromium from the autoclave material can be reduced or even completely suppressed by applying mineralizers of higher pH values like diluted aqueous KOH. Furthermore, the formation of chromates is favored by high reaction temperatures and long experiment times in aged, frequently used autoclaves.

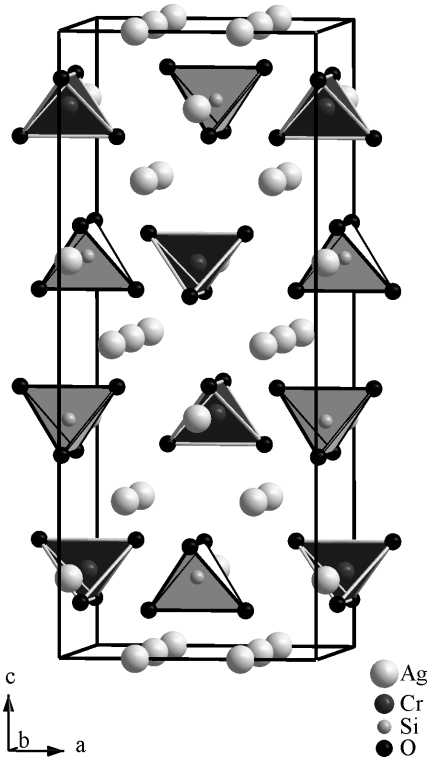

Fig. 1. Crystal structure of $Ag_6(CrO_4)(SiO_4)$ with CrO_4^{2-} (dark grey) and SiO_4^{4-} anions (light grey) drawn as tetrahedra.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	0.0184(7)	0.0204(7)	0.0259(7)	−0.0093(5)	0	0
Ag(2)	0.0111(10)	0.0550(15)	0.0456(14)	0	0	0
Cr	0.031(2)	U_{11}	0.056(5)	0	0	0
Si	0.010(2)	U_{11}	0.013(4)	0	0	0
O(1)	0.019(6)	0.017(5)	0.027(7)	0	−0.004(5)	0
O(2)	0.075(16)	0.064(15)	0.25(4)	−0.06(2)	0	0

Table 3. Anisotropic displacement parameters[a] in Å^2 for $Ag_6(CrO_4)(SiO_4)$.

[a] U_{ij} are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$.

	$Ag_6(CrO_4)(SiO_4)$ (M^{4+} = Si, M^{6+} = Cr)	$Ag_6(SO_4)(SiO_4)$ [15] (M^{4+} = Si, M^{6+} = S)	$Ag_6(SO_4)(GeO_4)$ [22] (M^{4+} = Ge, M^{6+} = S)
Distances			
M^{4+}–O(1) [4×]	1.652(12)	1.642	1.769
M^{6+}–O(2) [4×]	1.61(2)	1.464	1.472
Ag(1)–O(1) [2×]	2.218(7)	2.178	2.183
Ag(1)–O(2)^{vi} [2×]	2.571(18)	2.541	2.569
Ag(2)–O(2) [2×]	2.40(3)	2.395	2.394
Ag(2)–O(1) [2×]	2.424(12)	2.504	2.551
Ag(1)–Ag(1)^{ix}	2.974(3)	2.923	3.024
Angles			
O(1)–M^{4+}–O(1)^{i} [4×]	108.4(4)	109.0	108.9
O(1)– M^{4+}–O(1)^{v} [2×]	111.7(8)	110.5	110.7
O(2)– M^{6+}–O(2)^{i} [4×]	106.1(12)	109.6	109.1
O(2)– M^{6+}–O(2)^{ii} [2×]	116(3)	109.2	110.2
O(1)–Ag(1)–O(1)^{viii}	173.8(6)	174.1	177.0
Ag(1)–O(1)–Ag(1)^{x}	109.8(5)	108.2	109.9

Table 4. Selected bond lengths (Å) and angles (deg) for $Ag_6(CrO_4)(SiO_4)$ and isostructural compounds.

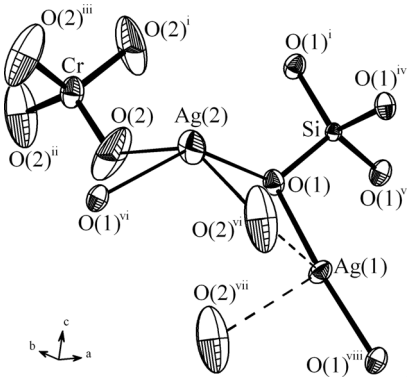

Fig. 2. Asymmetric unit and adjacent atoms of $Ag_6(CrO_4)(SiO_4)$, with ellipsoids drawn at 50 % probability level. Symmetry operations: [i] $3/4-y$, $3/4-x$, $1/4-z$; [ii] $-x$, $3/2-y$, z; [iii] $-3/4+y$, $3/4+x$, $1/4-z$; [iv] $1/4+y$, $-1/4+x$, $1/4-z$; [v] $1-x$, $1/2-y$, z; [vi] $-x$, $1/2-y$, z; [vii] $-x$, $-1/2+y$, $-z$; [viii] x, $-y$, $-z$.

$Ag_6(CrO_4)(SiO_4)$ crystallizes isostructurally to $Ag_6(SO_4)(SiO_4)$ [15] and $Ag_6(SO_4)(GeO_4)$ [22] with space group $I4_1/amd$ and consists of Ag^+ cations and isolated CrO_4^{2-} and SiO_4^{4-} tetrahedra (Fig. 1). While the SiO_4 geometry complies well with that known from related silicates [10, 16], the Cr–O distances appear shorter compared to other chromates [21, 23], and both MO_4 units – but particularly the CrO_4 units – are slightly flattened to form a bisphenoid with respect to their extension along the c axis (see Table 4). Two crystallographically independent silver cations are present in the structure, Ag(2) located slightly above the center of a square of four oxygen atoms and Ag(1) in a dumbbell-like coordination by two O(1) atoms with two more oxygen atoms at a larger distance (see Fig. 2). The dumbbells, exhibiting the shortest Ag–O bonds present in $Ag_6(CrO_4)(SiO_4)$, form zigzag $^1_\infty[AgO]^-$ chains along [100] and [010], respectively. The chains are interconnected by SiO_4 tetrahedra to give a three-dimensional, formally uncharged $^3_\infty[Ag_4SiO_4]$ framework (Fig. 3). The CrO_4^{2-} tetrahedron, bearing the lower charge among the two complex anions present, and the Ag(2) atoms are located in channels inside the "Ag_4SiO_4" framework, and the Ag–O bond lengths are slightly longer than those within the framework. No mixed occupation, neither of the Si, nor of the Cr site, has been found in the structure refinement, although both tetrahedral anions are of very similar size. Obviously the charge difference is sufficient to cause full ordering.

The different two- and fourfold silver coordinations observed in the new compound resemble that in the "parent" structures Ag_4SiO_4 and Ag_2CrO_4: the fourfold coordination of silver atoms by squares of oxygen atoms is also found in Ag_2CrO_4 [23], while in Ag_4SiO_4 the silver atoms are coordinated

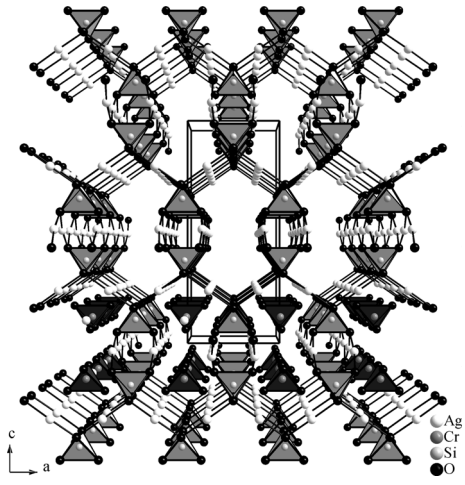

Fig. 3. Perspective view of the crystal structure of $Ag_6(CrO_4)(SiO_4)$. To emphasize the $^3_\infty[Ag_4SiO_4]_n$ network, Ag(1) atoms and SiO_4 tetrahedra are connected and, in the upper part, CrO_4 tetrahedra and Ag(2) atoms are removed.

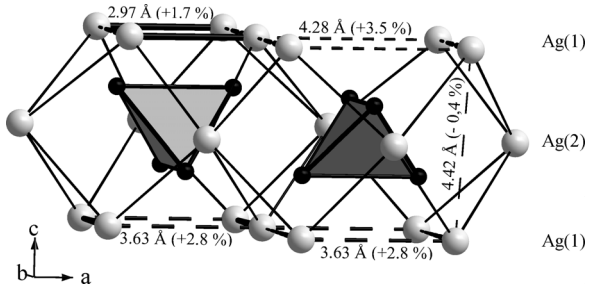

Fig. 4. Cuboctahedral surrounding of CrO_4 (dark grey) and SiO_4 (light grey) tetrahedra by Ag cations in $Ag_6(CrO_4)(SiO_4)$. Ag(1)–Ag(1) distances in [100], [010] and [001] directions are given with relative changes compared to $Ag_6(SO_4)(SiO_4)$ in brackets.

linearly [10]. As another characteristic feature of $Ag_6(CrO_4)(SiO_4)$, there is a striking analogy between the $^3_\infty[Ag_4SiO_4]$ framework and the crystal structure of Ag_4SiO_4, where helical $^1_\infty[AgO]^-$ chains are linked by SiO_4 units, but with a different connectivity pattern.

As frequently observed in silver-rich compounds [3, 4] a short distance of 2.97 Å between silver cations close to the interatomic distances in elemental silver (2.89 Å) is found.

Taken together, the cations form an ordered variant of a distorted cubic close packing with oxygen atoms in tetrahedral voids. Following from that cation packing both, the CrO_4^{2-} and SiO_4^{4-} tetrahedra, are surrounded by distorted cuboctahedra of silver atoms (Fig. 4). A

Table 5. Lattice parameters for $Ag_6(CrO_4)(SiO_4)$ and isostructural compounds.

Compound	*a* axis (Å)	*c* axis (Å)	unit cell volume (Å^3)	Ref. Ref.
$Ag_6(SO_4)(SiO_4)$	7.060	17.660	880.2	[15]
$Ag_6(SO_4)(GeO_4)$	7.149	18.063	923.2	[22]
$Ag_6(CrO_4)(SiO_4)$	7.256	17.584	925.9	this work

ccp array of the cations and similar cuboctahedral silver environments of tetrahedral MO_4 anions are also found in the α- and β-phases of Ag_3VO_4 [24, 25] and in Ag_4SiO_4 [10]. These compounds only differ in the arrangement of the occupied voids. In β-Ag_3VO_4 one kind of the tetrahedral voids is completely occupied, like in Sphalerite, while in α-Ag_3VO_4 and in $Ag_6(CrO_4)(SiO_4)$ half, and in Ag_4SiO_4 40 % of both kinds of tetrahedral voids are filled in different ordering schemes.

Compared to $Ag_6(SO_4)(SiO_4)$ [15], the unit cell volumes of the isostructural compounds $Ag_6(SO_4)(GeO_4)$ [22] and $Ag_6(CrO_4)(SiO_4)$ are larger, as is to be expected owing to the partially bigger cations (see Table 5). The volume increase is about 5 % in both cases. While for $Ag_6(SO_4)(GeO_4)$ the expansion is almost isotropic, surprisingly, in $Ag_6(CrO_4)(SiO_4)$ the volume increase exclusively results from elongation of the tetragonal *a* and *b* axes, while the *c* axis is even the shortest of all three compounds, slightly below the value for $Ag_6(SO_4)(SiO_4)$. Obviously the *c* axis is affected to a higher degree by the sizes of the SiO_4 and GeO_4 tetrahedra. This finding supports the structure description given as a rigid framework consisting of Ag_4MO_4 units (M = Si, Ge). As seen in Fig. 3, the SiO_4 tetrahedra act as a spacer in the [001] direction between the layers of Ag(1) atoms. These layers of Ag(1) atoms at the special 16*f* position with fixed *z* parameter (top and bottom positions in Fig. 4) define the upper and lower border of the cage including also CrO_4, *i. e.* in [001] direction the SiO_4^{4-} and the slightly larger CrO_4^{2-} tetrahedral have the same space available. As a consequence, the CrO_4^{2-} tetrahedron in the new compound appears flattened as stated above, while in $Ag_6(SO_4)(SiO_4)$ and in $Ag_6(SO_4)(GeO_4)$ all tetrahedral groups are almost undistorted [15, 22; see also Table 4]. The required additional space for the larger CrO_4^{2-} tetrahedron is created instead mainly in [100] and [010] directions, as can as well be seen from the Ag(1)–Ag(1) distances shown in Fig. 4. Note that in *a* and *b* directions the highest relative enlargement is

observed at the cuboctahedral edge which is part of the CrO_4 cuboctahedron only, and *vice versa* the smallest relative elongation at the short Ag–Ag distance which is only an edge of the cuboctahedron surrounding SiO_4. Considering the $^3_\infty[Ag_4SiO_4]$ framework, the discussed changes are reflected in the AgO zigzag chains as elongated Ag(1)–O(1) distances and slightly widened Ag(1)–O(1)–Ag(1) angles. As another consequence the "intercalated" Ag(2) atom and the CrO_4^{2-} tetrahedron show a higher degree of thermal motion expressed by the large displacement parameters of these atoms, particularly of the O(2) atoms. The O(2) ellipsoid has its largest extension (U_{33}) perpendicular to the Cr–O bond and almost parallel to the *c* axis, *i. e.* the direction of the tetrahedral distortion. Thus the large displacement parameters of these atoms seem to be an expression rather of the internal stress caused by the lack of space than of the lower fixation of the chromate tetrahedron.

Acknowledgements

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[1] M. Jansen, H. H. Käs *Angew. Chem.* **1980**, *92*, 386 – 387; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 386 – 387.
[2] C. Friebel, M. Jansen *Z. Naturforsch.* **1984**, *39b*, 739 – 743.
[3] M. Jansen *J. Less-Common Met.* **1980**, *76*, 285 – 292.
[4] M. Jansen *Angew. Chem.* **1987**, *99*, 1136 – 1149; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098 – 1110.
[5] M. Jansen *Acta Crystallogr.* **1977**, *B33*, 3584 – 3586.
[6] M. Jansen, K. Heidebrecht *Z. Allg. Anorg. Chem.* **1991**, *601*, 5 – 11.
[7] C. Linke, M. Jansen *Z. Allg. Anorg. Chem.* **1996**, *622*, 486 – 493.
[8] M. Jansen, H.-L. Keller *Angew. Chem.* **1979**, *91*, 500; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 464.
[9] C. Linke, M. Jansen *Inorg. Chem.* **1994**, *33*, 2614 – 2616.
[10] W. Klein, M. Jansen *Z. Allg. Anorg. Chem.* **2008**, *634*, 1077 – 1081.
[11] K. Heidebrecht, M. Jansen *Z. Allg. Anorg. Chem.* **1991**, *597*, 79 – 86.
[12] E. Thilo, F. Wodtcke *Z. Allg. Anorg. Chem.* **1958**, *295*, 247 – 261.
[13] F. Wodtcke, K.-H. Jost *Z. Allg. Anorg. Chem.* **1962**, *314*, 341 – 344.
[14] M. Jansen, K. Heidebrecht *Z. Kristallogr.* **1987**, *179*, 347 – 356.
[15] H.-L. Keller, H. K. Müller-Buschbaum *Z. Anorg. Allg. Chem.* **1974**, *408*, 205 – 208.
[16] W. Klein, M. Jansen *Z. Kristallogr. – New Cryst. Struct.* **2009**, *224*, 165.
[17] W. Klein, J. Curda, E.-M. Peters, M. Jansen *Z. Anorg. Allg. Chem.* **2006**, *632*, 1508 – 1513.
[18] a) G. M. Sheldrick SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick *Acta Crystallogr.* **1990**, *A46*, 467 – 473; b) G. M. Sheldrick SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick *Acta Crystallogr.* **2008**, *A64*, 112 – 122.
[19] W. Klein, J. Curda, K. Friese, M. Jansen *Acta Crystallogr.* **2002**, *C58*, i23 – i24.
[20] W. Klein, J. Curda, M. Jansen *Acta Crystallogr.* **2005**, *C61*, i63 – i64.
[21] J. Curda, E.-M. Peters, W. Klein, M. Jansen *Z. Kristallogr. – New Cryst. Struct.* **2001**, *216*, 180.
[22] K. Heidebrecht, M. Jansen *Z. Kristallogr.* **1991**, *196*, 294 – 295.
[23] M. L. Hackert, R. A. Jacobson *J. Solid State Chem.* **1971**, *3*, 364 – 368.
[24] T. A. Albrecht, C. L. Stern, K. R. Poeppelmeier *Inorg. Chem.* **2007**, *46*, 1704 – 1708.
[25] R. E. Dinnebier, A. Kowalevsky, H. Reichert, M. Jansen *Z. Kristallogr.* **2007**, *222*, 420 – 426.