

Seven new rare-earth transition-metal oxychalcogenides: Syntheses and characterization of Ln_4MnOSe_6 ($Ln = La, Ce, Nd$), Ln_4FeOSe_6 ($Ln = La, Ce, Sm$), and La_4MnOS_6

Ismail Ijjaali, Bin Deng, James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Received 22 December 2004; received in revised form 25 February 2005; accepted 27 February 2005

Available online 23 March 2005

Abstract

The quaternary oxychalcogenides Ln_4MnOSe_6 ($Ln = La, Ce, Nd$), Ln_4FeOSe_6 ($Ln = La, Ce, Sm$), and La_4MnOS_6 have been synthesized by the reactions of Ln ($Ln = La, Ce, Nd, Sm$), M ($M = Mn, Fe$), Se, and SeO_2 at 1173 K for the selenides or by the reaction of La_2S_3 and MnO at 1173 K for the sulfide. *Warning:* These reactions frequently end in explosions. These isostructural compounds crystallize with two formula units in space group $C_{6v}^4 - P6_3mc$ of the hexagonal system. The cell constants (a, c in Å) at 153 K are: La_4MnOSe_6 , 9.7596(3), 7.0722(4); La_4FeOSe_6 , 9.7388(4), 7.0512(5); Ce_4MnOSe_6 , 9.6795(4), 7.0235(5); Ce_4FeOSe_6 , 9.6405(6), 6.9888(4); Nd_4MnOSe_6 , 9.5553(5), 6.9516(5); Sm_4FeOSe_6 , 9.4489(5), 6.8784(5); and La_4MnOS_6 , 9.4766(6), 6.8246(6). The structure of these Ln_4MOQ_6 compounds comprises a three-dimensional framework of interconnected $LnOQ_7$ bicapped trigonal prisms, MQ_6 octahedra, and the unusual $LnOQ_6$ tricapped tetrahedra.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Synthesis; Crystal structure; Rare earth; Oxychalcogenide; Manganese; Iron

1. Introduction

Quaternary oxychalcogenides involving $3d$ transition metals and $4f$ elements are of considerable interest owing to their electrical [1–4], optical [5,6], and magnetic properties [7,8]. The $3d$ metal in most of the known phases is Cu or an early transition element, such as Ti, V, or Cr. With the exception of $La_3CuO_2S_3$ [9], the Cu-containing materials usually adopt a layered structure [10–12]. In contrast, those structures containing an early transition metal are composed of three-dimensional face- and edge-sharing polyhedra. Examples include $La_4Ti_2O_4Se_5$, $La_6Ti_3O_5Se_9$ [13], $La_6Ti_2S_8O_5$, $La_4Ti_3S_4O_8$ [14], $La_8Ti_{10}S_{24}O_4$ [15], $Ln_5V_3O_7S_6$ ($Ln = La, Ce, Pr, Nd$) [16,17], $Ln_4VO_4Se_8$ ($Ln = Nd, Sm, Gd$) [18], $LaCrOS_2$ [19], $CeCrOS_2$ [20], and $NdCrOS_2$ [7]. Ferromagnetic ordering occurs in $LaCrOQ_2$ ($Q = S,$

Se) and antiferromagnetic ordering occurs in $NdCrOS_2$ [7].

In the search for new $Ln/M/O/Q$ phases that might possess $3d-4f$ magnetic interactions, we have focused on the late transition metals Mn and Fe because these have more d electrons and higher magnetic moments than do Ti, V, or Cr. Recently, we synthesized the quaternary compound $CeMn_{0.5}OSe$ [21]. The short Mn–Mn distance (2.8465(5) Å) in this compound could result in magnetic ordering. We present here the syntheses and the structure of seven new Ln/Mn or $Fe/O/Q$ quaternary compounds. Magnetic studies are not presented owing to the lack of sufficient quantities of these Mn and Fe compounds.

2. Experimental

2.1. Syntheses

The following reactants were used as obtained: La (Alfa, 99.9%), Ce (Alfa, 99.9%), Nd (Alfa, 99.9%), Sm

*Corresponding author. Fax: +1 847 491 2976.

E-mail address: ibers@chem.northwestern.edu (J.A. Ibers).

(Alfa, 99.9%), Mn (Alfa, 99.9%), Fe (Alfa, 99.9%), Se (Alfa, 99.5%), SeO₂ (Aldrich, 99.9%), La₂S₃ (Strem, 99.9%), and MnO (Strem, 99%). The Ln₄MOSe₆ compounds were synthesized from reaction mixtures of 2 mmol of Ln, 1 mmol of M, 3 mmol of Se, and 1 mmol of SeO₂. La₄MnOS₆ was synthesized from a mixture of 1 mmol of La₂S₃ and 0.5 mmol of MnO. Those reaction mixtures were loaded into fused-silica tubes under an Ar atmosphere in a glovebox. The tubes were evacuated to about 10⁻⁴ Torr and sealed, and then placed in a computer-controlled furnace. The samples were heated to 1173 K in 72 h, kept at 1173 K for 5 days, cooled at 1.5 K/h to 953 K, and then cooled to room temperature in 10 h. *Warning:* The tubes often exploded during the cooling process. The products were washed with deionized water and dried with methanol. Qualitative elemental analyses of these compounds were carried out with an EDX-equipped Hitachi S-3500 SEM. In those reactions that did not explode the yields of desired products were about 2%. Crystals of La₄MnOS₆ are red; those of Ce₄FeOS₆ are dark red; the others are black.

2.2. Crystallography

Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [22]. The crystal-to-detector distance was 5.023 cm. Data were collected by a scan of 0.3° in ω in groups of 606 frames for each of the φ settings of 0°, 90°, 180°, and 270°. The exposure times were 15 s/frame. Intensity data were collected with the program SMART [22]. Cell refinement and data reduction were carried out with the use of the program SAINT [22], and face-indexed absorption corrections were performed numerically with the use of the program XPREP [23]. Then the program SADABS [22] was employed to make incident beam and decay corrections.

The structures were solved in the hexagonal space group $P6_3mc$ with the direct methods program SHELXS of the SHELXTL suite of programs [23] and refined by full-matrix least-squares techniques. Final refinements included anisotropic displacement parameters and a secondary extinction correction. The program TIDY [24] was used to standardize the positional parameters. Owing to the direction of the 6_3 axis in the particular crystal chosen relative to the laboratory coordinate system, these positional parameters occur in two sets, with Ce₄FeOS₆ and Nd₄MnOS₆ in one set and the other five compounds in the other. Additional experimental details are given in Table 1 and in Supporting information. Table 2 presents selected interatomic distances.

3. Results and discussion

The new compounds Ln₄MnOS₆ (Ln = La, Ce, Nd), Ln₄FeOS₆ (Ln = La, Ce, Sm), and La₄MnOS₆ are isostructural and crystallize in a new structure type that is closely related to the structure of K₅InTe₄·KCl [25]. Because there are no Q–Q bonds or Q–O bonds in these compounds, the oxidation states of Ln/M/O/Q are 3+/2+/2–/2–. The unit cell of Ln₄MOQ₆ is illustrated in Fig. 1. The main building units of the structure are a three-dimensional framework of interconnected LnOQ₇ and LnOQ₆ polyhedra and one-dimensional ∞ [MQ₃^{4–}] chains. The polyhedra are distinctly different for the two crystallographically independent Ln atoms (Ln1, site symmetry m and Ln2, site symmetry $3m$). Atom Ln1 is in a bicapped trigonal prism and atom Ln2 is in what may be described as a tetrahedron of three Q2 atoms and one O atom with each QQO face capped with a Q1 atom (Fig. 2). We can find no other examples of this coordination geometry among ternary and quaternary rare-earth oxychalcogenides. The six-coordinate M atom (site symmetry $3m$) is in an octahedron of Q1

Table 1
Crystal data and structure refinement for Ln₄MOQ₆^a (Q = Se, S)

	La ₄ MnOS ₆	La ₄ FeOS ₆	Ce ₄ MnOS ₆	Ce ₄ FeOS ₆	Nd ₄ MnOS ₆	Sm ₄ FeOS ₆	La ₄ MnOS ₆
FW	1100.34	1101.25	1105.18	1106.09	1121.66	1147.01	818.94
<i>a</i> (Å)	9.7596(3)	9.7388(4)	9.6795(4)	9.6405(3)	9.5553(5)	9.4489(5)	9.4766(6)
<i>c</i> (Å)	7.0722(4)	7.0512(5)	7.0235(5)	6.9888(4)	6.9516(5)	6.8784(5)	6.8246(6)
<i>V</i> (Å ³)	583.38(4)	579.17(5)	569.89(5)	562.51(4)	549.67(6)	531.84(6)	530.78(7)
ρ_c (g/cm ³)	6.264	6.315	6.441	6.530	6.777	7.163	5.124
μ (mm ⁻¹)	34.047	34.457	35.836	36.473	39.483	43.540	18.028
<i>p</i> ^c	0.013	0.012	0.040	0.014	0.040	0.023	0.012
<i>R</i> (<i>F</i>) ^b	0.0190	0.0165	0.0247	0.0195	0.0286	0.0188	0.0125
<i>R</i> _w (<i>F</i> ²) ^c	0.0523	0.0479	0.0729	0.0585	0.0825	0.0450	0.0297

^aFor all structures *Z* = 4, space group = $P6_3mc$, *T* = 153 (2) K, and λ = 0.71073 Å.

^b $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

^c $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (pF_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Selected interatomic distances (Å) for Ln_4MOQ_6

	La_4MnOSe_6	La_4FeOSe_6	Ce_4MnOSe_6	Ce_4FeOSe_6	Nd_4MnOSe_6	Sm_4FeOSe_6	La_4MnOS_6
$Ln1-O$	2.393(4)	2.401(4)	2.369(5)	2.372(4)	2.332(6)	2.319(3)	2.378(2)
$Ln1-Q1 \times 2$	3.0415(4)	3.0212(4)	3.0205(5)	2.9935(4)	2.9949(6)	2.9543(4)	2.9155(4)
$Ln1-Q2 \times 2$	3.0475(8)	3.0520(8)	3.0180(9)	3.0179(9)	2.979(1)	2.9522(7)	2.9359(9)
$Ln1-Q1$	3.096(1)	3.092(1)	3.069(1)	3.059(1)	3.021(2)	2.991(1)	2.995(1)
$Ln1-Q2 \times 2$	3.3014(7)	3.2888(7)	3.2830(9)	3.2628(8)	3.245(1)	3.2118(6)	3.2336(9)
$Ln2-O$	2.41(1)	2.39(1)	2.39(2)	2.37(1)	2.36(2)	2.30(1)	2.367(6)
$Ln2-Q2 \times 3$	2.980(1)	2.976(1)	2.955(1)	2.946(1)	2.909(1)	2.873(1)	2.845(1)
$Ln2-Q1 \times 3$	3.5223(8)	3.562(1)	3.480(1)	3.516(2)	3.420(1)	3.4136(7)	3.452(3)
$M-Q1 \times 3$	2.675(2)	2.652(2)	2.671(2)	2.640(2)	2.660(2)	2.629(1)	2.539(1)
$M-Q1 \times 3$	2.870(2)	2.805(2)	2.850(2)	2.778(2)	2.822(2)	2.741(2)	2.802(1)

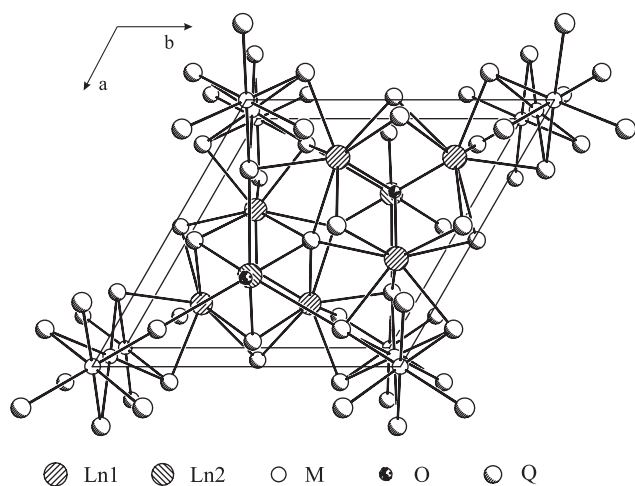


Fig. 1. Structure of Ln_4MOQ_6 viewed down [001].

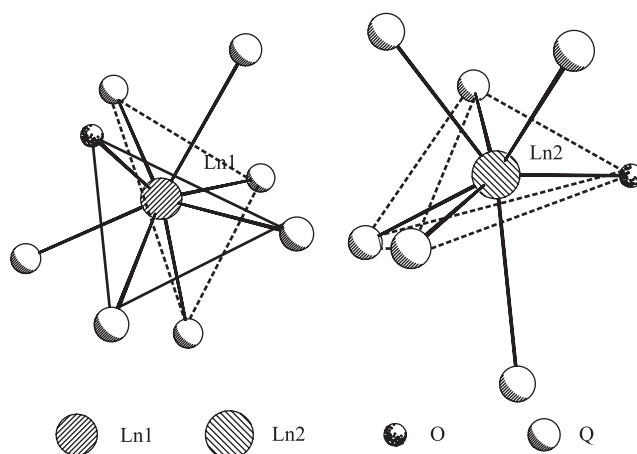


Fig. 2. Coordination geometries of the two independent Ln atoms in Ln_4MOQ_6 .

atoms. Because of the Peierls distortion for Mn^{2+} , this octahedron is more distorted for $M = Mn$ than for $M = Fe$. The one-dimensional ${}^1_{\infty}[MQ_3^{4-}]$ chain is formed by the face sharing of these MQ_6 octahedra along the hexagonal c -axis, as indicated in Fig. 3. Similar ${}^1_{\infty}[MQ_3^{4-}]$ chains are found in $La_6MnSi_2S_{14}$ [26] and La_3MnFeS_7 [27]. The three-dimensional structure of the present compounds results in the following surroundings of the O and Q atoms. Each O atom is surrounded by three $Ln(1)$ atoms and one $Ln(2)$ atom; each Q1 atom is coordinated by three $Ln(1)$ atoms, two M atoms, and one $Ln(2)$ atom; and each Q2 atom is surrounded by four $Ln(1)$ atoms and one $Ln(2)$ atom.

The $Ln-Ln$ distances are 3.9077(7) and 3.9200(9) Å in La_4MnOSe_6 ; 3.9108(9) and 3.9209(8) Å in La_4FeOSe_6 ; 3.8718(9) and 3.883(1) Å in Ce_4MnOSe_6 ; 3.868(1) and 3.8791(8) Å in Ce_4FeOSe_6 ; 3.8061(9) and 3.835(1) Å in Nd_4MnOSe_6 ; and 3.7744(6) and 3.7851(8) Å in Sm_4FeOSe_6 . The $Ln-M$ distance is 3.5915(9) Å in La_4MnOSe_6 , 3.5570(8) Å in La_4FeOSe_6 , 3.561(1) Å in Ce_4MnOSe_6 , 3.5189(9) Å in Ce_4FeOSe_6 , 3.516(1) Å in Nd_4MnOSe_6 , and 3.4562(7) Å in Sm_4FeOSe_6 . The $M-M$ distance is 3.536(1) Å in La_4MnOSe_6 , 3.526(2) Å

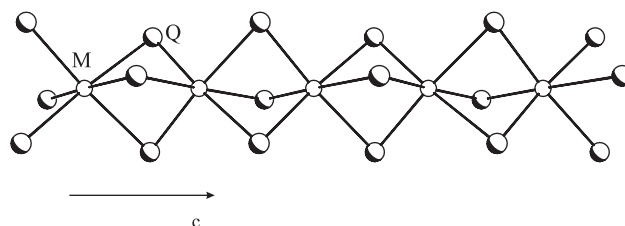


Fig. 3. The one-dimensional ${}^1_{\infty}[MQ_3^{4-}]$ chain of Ln_4MOQ_6 .

in La_4FeOSe_6 , 3.512(1) Å in Ce_4MnOSe_6 , 3.494(1) Å in Ce_4FeOSe_6 , 3.476(1) Å in Nd_4MnOSe_6 , and 3.439(2) Å in Sm_4FeOSe_6 .

Other selected interatomic distances for Ln_4MOQ_6 are given in Table 2. The $Ln-O$ distances, which range from 2.30(1) to 2.41(1) Å, are comparable to those in $LaCuOS$ ($La-O$ 2.367(5) Å) [28], $CeCrOS_2$ (2.354(2) and 2.428(3) Å) [29], $NdCrOS_2$ (2.301(1) and 2.405(2) Å) [7], and $Sm_3NbO_4Se_3$ (2.321(3)–2.512(2) Å) [30]. The $Ln1-Se1$ and $Ln2-Se2$ distances range from 2.873(1) to

3.096(1) Å. This range is normal compared to those of 2.862(1)–2.944(1) Å in LiLnSe_2 [31] and 2.8371(7)–3.0295(6) Å in RbLnSe_2 [32]. It is also normal compared to the Ln–Se distances in several oxyselenides, including distances of 3.010(1)–3.488(1) Å in $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ [13], 3.3295(8) Å in $\text{CeMn}_{0.5}\text{OSe}$ [21], 2.9037(6)–3.3211(6) Å in $\text{Nd}_7\text{VO}_4\text{Se}_8$ [18], and 2.923(1)–3.149(1) Å in $\text{Sm}_3\text{NbO}_4\text{Se}_3$ [30]. The Ln1–Q2 capping distances in the Ln1OQ_7 bicapped trigonal prisms of the present compounds are longer than the Ln1–Se1 distances, ranging from 3.2118(6) to 3.3014(7) Å. Concomitant with the unusual coordination geometry about atom Ln2 , the Ln2–Se1 capping distances are even longer, ranging from 3.4136(7) to 3.5223(8) Å. In addition to these, there are three other Se2 atoms located near the Ln2 atoms. These distances range from 3.615(7) to 3.707(5) Å. Thus, one can describe atom Ln2 as being seven coordinate (LnOSe_6) or ten coordinate (LnOSe_9), the former being closer to the usual coordination number for chalcogenide coordination of a rare earth. The M–Se distances range from 2.629(1) to 2.870(2) Å, consistent with the Mn–Se distances of 2.576(1)–2.847(2) Å for $\text{CeMn}_{0.5}\text{OSe}$ [21] and the Fe–Se distance of 2.722(3) Å for $\text{La}_2\text{Fe}_2\text{O}_3\text{Se}_2$ [33].

In La_4MnOS_6 , the La–La distances are 3.846(1) and 3.892(1) Å, the La–Mn distance is 3.472(1) Å, and the Mn–Mn distance is 3.412(1) Å. Table 2 also shows selected interatomic distances for La_4MnOS_6 . The La–O distances of 2.367(6) and 2.378(2) Å are consistent with those in $\text{La}_5\text{Cu}_6\text{O}_4\text{S}_7$ (2.343(2)–2.446(3) Å) [12]. The La1–S distances of 2.9155(4) and 2.995(1) Å are comparable to those of 3.054(2)–3.231(1) Å in $\text{La}_5\text{Cu}_6\text{O}_4\text{S}_7$ [12]. The La2–S2 distance of 2.845(1) Å is slightly shorter and the La2–S1 distance of 3.452(3) Å is somewhat longer. As they are for $\text{Q} = \text{Se}$, the La1–Q1 and La2–Q1 ($\text{Q} = \text{S}$) capping distances are very long. The Mn–S distances of 2.539(1) and 2.802(1) Å reflect the Peierls distortion expected for this Mn^{2+} center. Such a distortion is also observed in $\text{La}_6\text{MnSi}_2\text{S}_{14}$ (2.637(2) and 2.674(1) Å) [26] and $\text{La}_3\text{MnFeS}_7$ (2.773(2) and 2.816(3) Å) [27].

4. Supporting information

The crystallographic files in cif format have been deposited with FIZ Karlsruhe. The compounds and their CSD numbers are: $\text{La}_4\text{MnOSe}_6$, 391303; $\text{La}_4\text{FeOSe}_6$, 391306; $\text{Ce}_4\text{MnOSe}_6$, 391300; $\text{Ce}_4\text{FeOSe}_6$, 391301; $\text{Nd}_4\text{MnOSe}_6$, 391299; $\text{Sm}_4\text{FeOSe}_6$, 391304; La_4MnOS_6 , 391305. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysddata@fiz-karlsruhe.de (email).

Acknowledgments

This research was supported in part by the US National Science Foundation under Grant DMR00-96676. Use was made of the MRSEC Central Facilities supported by the National Science Foundation at the Materials Research Center of Northwestern University under Grant DMR00-76097.

References

- [1] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, H. Hosono, Appl. Phys. Lett. 77 (2000) 2701–2703.
- [2] H. Hiramatsu, K. Ueda, H. Ohto, M. Orita, M. Hirano, H. Hosono, Thin Solid Films 411 (2002) 125–128.
- [3] S. -Ichiro Inoue, K. Ueda, H. Hosono, N. Hamada, Phys. Rev. B: Condens. Matter 64 (2001) 245211–245215.
- [4] K. Ueda, H. Hosono, J. Appl. Phys. 91 (2002) 4768–4770.
- [5] A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 124 (2002) 13547–13553.
- [6] C. Boyer-Candalen, J. Derouet, P. Porcher, Y. Moëlo, A. Meerschaut, J. Solid State Chem. 165 (2002) 228–237.
- [7] M. Wintenberger, J. Dugué, M. Guittard, N.H. Dung, V.V. Tien, J. Solid State Chem. 70 (1987) 295–302.
- [8] M. Wintenberger, T. Vovan, M. Guittard, Solid State Commun. 53 (1985) 227–230.
- [9] I. Ijjaali, C.L. Haynes, A.D. McFarland, R.P. Van Duyne, J.A. Ibers, J. Solid State Chem. 172 (2003) 257–260.
- [10] A.M. Kusainova, P.S. Berdonosov, L.G. Akselrud, L.N. Kholodkovskaya, V.A. Dolgikh, B.A. Popovkin, J. Solid State Chem. 112 (1994) 189–191.
- [11] P.S. Berdonosov, A.M. Kusainova, L.N. Kholodkovskaya, V.A. Dolgikh, L.G. Akselrud, B.A. Popovkin, J. Solid State Chem. 118 (1995) 74–77.
- [12] F.Q. Huang, P. Brazis, C.R. Kannewurf, J.A. Ibers, J. Solid State Chem. 155 (2000) 366–371.
- [13] O. Tougaard, J.A. Ibers, J. Solid State Chem. 157 (2001) 289–295.
- [14] J.A. Cody, J.A. Ibers, J. Solid State Chem. 114 (1995) 406–412.
- [15] L. Cario, C. Deudon, A. Meerschaut, J. Rouxel, J. Solid State Chem. 136 (1998) 46–50.
- [16] J. Dugué, T. Vovan, P. Laruelle, Acta Crystallogr. C: Cryst. Struct. Commun. 41 (1985) 1146–1148.
- [17] T. Vovan, J. Dugué, M. Guittard, C.R. Acad. Sci., Sér. 2 292 (1981) 957–959.
- [18] O. Tougaard, J.A. Ibers, J. Solid State Chem. 154 (2000) 564–568.
- [19] J. Dugué, T. Vovan, J. Villers, Acta Crystallogr. B: Struct. Crystallogr. Cryst. Chem. 36 (1980) 1291–1294.
- [20] J. Dugué, T. Vovan, J. Villers, Acta Crystallogr. B: Struct. Crystallogr. Cryst. Chem. 36 (1980) 1294–1297.
- [21] I. Ijjaali, K. Mitchell, C.L. Haynes, A.D. McFarland, R.P. Van Duyne, J.A. Ibers, J. Solid State Chem. 176 (2003) 170–174.
- [22] Bruker, SMART Version 5.054 data collection and SAINT-Plus Version 6.45a data processing software for the SMART system, Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2003.
- [23] G.M. Sheldrick, SHELXTL Version 6.14, Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2003.
- [24] L.M. Gelato, E. Parthé, J. Appl. Crystallogr. 20 (1987) 139–143.
- [25] S. Sportouch, C. Belin, M. Tillard-Charbonnel, Acta Crystallogr. C: Cryst. Struct. Commun. 50 (1994) 1861–1862.
- [26] G. Collin, P. Laruelle, C. R. Seances Acad. Sci., Ser. C 270 (1970) 410–412.
- [27] K.S. Nanjundaswamy, J. Gopalakrishnan, J. Solid State Chem. 49 (1983) 51–58.

- [28] M. Palazzi, S. Jaulmes, *Acta Crystallogr. B: Struct. Crystallogr. Cryst. Chem.* 37 (1981) 1337–1339.
- [29] T.V. Van, D.N. Huy, *C. R. Acad. Sci., Sér. 2* 293 (1981) 933–936.
- [30] A. Meerschaut, C. Boyer, A. Lafond, L. Cario, J. Rouxel, *J. Solid State Chem.* 137 (1998) 122–126.
- [31] T. Ohtani, H. Honjo, W. Hironobu, *Mater. Res. Bull.* 22 (1987) 829–840.
- [32] B. Deng, D.E. Ellis, J.A. Ibers, *Inorg. Chem.* 41 (2002) 5716–5720.
- [33] J.M. Mayer, L.F. Schneemeyer, T. Siegrist, J.V. Waszczak, B. Van Dover, *Angew. Chem.* 104 (1992) 1677–1678.