ARTICLE

Synthesis and Structural Characterization of Cs$_2$Ga$_2$Se$_5$

Daniel Friedrich,[a] Marc Schlosser,[a] and Arno Pfitzner*[a]

Dedicated to Professor Reinhard Nesper on the Occasion of His 65th Birthday

Abstract. Cs$_2$Ga$_2$Se$_5$ was obtained by the reaction of CsN$_3$ with stoichiometric amounts of GaSe and Se at elevated temperature. It forms yellow crystals embedded in a pure orange microcrystalline powder. The crystal structure of Cs$_2$Ga$_2$Se$_5$ was determined by single-crystal X-ray diffraction at 123 K. The compound crystallizes monoclinically in the space group $C2/c$ (No. 15) with a = 15.3911(5) Å, b = 7.3577(2) Å, c = 12.9219(3) Å, β = 126.395(3)°, V = 1177.89(7) Å^3, and Z = 4. The structure features one-dimensional chains $^1_\infty$[Ga$_2$Se$_3$(Se$_2$)$^{2-}$], consisting of edge- and corner sharing GaSe$_4$ tetrahedra. Raman spectroscopic measurements reveal vibrational bands of the Se$_2^{2-}$ units at 236 cm^{-1}, and the bands of Ga–Se vibrations at 254 and 273 cm^{-1}. UV/Vis diffuse reflectance spectroscopy shows the bandgap at about 1.95 eV.

Introduction

Chalcogenometallates of group 13 metals show a large variety of compounds. A certain number of them containing alkali metal cations have already been investigated.[1] The crystal structures of known phases in the ternary systems of alkali metal, triel and chalcogen mostly consist of MQ_4-tetrahedra (M = Al, Ga, In; Q = S, Se, Te) embedded in a cationic surrounding. The anionic units composed of these tetrahedra range from discrete tetrahedra to more complex one-, two- and three-dimensional networks. With the exception of CsGaSe$_2$-II[2] (two-dimensional layers, KInS$_2$[3] structure type), all known phases in the ternary system caesium, gallium, and selenium contain one-dimensional selenogallate anions. CsGaSe$_2$-I[2] and CsGaSe$_3$[4] show infinite anionic chains, whereas Cs$_6$Ga$_2$Se$_6$,[5] Cs$_8$Ga$_4$Se$_{10}$,[6] and Cs$_{10}$Ga$_6$Se$_{14}$[6] exhibit dimeric, tetrameric, and hexameric selenogallate units, respectively. CsGaQ_3 (Q = S, Se)[7,4] and K$_9$InSe$_7$[8] are the only examples containing polychalcogenide units among ternary group 13 chalcogenides with alkali metal cations.

In this paper we report on the synthesis and characterization of Cs$_2$Ga$_2$Se$_5$, a new member of this group, which contains polyselenide ions. The title compound as well as the recently reported Cs$_2$Ga$_2$S$_5$[9] are the first examples of anionic chains $^1_\infty$[M_2Q$_3$(Q$_2$)$^{2-}$] (M = Al, Ga, In; Q = S, Se, Te) among group 13 chalcogenometallates containing alkali metal cations. Analogous $^1_\infty$[M_2Q$_3$(Q$_2$)$^{2-}$] chains have been reported in [C$_6$H$_{16}$N$_2$][In$_2$Se$_3$(Se$_2$)],[10]   [M(C$_{12}$H$_8$N$_2$)$_3$][In$_2$Se$_3$(Se$_2$)]H$_2$O

(M = Ni, Fe),[11] [C$_4$H$_{14}$N$_2$][Ga$_2$Se$_3$(Se$_2$)],[12] [C$_6$H$_{16}$N$_2$]-[Ga$_2$Se$_3$(Se$_2$)],[13] and [Mn(C$_2$H$_8$N$_2$)$_3$][In$_2$Se$_3$(Se$_2$)],[14] using organic cations as structure directing agents.

Results and Discussion

Crystal Structure

Cs$_2$Ga$_2$Se$_5$ forms yellow crystals. Its crystal structure was determined by single-crystal X-ray diffraction of a suitable rod shaped crystal. The compound crystallizes monoclinically in the space group $C2/c$ (No. 15) with a = 15.3911(5) Å, b = 7.3577(2) Å, c = 12.9219(3) Å, β = 126.395(3)°, and Z = 4. The crystal structure was solved by charge flipping methods using SUPERFLIP[15] and was subsequently refined by full-matrix least-squares methods using Jana2006.[16] The refinement converged at R_1 = 0.0322 and at wR_2 = 0.0641 for all data. At this stage one significant electron density maximum remained in the final difference Fourier synthesis. It was located in the center of the diselenide unit with reasonable distances to the neigboring gallium atoms. Therefore an additional selenium site was introduced and refined by using a constraint for the occupation of this position and the original diselenide position (see Figure 1). Thus charge balance was ensured. The final structure model contained 96.33% Se$_2^{2-}$
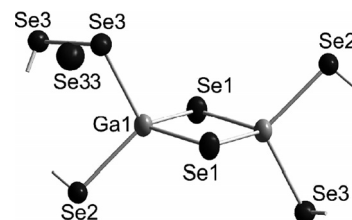

Figure 1. Local coordination of Ga with respect to disordered Se$_2^{2-}$ and Se^{2-} (ellipsoids represent 90% probability).

* Prof. Dr. A. Pfitzner
  Fax: +49-941-943814551
  E-Mail: arno.pfitzner@chemie.uni-regensburg.de
[a] Institut für Anorganische Chemie
  Universität Regensburg
  Universitätsstraße 31
  93040 Regensburg, Germany

and 3.67 % Se^{2-} ions at this position. After taking this disorder into account, the R values dropped to $R_1 = 0.0303$ and $wR_2 = 0.0584$ (for all data), and the peak in the final difference Fourier synthesis disappeared. Several crystals were investigated and showed the same disorder of Se_2^{2-} and Se^{2-} at this position. Therefore we assume that this is an intrinsic phenomenon for the title compound. The final crystallographic data and details of the structure solution and refinement for $Cs_2Ga_2Se_5$ are listed in Table 1. Table 2 and Table 3 show the atomic coordinates and displacement parameters. Interatomic distances and angles are listed in Table 4.

The crystal structure of $Cs_2Ga_2Se_5$ represents a new structure type. It consists of infinite chains $^1_\infty[Ga_2Se_3(Se_2)^{2-}]$ parallel [101] (Figure 2). These anionic selenogallate chains are separated by caesium atoms. Gallium is trivalent and has a slightly distorted tetrahedral coordination formed by three Se^{2-} and one Se atom of the Se_2^{2-} unit. The bond lengths Ga–Se range from d(Ga–Se) = 2.3828(5) Å to d(Ga–Se) = 2.4208(5) Å with a mean bond length of $\bar{d}$(Ga–Se) = 2.41(1) Å. Gallium forms shorter bonds with selenide ions than with diselenide ions as already observed in $CsGaSe_3$.[4] The angles Se–Ga–Se range from 102.15(2)° to 116.37(2)°. The observed bond lengths and angles are in good agreement with values reported for similar compounds.[2,4–6] The bond length

Table 1. Crystallographic data for $Cs_2Ga_2Se_5$.

	$Cs_2Ga_2Se_5$
Formula weight /g·mol^{-1}	800.07
Color and shape	yellow rod
Crystal system, space group	monoclinic, $C2/c$ (No.15)
Lattice constants	
a /Å	15.3911(5)
b /Å	7.3577(2)
c /Å	12.9219(3)
β /°	126.395(3)
Volume V/Å^3	1177.89(7)
Number of formula units, Z	4
Calculated density ρ_{calc}/g·cm^{-3}	4.51
Temperature T /K	123
Diffractometer	Agilent Supernova
Wavelength λ /Å	0.71073
Absorption coeff. μ (Mo-K_α) /mm^{-1}	26.069
θ Range of data collection /°	3.22–32.2
Index ranges	$-23 \leq h \leq 22$
	$-10 \leq k \leq 10$
	$-19 \leq l \leq 19$
Absorption correction	Analytical, CrysAlisPro[17]
No. of reflections collected	13623
Independent reflections	2050
R_{int}	0.0468
Completeness to $\theta_{max} = 32.528$	94.5 %
Structure solution	Charge flipping, Superflip[15]
Structure refinement	Jana2006[16]
No. of refined parameters	48
No. of constraints	1
GooF	1.34
R_1, wR_2 [$I > 2\sigma$ (I)]	0.0249, 0.0553
R_1, wR_2 [all data]	0.0303, 0.0584
Largest diff. peak and hole /e·Å^{-3}	1.81, -1.09

Table 4. Selected bond lengths /Å and angles /° for $Cs_2Ga_2Se_5$.

Ga–Se1	2.4130(7)	Se1–Ga–Se1^{vii}	102.15(2)
Ga–Se1^{vii}	2.4118(7)	Se1^{vii}–Ga–Se2	116.37(2)
Ga–Se2	2.3828(5)	Se1–Ga–Se3	112.89(2)
Ga–Se3	2.4208(5)	Se3^{vii}–Ga–Se1	104.38(3)
Ga–Se33	2.496(15)	Se3–Ga–Se2	109.78(2)
		Se2–Ga–Se1^{iii}	111.03(2)
Se3–Se3	2.3644(7)		
Ga–Ga^{vii}	3.0315(6)	Ga–Se1–Ga^{vii}	77.85(2)
Ga–Ga^{v}	3.5097(5)		
Cs–Se1	3.9243(6)		
Cs–Se1^{i}	3.7139(5)		
Cs–Se1^{ii}	3.8962(5)		
Cs–Se1^{iv}	3.7337(6)		
Cs–Se2	4.0647(4)		
Cs–Se2^{ii}	3.7855(4)		
Cs–Se3^{i}	3.8037(6)		
Cs–Se3^{v}	3.9358(6)		
Cs–Se3^{vi}	3.6878(5)		
Cs–Se3^{viii}	3.9509(5)		
Cs–Se33^{i}	3.73(1)		

Symmetry codes used to generate equivalent atoms: (i) $1-x$, $-y$, $-z$; (ii) $1-x$, $1-y$, $-z$; (iii) $1.5-x$, $0.5-y$, $-z$; (iv) $0.5+x$, $0.5-y$, $0.5+z$; (v) $1-x$, y, $0.5-z$; (vi) x, $-y$, $-0.5+z$; (vii) $0.5-x$, $0.5-y$, $-z$; (viii) $0.5+x$, $0.5+y$, z.

Table 2. Atomic coordinates, occupancies, and equivalent isotropic displacement parameters U_{eq} /Å^2 for $Cs_2Ga_2Se_5$.

Atom	Wyck.	Sof.	x	y	z	U_{eq} a)
Cs	8f	1	0.6142(1)	0.2766(1)	0.0522(1)	0.0185(1)
Ga	8f	1	0.3608(1)	0.2279(1)	0.1264(1)	0.0126(2)
Se1	8f	1	0.3093(1)	0.2106(1)	$-0.0898(1)$	0.0152(1)
Se2	4e	1	½	0.4467(1)	¼	0.0161(1)
Se3	8f	0.963(1)	0.4167(1)	$-0.0624(1)$	0.2359(1)	0.0135(2)
Se33	4e	0.018	½	$-0.013(3)$	¼	0.031(8)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters U_{ij} (in Å$^2 \times 10^3$) for $Cs_2Ga_2Se_5$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	22.4(1)	18.3(1)	13.7(1)	$-0.7(1)$	10.1(1)	$-0.4(1)$
Ga	12.2(1)	14.5(2)	9.4(1)	0.9(1)	5.4(1)	$-0.0(1)$
Se1	14.0(1)	21.4(1)	10.9(1)	1.4(1)	7.8(1)	$-0.5(1)$
Se2	15.2(2)	13.0(2)	13.0(2)	0	4.4(1)	0
Se3	13.4(1)	13.4(1)	14.2(1)	$-0.2(1)$	8.5(1)	0.1(1)
Se33	23(8)	53(1)	15(7)	0	1.0(7)	0

Dedicated Cluster

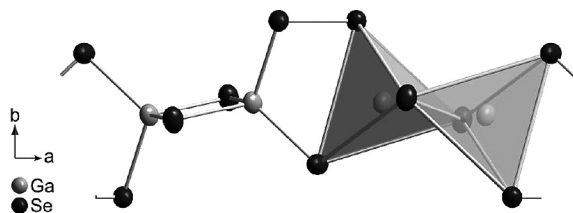within the diselenide ion $d(Se–Se) = 2.3743(7)$ Å is in good agreement with comparable compounds.[4,10–14]

Figure 2. Section of the one-dimensional anionic chain $\frac{1}{\infty}[Ga_2Se_3(Se_2)^{2-}]$, showing the linkage of Ga_2Se_2 and of Ga_2Se_3 rings and coordination polyhedra, respectively (ellipsoids represent 90% probability). The disorder of the Se3/Se33 site is omitted for clarity.

Two $GaSe_4$ tetrahedra are linked by one common edge to form Ga_2Se_6 double tetrahedra. These Ga_2Se_6 units share one common corner and one diselenide dumbbell to the next double tetrahedron and thus form infinite one-dimensional anionic chains along [101]. Alternatively the anionic chains can be described as alternating four-membered Ga_2Se_2 and five-membered $Ga_2Se(Se_2)$ rings connected by common corners. Due to this alternating connection mode in the chains two different Ga–Ga distances of $d(Ga–Ga) = 3.0315(6)$ Å and $d(Ga–Ga) = 3.5097(5)$ Å are observed. The shorter distance is present in the four-membered rings Ga_2Se_2. The anionic chain in $Cs_2Ga_2Se_5$ is related to the chains present in $CsGaSe_2$-I[2] and $CsGaSe_3$.[4] The anions $\frac{1}{\infty}[GaSe_2^{-}]$ and $\frac{1}{\infty}[GaSe_3^{-}]$ can be converted to $\frac{1}{\infty}[Ga_2Se_3(Se_2)^{2-}]$ by replacing a Se^{2-} ion by a Se_2^{2-} ion in a $\frac{1}{\infty}[Ga_2Se_4^{2-}]$ chain or by replacing a Se^{2-} ion with a Se^{2-} ion in a $\frac{1}{\infty}[Ga_2Se_2(Se_2)^{2-}]$ chain. This structure description holds for the majority part assuming fully occupied Se3 positions and neglecting the Se33 position. However, the position Se33 is partially occupied by about 2% and in then the position Se3 has to be unoccupied. In this case gallium still has fourfold coordination and the coordination number of cesium is reduced by one within a sphere of 4.1 Å.

Analogous $\frac{1}{\infty}[M_2Se_3(Se_2)^{2-}]$ chains have been recently reported for $[C_6H_{16}N_2][In_2Se_3(Se_2)]$,[10] $[M(C_{12}H_8N_2)_3][In_2Se_3(Se_2)]H_2O$ (M = Ni, Fe),[11] $[C_4H_{14}N_2][Ga_2Se_3(Se_2)]$,[12] $[C_6H_{16}N_2][Ga_2Se_3(Se_2)]$,[13] and $[Mn(C_2H_8N_2)_3][In_2Se_3(Se_2)]$.[14] $Cs_2Ga_2Se_5$ however represents the first example for a gallium polyselenide $\frac{1}{\infty}[Ga_2Se_3(Se_2)^{2-}]$ with alkali metal counterions.

Caesium is tenfold coordinated by selenium atoms arranged as an irregular coordination polyhedron. The bond lengths Cs–Se range from $d(Cs–Se) = 3.6878(5)$ Å to $d(Cs–Se) = 4.0647(4)$ Å with a mean bond length of $3.85(1)$ Å. These data are in good agreement with comparable compounds.[2,4–6] The cesium atoms form some complex topological network (Figure 3) with Cs–Cs distances ranging from $d(Cs–Cs) = 4.3991(4)$ Å to $d(Cs–Cs) = 6.4896(4)$ Å. The anionic chains are hexagonally arranged along [101] (Figure 3).

Vibration Spectroscopy

The Raman spectrum of $Cs_2Ga_2Se_5$ is displayed in Figure 4. It shows bands at 129, 140, 196, 236, 254, and 273 cm^{-1}. The
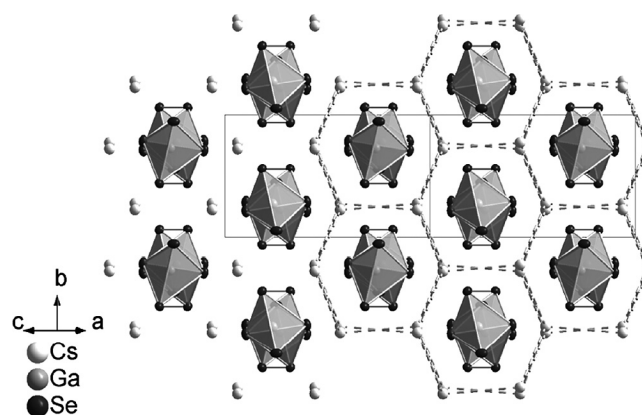

Figure 3. The hexagonal packing of the $\frac{1}{\infty}[Ga_2Se_3(Se_2)^{2-}]$ chains oriented along [101] (ellipsoids at 90% probability). The cationic network is indicated by fragmented lines. Disorder of the Se3/Se33 site is omitted for clarity.

peaks at 129, 140, and 196 cm^{-1} most likely result from Cs–Se stretching vibrations or lattice vibrations. The band at 236 cm^{-1} can be assigned to Se–Se stretching vibrations,[4,18] whereas the peaks at higher wavenumbers all can be assigned to Ga–Se stretching modes.
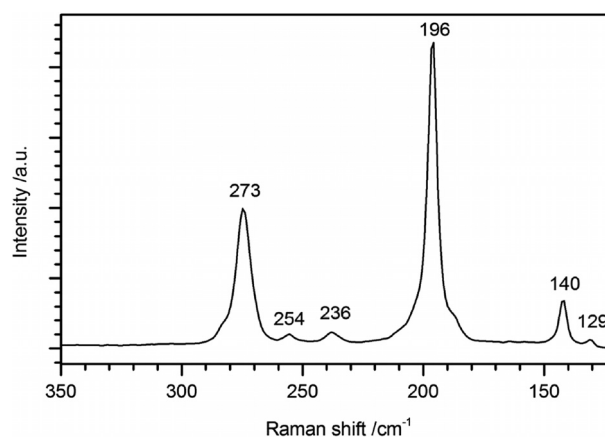

Figure 4. Raman spectrum of $Cs_2Ga_2Se_5$.

Optical Properties

The optical bandgap of $Cs_2Ga_2Se_5$ was determined by using solid-state UV/Vis diffuse reflectance spectroscopy. The absorption data were calculated by a modified Kubelka-Munk function.[19] The optical bandgap was obtained by extrapolation of the linear part onto the baseline (see Figure 5). The measurement confirmed the wide bandgap character of $Cs_2Ga_2Se_5$ with a bandgap of 1.95 eV (636 nm).

The bandgap of $Cs_2Ga_2Se_5$ is in the range of comparable compounds containing $\frac{1}{\infty}[Ga_2Se_3(Se_2)^{2-}]$ chains.[12,13] The considerably smaller bandgaps of $Cs_2Ga_2Se_5$ (1.95 eV) and $CsGaSe_3$ (2.25 eV)[4] compared to $CsGaSe_2$ (ca. 3.5 eV)[6] further suggest that the Se_2^{2-} units have a significant influence on the size of the bandgap as already proposed by *Vaqueiro*.[13]
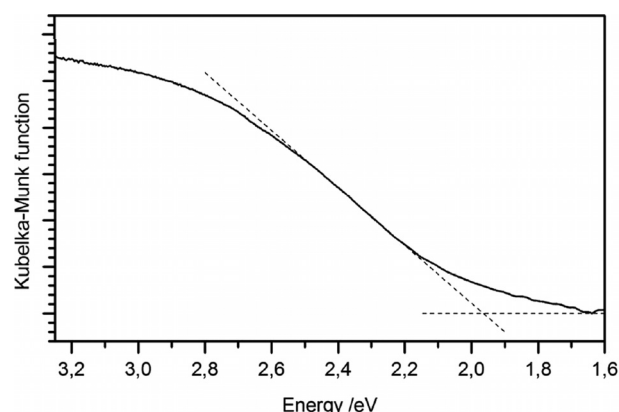
Figure 5. Diffuse reflectance spectrum of Cs$_2$Ga$_2$Se$_5$. The dashed lines show the extrapolation of the linear parts of the modified Kubelka-Munk function onto the baseline used to determine the optical bandgap.

Conclusions

Cs$_2$Ga$_2$Se$_5$, a new phase in the ternary systems consisting of alkali metal, gallium, and selenium, was obtained by the reaction of stoichiometric amounts of CsN$_3$, GaSe, and Se. The crystal structure was solved from single-crystal X-ray diffraction data. The title compound was further characterized by Raman and UV/Vis spectroscopy. Vibration spectra are dominated by the vibration modes of Ga–Se and Se$_2$ units. A comparably small bandgap is observed due to the Se$_2$ units. The anionic chains in Cs$_2$Ga$_2$Se$_5$ and in the homologous Cs$_2$Ga$_2$S$_5$[9] are the first examples of $\frac{1}{\infty}[Ga_2Q_3(Q_2)^{2-}]$ (Q = S, Se) chains in the systems of alkali metal, group 13 metal, and chalcogen.

Experimental Section

Commercially available gallium (Chempur 99.99 %) and selenium (Chempur 99.999 %) were used without further treatment. GaSe was prepared by chemical vapor transport using iodine (Sigma-Aldrich 99.8 %) as transporting agent. CsN$_3$ was obtained by passing gaseous hydrazoic acid (produced by acidifying an aqueous solution of NaN$_3$ (Sigma-Aldrich, 99.0 %) into an aqueous solution of Cs$_2$CO$_3$ (Sigma-Aldrich, 99.9 %).

Attention: HN$_3$ is highly explosive in condensed form. Tools made from transition metals should be avoided.

Synthesis of Cs$_2$Ga$_2$Se$_5$: The title compound was obtained by thermal decomposition of CsN$_3$ mixed with stoichiometric amounts of GaSe and Se in a quartz ampoule under dynamical vacuum conditions. The flame sealed ampoule containing the raw product was annealed for several days at 873 K in a tube furnace.

X-ray Crystallography: Suitable crystals for single crystal X-ray diffraction were placed on top of a glass fiber. Data collection was per-

formed at 123 K with an Agilent Supernova using monochromatized Mo-K_α radiation (λ = 0.71073 Å). Experimental parameters are listed in Table 1. The data were processed with the CrysAlisPro[17] software package. The crystal structure was solved by charge flipping using SUPERFLIP[15] and refined with Jana2006.[16] The disorder present in the structure was taken into account by a constrained refinement of the occupation factors of Se3 and Se33.

Raman-Spectroscopy: Raman spectra were recorded with a Varian FTS 7000e spectrometer with a Varian FT-Raman unit in the region of 120–4000 cm^{-1} with a resolution of 1 cm^{-1}. The instrument is equipped with a Nd:YAG laser providing an excitation wavelength of 1064 nm.

Diffuse Reflectance Spectroscopy: The measurements were performed with a Bruins Omega 20 UV/Vis spectrometer using BaSO$_4$ as a reference (100 % reflectance). Absorption data were calculated by using a modified Kubelka-Munk function.[19]

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-427420.

References

[1] B. Krebs, *Angew. Chem.* **1983**, *95*, 113.
[2] A. Kyas, Dissertation, TH Aachen **1981**.
[3] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *195*, 318.
[4] J. Do, M. G. Kanatzidis, *Z. Anorg. Allg. Chem.* **2003**, *629*, 621.
[5] H. J. Deiseroth, F. S. Han, *Z. Naturforsch.* **1983**, *38b*, 181.
[6] H. J. Deiseroth, *Z. Kristallogr.* **1984**, *166*, 283–295.
[7] M. S. Devi, K. Vidyasagar, *J. Chem. Soc. Dalton Trans.* **2002**, 4751.
[8] J. Heine, S. Dehnen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2303.
[9] D. Friedrich, A. Pfitzner, M. Schlosser, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1572.
[10] S. J. Ewing, A. V. Powell, P. Vaqueiro, *J. Solid State Chem.* **2011**, *184*, 1800.
[11] X. Zhang, Z.-X. Lei, W. Luo, W.-Q. Mu, X. Zhang, Q.-Y. Zhu, J. Dai, *Inorg. Chem.* **2011**, *50*, 10872.
[12] W.-W. Xiong, J.-R. Li, M.-L. Feng, X.-Y. Huang, *CrystEngComm* **2011**, *13*, 6206.
[13] S. J. Ewing, M. L. Romero, J. Hutchinson, A. V. Powell, P. Vaqueiro, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2526.
[14] H.-G. Yao, M. Ji, S.-H. Ji, Y.-L. An, *Z. Anorg. Allg. Chem.* **2012**, *638*, 683.
[15] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
[16] V. Petricek, M. Dusek, L. Palatinus, *Jana2006*, The Crystallographic Computing System; Institute of Physics: Praha, Czech Republic, **2006**.
[17] *CrysAlisPro*, Agilent Technologies, XRD Products, **2010**.
[18] C. Bartsch, T. Doert, *Solid State Sci.* **2012**, *14*, 515.
[19] H. Kisch, *Angew. Chem. Int. Ed.* **2013**, *52*, 812.

Dedicated Cluster