Solid State Sciences 37 (2014) 164–169

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Dimorphic cerium(III) oxoarsenate(III) $Ce[AsO_3]$

Florian Ledderboge [a], Sebastian J. Metzger [a], Gunter Heymann [b], Hubert Huppertz [b], Thomas Schleid [a, *]

[a] Institute for Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
[b] Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 80 – 82, 6020 Innsbruck, Austria

ARTICLE INFO

Article history:
Received 11 June 2014
Received in revised form
6 August 2014
Accepted 11 August 2014
Available online 20 August 2014

Keywords:
Lanthanoids
Cerium
Arsenic
Oxoarsenates(III)
Crystal structures
Raman spectroscopy

ABSTRACT

Colourless, water- and air-stable single crystals of cerium(III) oxoarsenate(III) $Ce[AsO_3]$ were prepared by the reaction of cerium metal (Ce) and arsenic sesquioxide (As_2O_3) in the presence of cesium chloride (CsCl) as fluxing agent at 750 °C in an evacuated silica ampoule. $Ce[AsO_3]$ crystallizes monoclinically ($a = 902.89(8)$, $b = 782.54(7)$, $c = 829.68(7)$ pm, $\beta = 103.393(3)°$, $Z = 8$) in the space group $P2_1/c$ and is isotypic with α-$Pb[SeO_3]$. There are two crystallographically different Ce^{3+} positions. $(Ce1)^{3+}$ is coordinated by nine oxygen atoms (d(Ce–O) = 244–286 pm) and $(Ce2)^{3+}$ by only eight (d(Ce–O) = 239–273 pm). Both crystallographically different As^{3+} cations form discrete ψ^1 tetrahedra $[AsO_3]^{3-}$ (d(As–O) = 174–179 pm), which are attached to the Ce^{3+} cations via edges and corners. The second monoclinic modification of $Ce[AsO_3]$ with the lattice parameters $a = 439.32(4)$, $b = 529.21(5)$, $c = 617.34(6)$ pm and $\beta = 105.369(3)°$ with $Z = 2$ was obtained by high-pressure synthesis (11 GPa, 1200 °C) and has both a higher density (6.31 vs. 6.13 g · cm^{-3}) and a higher calculated Madelung part of the lattice energy (15,155 vs. 15,132 kJ · mol^{-1}). It adopts the space group $P2_1/m$, crystallizing isotypically with $La[AsO_3]$, β-$Pb[SeO_3]$, $Pb[SO_3]$ (*scotlandite*) or $K[ClO_3]$ and exhibits nine-fold coordinated Ce^{3+} cations exclusively (d(Ce–O) = 254–287 pm) along with tripodal $[AsO_3]^{3-}$ anions (d(As–O) = 175–176 pm). *Raman* spectroscopy on both phases of $Ce[AsO_3]$ shows stretching vibrations between 769 and 731 cm^{-1} as well as asymmetric vibrations in the range of 659–617 cm^{-1}. The symmetric bending mode vibrations emerge in an interval from 340 to 410 cm^{-1} and the asymmetric bending modes range between 230 and 290 cm^{-1}.

1. Introduction

Ternary lanthanoid(III) oxoarsenates(V) with the composition $Ln[AsO_4]$ are well known since 1934 [1] and crystallize with coordination numbers (C.N.) of eight plus one for the Ln^{3+} cations involved in the monoclinic *monazite*-type structure (space group: $P2_1/n$), which is restricted to the light lanthanoids (Ln = La – Nd) [2–5] with largest cationic radii. Eightfold coordination is found in both, the tetragonal *xenotime*- (Ln = Pm – Lu, space group: $I4_1/amd$) [1–3,6–10] and the *scheelite*-type crystal structures (Ln = La, Ce, Pr, Nd, Sm, Tb, Dy, Er, Yb, Lu, space group: $I4_1/a$) [11,12]. On the other hand lanthanoid(III) oxoarsenates(III) were only known with the composition $Ln_4[As_2O_5]_2[As_4O_8]$ (Ln = Nd and Sm) [13,14] for a long time without containing discrete $[AsO_3]^{3-}$ units. Oxoarsenates(III), where isolated $[AsO_3]^{3-}$ units were observed, typically contain chloride anions, as it is the case for $Ln_5Cl_3[AsO_3]_4$ (Ln = La, Pr and Nd) [15,16] or the oxide-halide derivates $Ln_3OCl[AsO_3]_2$ (Ln = La, Ce, Gd and Tb) [5,17,18], as well as $La_3OBr[AsO_3]_2$ [19] and $Ln_5O_4Cl[AsO_3]_2$ (Ln = Pr and Nd) [20,21]. The simple composition $Ln[AsO_3]$ (Ln = La) [22] was first realized by high-pressure (11.5 GPa) and high-temperature (1000 °C) synthesis from lanthanum sesquioxide and arsenic sesquioxide in 2012. $La[AsO_3]$ adopts the monoclinic space group $P2_1/m$, crystallizes isotypically with β-$Pb[SeO_3]$ [23], $Pb[SO_3]$ (*scotlandite*) [24] or $K[ClO_3]$ [25,26] and exhibits nine-fold coordinated La^{3+} cations.

2. Experimental, material and methods

For preparing α-$Pb[SeO_3]$-type $Ce[AsO_3]$, cerium powder (Ce: 99.9%, ChemPur, Karlsruhe, Germany), arsenic sesquioxide (As_2O_3: 99.99% Alfa Aesar, Ward Hill, MA, USA) and cesium chloride (CsCl: suprapur, Merck, Darmstadt, Germany) were filled into silica tubes in molar ratios of 3:3:2 and sealed under dynamic vacuum. The mixture was heated up to 750 °C within 2 days, kept at this temperature for 4 days and cooled down to room temperature within 7 days. After this treatment colourless crystals of $Ce[AsO_3]$ were

* Corresponding author.
E-mail address: schleid@iac.uni-stuttgart.de (T. Schleid).

http://dx.doi.org/10.1016/j.solidstatesciences.2014.08.005
1293-2558/

Table 1
Crystallographic data for both forms of $Ce[AsO_3]$ and their isotypic relatives.

		α-Pb[SeO$_3$]	Ce[AsO$_3$][a]	Ce[AsO$_3$][a]	La[AsO$_3$]	K[ClO$_3$]	β-Pb[SeO$_3$]
Crystal system		--- all monoclinic ---		--- all monoclinic ---			
Space group		--- $P2_1/c$ (no. 14) ---		--- $P2_1/m$ (no. 11) ---			
Lattice parameters:	*a* (pm)	915.87(1)	902.89(8)	439.32(4)	442.91(4)	465.35(2)	455.2(1)
	b (pm)	809.02(1)	782.54(7)	529.21(5)	531.40(5)	558.41(3)	552.5(2)
	c (pm)	879.32(1)	829.68(7)	617.34(6)	622.83(6)	705.15(5)	663.3(3)
	β (°)	103.032(1)	103.392(3)	105.369(3)	105.564(3)	108.723(6)	106.40(3)
Number of formula units, *Z*		8	8	2	2	2	2
Calculated density, D_x (g · cm^{-3})		6.99	6.13	6.31	6.16	2.35	6.93

[a] Further details for both crystal structure investigations of dimorphic $Ce[AsO_3]$ may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition numbers CSD-423417 for K[ClO$_3$]-type Ce[AsO$_3$] and CSD-426720 for α-Pb[SeO$_3$]-type Ce[AsO$_3$] (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de; internet: http://www.fiz-karlsruhe.de/request_for_deposited_data.html)

obtained, which proved to be stable against water and air. A big single crystal of elemental arsenic at the top of the ampoule could be observed as by-product according to $Ce + As_2O_3 \rightarrow Ce[AsO_3] + As$.

For the synthesis of K[ClO$_3$]-type $Ce[AsO_3]$, cerium(IV) oxide (CeO_2: 99.99%, ChemPur, Karlsruhe, Germany) and arsenic sesquioxide (As_2O_3: 99.995%, Merck, Darmstadt, Germany) in 2:1 M ratio were filled into cylindrical boron-nitride crucibles (BN) with a fitting plate. Single crystals were obtained in a modified *Walker*-type module in combination with a 1000 ton press. Precast magnesium oxide octahedra (MgO) with edge lengths of 14 mm were applied as pressure medium. Eight tungsten carbide cubes (WC) with a truncation edge length of 8 mm compressed the octahedra. Further information on the construction of the assemblies is given in references (*Walker* [27,28], *Huppertz* [29], *Rubie* [30], *Kawai and Endo* [31]). The mixture was compressed up to 11 GPa in 5.4 h, subsequently heated to 1200 °C within 15 min and kept there for another 15 min. After cooling down the sample to 500 °C within 150 min it was quenched to room temperature by turning off the heating. The recovered MgO octahedron was broken apart and the sample was carefully separated from the surrounding BN crucible. Besides cerium(III) oxoarsenate(V) $Ce[AsO_4]$ in the *scheelite*-type structure [11] K[ClO$_3$]-type $Ce[AsO_3]$ could be found, both as colourless single crystals, formed according to $2\ CeO_2 + As_2O_3 \rightarrow Ce[AsO_4] + Ce[AsO_3]$.

Table 2
Structure refinement for both forms of $Ce[AsO_3]$.

Structure type	α-Pb[SeO$_3$]	K[ClO$_3$]
Space group	$P2_1/c$ (no. 14)	$P2_1/m$ (no. 11)
Collected reflections	18,181	2573
Unique reflections	1727	371
R_{int}/R_σ	0.088/0.044	0.059/0.031
R_1/wR_2 (for all reflections)	0.061/0.116	0.021/0.042
Goodness of fit (GooF)	1.066	1.062
Radiation	Mo-Kα ($\lambda = 71.07$ pm)	
Instrument	κ-CCD (Bruker-Nonius)	
Structure solution & refinement	Program SHELX 97 [32]	

Table 3
Atomic positions and equivalent isotropic displacement parameters for both forms of $Ce[AsO_3]$.

Atom	site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/pm^2
α-Pb[SeO$_3$]-type Ce[AsO$_3$]					
Ce1	4*f*	0.40289(8)	0.16544(9)	0.27132(9)	95(2)
Ce2	4*f*	0.00934(8)	0.31088(9)	0.34377(9)	87(2)
As1	4*f*	0.20511(15)	0.51457(16)	0.04892(16)	89(3)
As2	4*f*	0.31219(15)	0.59181(16)	0.43871(16)	92(3)
O1	4*f*	0.3973(11)	0.4595(12)	0.0941(12)	130(19)
O2	4*f*	0.1544(11)	0.0335(12)	0.3340(12)	136(19)
O3	4*f*	0.1315(11)	0.3239(12)	0.1167(12)	111(18)
O4	4*f*	0.6245(11)	0.3646(12)	0.3509(12)	127(19)
O5	4*f*	0.3148(11)	0.3647(12)	0.4553(12)	119(18)
O6	4*f*	0.1101(11)	0.6093(11)	0.4097(12)	119(18)
K[ClO$_3$]-type Ce[AsO$_3$]					
Ce	2*e*	0.33667(8)	$^1/_4$	0.70369(6)	121(2)
As	2*e*	0.07900(14)	$^1/_4$	0.14520(11)	120(2)
O1	2*e*	0.6715(11)	$^1/_4$	0.1189(8)	197(12)
O2	4*f*	0.1913(7)	0.0023(7)	0.3404(5)	134(8)

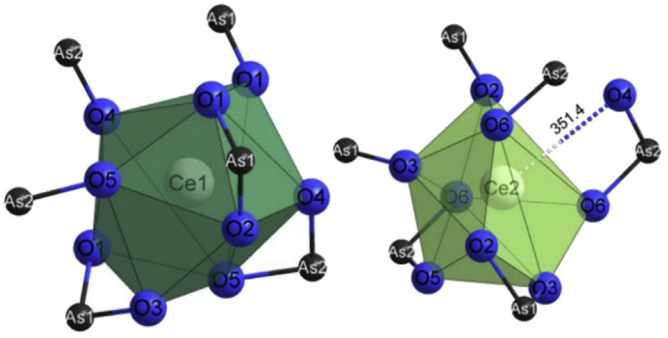

Fig. 1. Oxygen coordination polyhedra around $(Ce1)^{3+}$ (*left*) and $(Ce2)^{3+}$ (*right*) in α-Pb[SeO$_3$]-type $Ce[AsO_3]$.

Table 4
Selected interatomic distances (*d*/pm) and angles (∢/°) in α-Pb[SeO$_3$]-type $Ce[AsO_3]$.

$[(Ce1)O_9]^{15-}$ polyhedron		$[(Ce2)O_8]^{13-}$ polyhedron	
Ce1 – O5	244.1	Ce2 – O3	239.6
Ce1 – O1	248.3	Ce2 – O3	251.0
Ce1 – O4	250.1	Ce2 – O6	252.0
Ce1 – O4	255.3	Ce2 – O2	252.7
Ce1 – O5	256.8	Ce2 – O2	254.6
Ce1 – O2	262.9	Ce2 – O6	260.0
Ce1 – O1	272.5	Ce2 – O6	265.0
Ce1 – O3	278.1	Ce2 – O5	273.1
Ce1 – O1	286.2		
$[(As1)O_3]^{3-}$ ψ^1 tetrahedron		$[(As2)O_3]^{3-}$ ψ^1 tetrahedron	
As1 – O1	174.2	As2 – O4	174.0
As1 – O2	177.6	As2 – O5	178.2
As1 – O3	177.7	As2 – O6	179.0
O1 – As1 – O2	100.2	O4 – As2 – O5	97.1
O1 – As1 – O3	98.7	O4 – As2 – O6	102.0
O2 – As1 – O3	96.4	O5 – As2 – O6	94.7