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Synthesis and structure of the first cerium iodothiosilicate: $Ce_3(SiS_4)_2I$

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Abstract

The first cerium iodothiosilicate, $Ce_3(SiS_4)_2I$, has been synthesized from the reaction at 900°C between cerium sulfide, silicon, iodine and sulfur in a $Ce_2S_3/Si/S/I=3:6:11:2$ ratio. This compound crystallises in the monoclinic space group *C2/c* ($Z=4$) with the powder refined cell parameters: $a=15.9634(5)$ Å, $b=7.8502(2)$ Å, $c=10.8664(3)$ Å, $\beta=97.931(2)°$. The structure was solved from single crystal X-Ray diffraction analysis ($R(\%)=2.17$ and $R_w(\%)=2.60$). The $Ce_3(SiS_4)_2I$ structure is quite different from those of the other already known rare earth thiosilicates because of the template role of iodine, leading to the occurrence of tunnels. In these tunnels are found the iodide anions which are surrounded by three cerium, so as to form $[ICe_3]$ isosceles triangular entities. Around the tunnels is found a three-dimensional network consisting of $(CeIS_8)$ polyhedra (trigonal prisms of sulfur tricapped by two sulfur and one iodine atom) linked to (SiS_4) tetrahedra. © 1998 Elsevier Science S.A.

Keywords: Cerium; $Ce_3(SiS_4)_2I$; Iodothiosilicate; Structure

1. Introduction

Rare-earth (RE) chalcogenides possess a rich structural chemistry [1–3] and a wide variety of interesting physical properties [4–7] based, respectively, on the common high coordination of RE elements and the occurrence of unsaturated f subshells. Indeed, in the lanthanide series, the low spatial extension of the f orbitals associated with localized energy levels may give rise to high magnetic moments (for elements such as Tb, Dy, Ho and Er), narrow band emission and absorption spectra, etc. These interesting magnetic and optical properties make it possible to use the RE chalcogenides as phosphors [4,5], magneto-optical [6], optical window [7] materials and, more recently, industrial pigments [5].

Since the end of the 1980s, research on quaternary compounds has received much attention leading to new chalcogenides containing an alkali- or alkaline-earth metal, a lanthanide, and a main group metal or a transition metal [8]. This new interest in RE solid state chemistry is partially related to the discovery of high temperature superconducting cuprates containing an RE element and attempts to extend the superconducting properties of oxides to chalcogenides. Moreover, this development has been highly favored by the ability of the (A_2Q_x) reactive flux method (A=alkali metal or alkaline-earth metal, Q=chalcogen) to stabilize metastable structural arrangements in ternary and quaternary systems. This synthesis route, mostly dedicated at first to new transition element or main group element chalcogenide preparation [9], has been extended to RE elements with success, yielding new materials with novel structures, new stoichiometries and interesting properties [10].

In view of these new fascinating RE element chemistry developments, we have embarked on the synthesis of phases in RE–A–X–Q (A=14 elements, X=halogen and Q=chalcogen). We report here the synthesis and structural characterization of the first iodothiosilicate of cerium.

2. Experimental

2.1. Synthesis

$Ce_3(SiS_4)_2I$ was prepared from a mixture of silicon (88.4 mg, 3.15 mmol, Koch-Light Laboratories, 99.99%), sulfur (185.2 mg, 5.775 mmol, Fluka, puriss >99.999%), iodine (133.2 mg, 0.525 mmol, Aldrich Chem., 99.99+%), and Ce_2S_3 (593 mg, 1.575 mmol Cerac, −325 mesh powder, 99.9%), handled under inert atmosphere. The mixture corresponded to the ratio $Ce/Si/I/S=3:3:1:10$ ($Ce_3(SiS_4)_2I/SiS_2=1:1$). The starting materials were

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placed in a quartz tube evacuated to 10^{-3} Torr, then sealed and heated at 700°C for 4 days. The sample was then cooled slowly to room temperature, finely ground and heated to 900°C. This two step reaction led to the pure well-crystallized and air-stable $Ce_3(SiS_4)_2I$ product. The SiS_2 excess was eliminated by sublimation at the coldest end of the reaction tube. Within an homogeneous pale-yellowish powder, crystals of a suitable size for crystallographic analysis could be obtained. Microprobe analysis of several crystals using energy dispersive X-spectroscopy (EDS) performed with a JEOL 5800-LV SEM equipped with a PGT IMIX detector gave the chemical formula $Ce_3Si_{2.1}I_{0.9}S_{7.8}$, in satisfactory agreement with the title composition.

2.2. X-ray structure determination

A suitable single crystal was mounted on a STOE image plate X-ray diffractometer. Images were recorded over the $0.0° < Ø < 249.2°$ range with 1.4° increment angle. Indexing was performed using the program INDEX [11]. Cell parameters were determined from a least squares analysis of the setting angles of 4876 reflections in the $2.9° \leq 2\theta \leq 48.4°$ range. Accurate cell constants were extracted from a full pattern matching refinement (FULLPROF [12]) from a powder diagram recorded on a CPS 120 INEL X-ray powder diffractometer using Cu KL_2 monochromatized radiation. The powder was first sieved at 20 μm and then introduced into a Lindemann capillary (Ø=0.1 mm). Diagram refinement confirmed the purity of the sample, at least at the X-ray diffraction detection threshold. Refined cell constants and additional relevant data of this refinement are given in Table 1.

The structure was solved with a direct method using the SHELXTL program [13] followed by successive obs-Fourier and diff-Fourier synthesis using the JANA96 [14] structure determination package. Conventional atomic and anomalous scattering factors were taken from the usual sources.

Data analysis indicated the *C2/c* space group. The refinement, conducted with anisotropic atomic displacement parameters and isotropic secondary extinction parameters, yielded $R_F = 2.17\%$ and $R_{wF} = 2.60\%$ with meaningless residues. The crystal data and the details of the

Table 1
Crystallographic data and experimental details for $Ce_3(SiS_4)_2I$

Physical and crystallographic data	
Formula	$Ce_3(SiS_4)_2I$
Molar weight	859.917
Color	Yellowish
Crystal size (mm^3)	0.17×0.06×0.03
System	Monoclinic
Space group	*C2/c* (15)
Cell parameters (powder refinement, $T = 300$ K)	$a = 15.9634(5)$ Å $b = 7.8502(2)$ Å $c = 10.8664(3)$ Å $\beta = 97.931(2)°$ $V = 1348.7(1)$ Å^3 $Z = 4$
Density (calc.)	4.201 g cm^{-3}
Absorption coefficient	$\mu(\lambda\text{Mo K}\alpha) = 137\ cm^{-1}$
Recording conditions	
Temperature	300 K
Radiation	$\lambda_{\text{Mo K}\alpha} = 0.71069$ Å
Diffractometer	STOE image plate
Angular range 2θ (deg)	2.9–48.4
hkl range	$-18 \leq h \leq 18,\ -8 \leq k \leq 8,\ -11 \leq l \leq 11$
Data reduction	
Total recorded reflections	10 692
Observed reflections ($I > 3\sigma(I)$)	4032
Independent reflections ($I > 3\sigma(I)$)	853
R_{int} (%)	4.55
Refinement	
Weighting scheme	$w = 1/(\sigma^2\|Fo\| + (0.01 \times 1.5\|Fo\|)^2)$
No. of refined parameters	66
Refinement results	$R(\%) = 2.17$ $R_w(\%) = 2.60$ g.o.f. = 0.87
Secondary extinction coefficient	0.119(6)
Type	Isotropic, type I, Gaussian distribution
Residual electronic density	$[-1.85, +0.89]$ e^- Å^{-3}

Table 2
Fractional coordinates and equivalent isotropic atomic displacement parameters of $Ce_3(SiS_4)_2I$

Atom	x	y	z	U_{eq} (Å^2)
Ce(1)	0.19688(2)	0.12029(5)	0.68020(4)	0.0093(2)
Ce(2)	1/2	0.09620(7)	3/4	0.0114(2)
I	0	0.98401(8)	1/4	0.0211(3)
Si	0.1596(1)	0.4628(2)	0.0292(2)	0.0097(6)
S(1)	0.1446(1)	0.2557(2)	0.1463(2)	0.0119(6)
S(2)	0.28161(9)	0.5690(2)	0.0857(2)	0.0111(5)
S(3)	0.0682(1)	0.6538(2)	0.0426(2)	0.0117(6)
S(4)	0.1501(1)	0.3994(2)	−0.1605(2)	0.0111(6)

acquisition and of the structural analysis are summarized in Table 1. Final values of the atomic parameters and anisotropic thermal parameters are given in Tables 2 and 3. Selected bond distances and angles can be found in Table 4.

3. Structural results

$Ce_3(SiS_4)_2I$ exhibits a tridimensional structure based on a $Ce_3Si_2S_8$ skeleton defining 6.6 Å diameter tunnels filled by iodide. A view down the c-axis is given in Fig. 1. Owing to the high Ce^{III} ($4f^1$) stability in chalcogenides, the $Ce_3^{III}Si_2^{IV}I^{-I}S_8^{-II}$ charge balance can be a priori proposed.

Ce(1) and Ce(2) environments are chemically equivalent. Both cerium atoms are surrounded by eight sulfide and one iodide ion in (CeS_8I) polyhedra that can be regarded, in a first approximation, as (CeS_6) triangular prisms capped by two additional chalcogens and one halogen. The mean Ce–S distances (Ce(1)–S, 3.007(2) Å; Ce(2)–S, 3.096(2) Å) agree with those reported in the literature (from 2.901(2) to 3.092(2) Å for γ-Ce_2S_3 [15]). They correspond well to the sum of the ionic radii ($d Ce^{III}$–S^{-II}=3.036 Å) [16]. The smallest S–S bond distance (3.298(2) Å) is a little shorter than the expected S^{-II}–S^{-II} contact (about 3.46 Å in TiS_2, for example [17]). Nevertheless, it remains sufficiently elongated to be attributed to S^{-II}–S^{-II} interactions. Such a deviation, which probably originates from steric interactions associated with the high coordination of Ce, seems to be quite current (d_{min}S–S= 3.035 Å in $CePS_4$ [18]).

Table 4
Selected bond distances (Å) and angles (deg) for $Ce_3(SiS_4)_2I$

Environment of Ce(1)		Environment of Si	
Ce(1)–S(1)	3.096(2)	Si–S(1)	2.099(3)
Ce(1)–S(1)	3.075(2)	Si–S(2)	2.130(2)
Ce(1)–S(2)	2.925(2)	Si–S(3)	2.111(3)
Ce(1)–S(2)	2.983(2)	Si–S(4)	2.106(3)
Ce(1)–S(2)	3.036(2)	S(1)–Si–S(2)	107.7(1)
Ce(1)–S(3)	2.958(2)	S(1)–Si–S(3)	111.8(1)
Ce(1)–S(4)	2.952(2)	S(1)–Si–S(4)	114.3(1)
Ce(1)–S(4)	3.027(2)	S(2)–Si–S(3)	108.4(1)
Ce(1)–I	3.4324(4)	S(2)–Si–S(4)	108.3(1)
		S(3)–Si–S(4)	106.2(1)

Environment of Ce(2)		Environment of I	
Ce(2)–S(1)	2.945(2) (×2)	I–Ce(1)	3.4324(4) (×2)
Ce(2)–S(3)	3.248(2) (×2)	I–Ce(2)	3.2954(9)
Ce(2)–S(3)	3.285(2) (×2)	Ce(1)–I–Ce(2)	103.80(1) (×2)
Ce(2)–S(4)	2.904(2) (×2)	Ce(1)–I–Ce(1)	152.40(2)
Ce(2)–I	3.2954(9)		

Each iodide is surrounded by three cerium cations to form isosceles (ICe_3) triangles. The Ce–I distances (Ce(1)–I, 3.4324(4) Å (×2); Ce(2)–I, 3.2954(9) Å) agree with those observed in CeSI (from 3.301(1) to 3.4368(4)) [19]. Again, these values compare satisfactorily with the sum of the ionic radii ($d Ce^{III}$–I^-=3.396 Å) [16].

As expected, silicon cations are in tetrahedral sites with Si–S bonds and S–Si–S angles ranging from 2.099(3) to 2.130(2) Å and from 106.2(1) to 114.3(1)°, respectively. These values are close to those observed in $Na_4Si_4S_{10}$, for example (Si–S distances from 2.025 to 2.162 Å and S–Si–S angles from 108.07 to 111.51°) [20].

The physical properties of the family are published elsewhere [21]. Note that the phase is semiconducting and paramagnetic.

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Table 3
Anisotropic atomic displacement parameters of $Ce_3(SiS_4)_2I$

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Ce(1)	0.0083(2)	0.0116(3)	0.0081(3)	0.0012(1)	0.0015(2)	0.0007(1)
Ce(2)	0.0055(3)	0.0146(3)	0.0141(4)	0	0.0020(2)	0
I	0.0107(3)	0.0150(4)	0.0396(5)	0	0.105(3)	0
Si	0.0070(8)	0.012(1)	0.011(1)	0.0005(7)	0.0017(7)	0.0014(8)
S(1)	0.0095(8)	0.0125(9)	0.014(1)	0.0012(6)	0.0039(6)	0.0028(7)
S(2)	0.0071(7)	0.0152(9)	0.011(1)	−0.0019(7)	0.0007(6)	0.0010(7)
S(3)	0.0075(8)	0.0125(9)	0.015(1)	0.0002(6)	−0.0000(7)	−0.0020(7)
S(4)	0.0095(8)	0.0142(9)	0.010(1)	0.0013(6)	0.0012(6)	−0.0015(7)

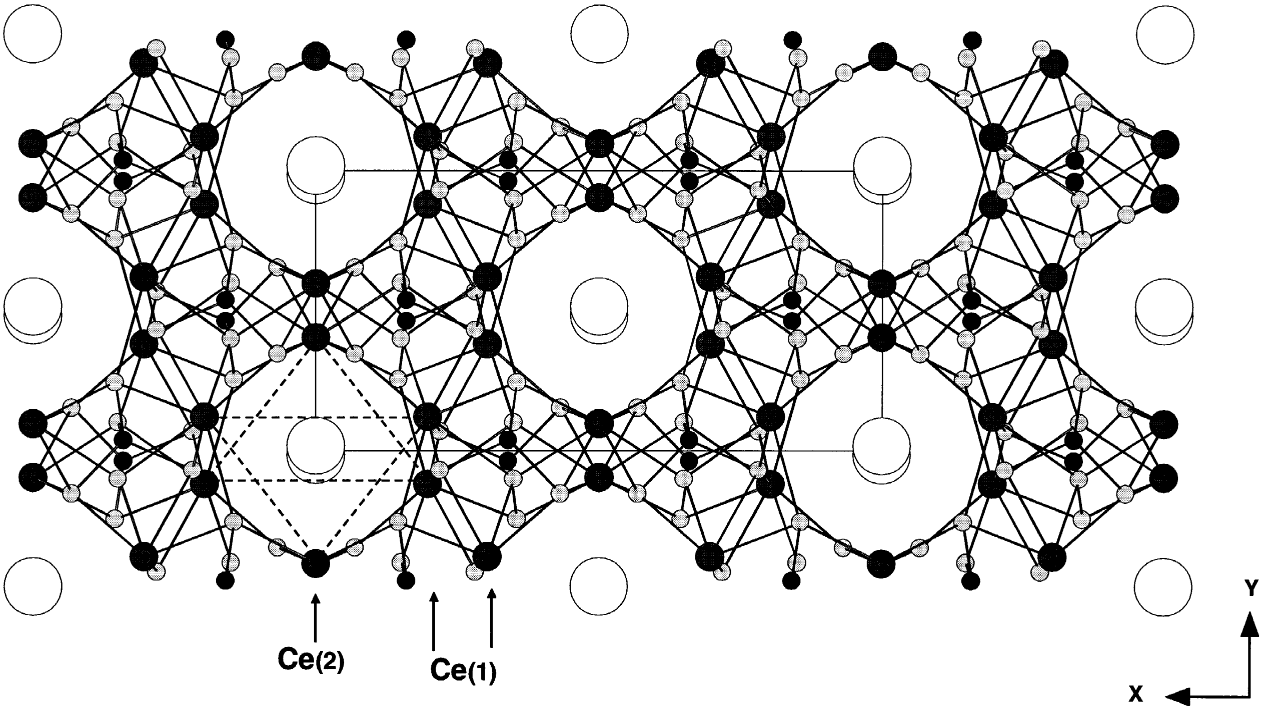

Fig. 1. View of $Ce_3(SiS_4)_2I$ down the *c*-axis. Black atoms are Si, dark gray Ce, light gray S and white I.

Région des Pays de Loire and Rhône-Poulenc Chimie, respectively.

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