

Rare Earth Site Preference in the Doped Laser Host Material Sc_2SiO_5 . A Single-Crystal X-Ray Study

Ute Ch. Rodewald^a, Lihe Zheng^b, Birgit Heying^a, Xiaodong Xu^b, Liangbi Su^b, Jun Xu^b, and Rainer Pöttgen^a

^a Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, 48149 Münster, Germany

^b Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **2012**, *67b*, 113–117; received January 17, 2012

Single crystals of the laser host material Sc_2SiO_5 as well as thulium- (4 at.-%) and ytterbium- (5 at.-%) doped samples were prepared by the Czochralski technique. The structures of Sc_2SiO_5 , $\text{Tm}^{3+}:\text{Sc}_2\text{SiO}_5$, and $\text{Yb}^{3+}:\text{Sc}_2\text{SiO}_5$ were refined on the basis of high-quality single-crystal X-ray diffraction data: monoclinic Y_2SiO_5 type, space group $C2/c$. The X-ray data unambiguously show that the larger rare earth cations exclusively occupy the $8f$ site with oxygen coordination number 7.

Key words: Crystal Structure, Scandium Silicate, Rare Earth Doping, Laser Material

Introduction

The scandium silicate Sc_2SiO_5 (SSO) was detected in early phase-analytical work, when establishing the equilibrium diagram of the Sc_2O_3 - SiO_2 system [1]. The only structural information from that investigation were d spacings and approximate intensities obtained from powder X-ray data. More detailed studies by ^{45}Sc solid-state NMR spectroscopy and Rietveld analyses showed that Sc_2SiO_5 adopts the monoclinic Y_2SiO_5 type, space group $C2/c$ [2, 3].

During the last ten years, Sc_2SiO_5 has intensively been discussed as host material for rare earth doping with respect to laser materials [4–7]. Sc_2SiO_5 is a stable compound for such applications since it exhibits a high lattice energy accompanied with a high melting point and a moderately high thermal conductivity [8, 9]. Many investigations subsequently focused on the substitution of Sc^{3+} by mainly Tm^{3+} and Yb^{3+} . These are the smallest possible ions with suitable f levels. The Sc_2SiO_5 structure offers two crystallographically independent scandium sites, both on Wyckoff positions $8f$. These sites have oxygen coordination numbers (CN) 6 and 7 for Sc2 and Sc1, respectively, both suitable for substitution. During systematic ^{45}Sc solid state NMR spectroscopic studies of intermetallic [10] and oxidic [11–13] compounds we also investigated the solid solution $\text{Lu}_{2-x}\text{Sc}_x\text{SiO}_5$ [14]. Single-crystal data of $\text{Lu}_{1.12}\text{Sc}_{0.88}\text{SiO}_5$, $\text{Lu}_{1.23}\text{Sc}_{0.77}\text{SiO}_5$, and

$\text{Lu}_{1.50}\text{Sc}_{0.50}\text{SiO}_5$ showed Lu / Sc mixing for both $8f$ sites, and, as expected from radii criteria, always with higher lutetium content for the CN-7 site.

Large high-quality crystals of neodymium-, thulium-, and ytterbium-doped Sc_2SiO_5 have recently been grown *via* the Czochralski technique [15–17] with doping quantities up to 5 at.-%. In the light of our results on the solid solution $\text{Lu}_{2-x}\text{Sc}_x\text{SiO}_5$ it was desirable to determine the site occupancy parameters by single-crystal X-ray diffraction. Herein we report on first single-crystal data for Sc_2SiO_5 and the doped compounds $\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$ and $\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$.

Experimental Section

Synthesis

The Tm- and Yb-doped SSO single crystals were grown by the Czochralski method in inductively heated iridium crucibles under nitrogen atmosphere. The starting materials were SiO_2 with 4N purity, Sc_2O_3 with 5N purity, Tm_2O_3 with 4N purity and Yb_2O_3 with 4N5 purity. The powders were weighed, mixed and pressed into tablets under 200 MPa pressure. The tablets were sintered at 1400 °C for 24 h before loaded into the iridium crucibles. A Yb: Lu_2SiO_5 seed crystal was employed to grow the Yb: Sc_2SiO_5 crystal, and a Yb: Sc_2SiO_5 seed crystal was applied to obtain the Tm: Sc_2SiO_5 crystal. The pulling rate was set at 0.5–3 mm h⁻¹ and the rotation rate at 10–30 rpm. After the growth procedure the crystal was cooled to r. t. within 40 h.

Table 1. Crystal data and structure refinement for Sc_2SiO_5 , $\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$ and $\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$, space group $C2/c$, $Z = 8$.

Compound	Sc_2SiO_5	$\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$	$\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$
Lattice parameters (Guinier powder data)			
a , pm	1367.9(1)	1369.4(1)	1373.7(3)
b , pm	642.57(6)	643.16(6)	644.9(1)
c , pm	996.7(1)	996.9(2)	999.8(2)
β , deg	121.12(1)	121.18(1)	121.18(1)
V , pm ³	0.7500	0.7512	0.7578
Formula weight, g mol ⁻¹	198.01	206.53	203.77
Calculated density, g cm ⁻³	3.51	3.65	3.57
Crystal size, μm^3	$20 \times 100 \times 100$	$70 \times 100 \times 140$	$20 \times 60 \times 100$
Transm. ratio (max / min)	0.893 / 0.722	0.714 / 0.468	0.920 / 0.808
Absorption coefficient, mm ⁻¹	3.8	5.3	4.8
Detector distance, mm	80	80	80
Exposure time, min	5	5	6
ω range; increment, deg	0–180, 1.0	0–180, 1.0	0–180, 1.0
Integr. param. A, B, EMS	12.8; 2.8; 0.012	13.0; 2.9; 0.012	13.0; 2.9; 0.012
$F(000)$, e	768	794	786
θ range for data collection, deg	3–32	3–32	3–32
Range in hkl	$\pm 20, \pm 9, \pm 14$	$\pm 20, \pm 9, \pm 14$	$\pm 20, \pm 9, \pm 14$
Total no. reflections	4519	4702	4308
Independent reflections / R_{int}	1288 / 0.0385	1292 / 0.0389	1294 / 0.0300
Reflections with $I \geq 2\sigma(I) / R_{\sigma}$	1158 / 0.0281	1215 / 0.0236	1133 / 0.0271
Data / ref. parameters	1288 / 74	1292 / 75	1294 / 75
Goodness-of-fit on F^2	1.050	1.168	0.938
$R1 / wR2$ for $I \geq 2\sigma(I)$	0.0215 / 0.0514	0.0150 / 0.0410	0.0164 / 0.0367
$R1 / wR2$ for all data	0.0255 / 0.0524	0.0167 / 0.0414	0.0227 / 0.0377
Extinction coefficient	0.0129(8)	0.0358(10)	0.0103(4)
Largest diff. peak / hole, e \AA^{-3}	0.79 / -0.69	0.46 / -0.55	0.45 / -0.52

The segregation coefficient of the Yb^{3+} ions in the SSO host structure was determined to be 0.96. The segregation coefficient of Tm^{3+} in the SSO host was measured by the ICP-AES method and calculated to be 0.72. For further details see [15] and [17]. Additionally a 1 at.-% Nd:SSO crystal was used [16].

EDX data

The cut pieces of the bulk samples from which small single crystals were selected by mechanical fragmentation were studied by semiquantitative EDX analyses using a Zeiss EVO MA10 scanning electron microscope with NdF_3 , TmF_3 , YbF_3 , Sc, and SiO_2 as standards. No impurity elements were detected. The thulium- and ytterbium-containing crystal fragments showed homogeneous rare earth distributions. Within the detection limit of the instrument, no neodymium was detected in the attempted $\text{Nd}^{3+}:\text{Sc}_2\text{SiO}_5$ sample, in agreement with the single-crystal X-ray data (*vide infra*).

X-Ray diffraction

Pieces of the Czochralski grown crystals were crushed, ground in an agate mortar and characterized by Guinier patterns (imaging plate detector, Fujifilm BAS-1800) with $\text{CuK}\alpha_1$ radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as

an internal standard. Correct indexing of the patterns was ensured by intensity calculations [18]. Micrometer-sized crystal fragments were then selected, glued to thin quartz fibers using bees wax and first tested by Laue photographs on a Buerger camera (using white Mo radiation). The data collections of three suitable crystals were carried out in oscillation mode on a Stoe IPDS II diffractometer using $\text{MoK}\alpha$ radiation. Numerical absorption corrections were applied to the data sets. Details about the data collections and crystallographic parameters are summarized in Table 1.

Structure refinements

The data sets showed C -centered monoclinic lattices, and the observed extinction conditions were compatible with the centrosymmetric space group $C2/c$ in agreement with previous work on $\text{Sc}_{0.88}\text{Lu}_{1.12}\text{SiO}_5$ [14]. The atomic parameters of the latter compound were taken as starting values, and the three structures were refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on F_o^2) [19]. The occupancies of both $8f$ scandium sites were refined in separate series of least-squares cycles in order to determine the degree of doping with the heavier rare earth element. Both scandium sites of the crystal from the 1 at.-% Nd:SSO sample were fully occupied with scandium within two standard deviations. For

Table 2. Atomic coordinates^a and equivalent isotropic displacement parameters (pm^2)^b for Sc_2SiO_5 , $\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$ and $\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$.

Atom	Occupancy (%)	x	y	z	U_{eq}
Sc_2SiO_5					
Sc1	100	0.54467(2)	0.75500(4)	0.48540(3)	57(1)
Sc2	100	0.14095(2)	0.38305(4)	-0.15617(3)	50(1)
Si	100	0.31852(3)	0.59675(6)	0.19143(4)	42(1)
O1	100	0.41809(9)	0.5276(2)	0.3661(1)	82(2)
O2	100	0.3713(1)	0.7949(2)	0.1471(1)	80(2)
O3	100	0.20173(9)	0.6549(2)	0.1871(1)	78(2)
O4	100	0.2975(1)	0.4163(2)	0.0662(1)	76(2)
O5	100	0.0140(1)	0.4043(2)	-0.1070(1)	73(2)
$\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$					
Sc1/Tm	93.1(1)/6.9(1)	0.54345(1)	0.75378(3)	0.48135(2)	68(1)
Sc2	100	0.14082(2)	0.38248(3)	-0.15663(2)	49(1)
Si	100	0.31814(3)	0.59613(5)	0.19156(3)	44(1)
O1	100	0.41767(7)	0.5262(1)	0.36592(9)	94(2)
O2	100	0.37149(8)	0.7948(1)	0.1490(1)	95(2)
O3	100	0.20149(7)	0.6537(1)	0.18679(9)	80(2)
O4	100	0.29744(7)	0.4167(1)	0.06578(9)	78(2)
O5	100	0.01447(7)	0.4043(1)	-0.10697(9)	72(2)
$\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$					
Sc1/Yb	95.5(1)/4.5(1)	0.54382(2)	0.75421(3)	0.48253(3)	66(1)
Sc2	100	0.14087(2)	0.38255(4)	-0.15654(3)	48(1)
Si	100	0.31829(3)	0.59639(6)	0.19150(4)	50(1)
O1	100	0.41784(9)	0.5264(2)	0.3659(1)	94(2)
O2	100	0.37146(10)	0.7946(2)	0.1485(1)	96(2)
O3	100	0.20150(9)	0.6541(2)	0.1867(1)	87(2)
O4	100	0.29758(10)	0.4167(1)	0.0662(1)	83(2)
O5	100	0.01420(9)	0.4044(2)	-0.1071(1)	78(2)

^a All atoms lie on the Wyckoff positions $8f$; ^b U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

the Tm:SSO and Yb:SSO crystals we observed thulium, respectively ytterbium only on the $8f$ site with CN = 7. These mixed occupancies were refined as least-squares variables. The refined atomic positions, equivalent isotropic displacement parameters, and interatomic distances are given in Tables 2 and 3. Refinement of the other occupancy parameters of the ytterbium-containing crystal showed small defects on the silicon site (fully occupied only within seven standard deviations), although the crystal was transparent. The origin of this is not yet clear.

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-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-424016 (Sc_2SiO_5), CSD-424017 ($\text{Sc}_{1.931}\text{Tm}_{0.069}\text{SiO}_5$), and CSD-424018 ($\text{Sc}_{1.955}\text{Yb}_{0.045}\text{SiO}_5$).

Results and Discussion

The structure of Sc_2SiO_5 has been refined for the first time from high-quality single-crystal X-ray diffractometer data. Our results fully confirm the

data recently obtained from a powder Rietveld refinement [2], however, with much higher precision. The Sc_2SiO_5 structure has simple monomeric building units, *i. e.* Sc1O_7 mono-capped octahedra, distorted Sc2O_6 octahedra, and SiO_4 tetrahedra. The connectivity pattern of these building units has been discussed in detail in our previous work on the solid solution $\text{Lu}_{2-x}\text{Sc}_x\text{SiO}_5$. For further details we refer to a review article on rare earth silicates [20].

The two different scandium coordinations in Sc_2SiO_5 are presented in Fig. 1. The Sc1 atoms

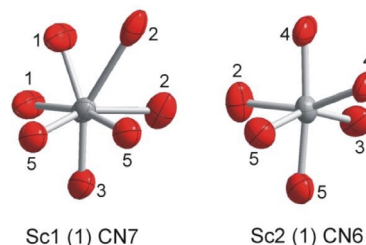


Fig. 1 (color online). Oxygen coordination of the scandium atoms in Sc_2SiO_5 . The site symmetries and atom designations are given.

Table 3. Interatomic distances (Å), bond valence (BV) and bond valence sums (BVS)^a for Sc_2SiO_5 , $\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$ and $\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$.

		Distance	BV			Distance	BV	BV			Distance	BV	BV	
Sc_2SiO_5					$\text{Sc}_{1.931(1)}\text{Tm}_{0.069(1)}\text{SiO}_5$						$\text{Sc}_{1.955(1)}\text{Yb}_{0.045(1)}\text{SiO}_5$			
		Sc1						Sc1 Tm						
Sc1:	O5	201.0	0.647	Sc1/Tm:	O5	204.0	0.597	0.898	Sc1/Yb:	O5	203.8	0.600	0.821	
	O1	210.2	0.505		O1	209.3	0.517	0.778		O1	210.3	0.503	0.689	
	O3	212.8	0.470		O3	215.5	0.437	0.658		O3	215.2	0.441	0.603	
	O2	216.8	0.422		O2	216.4	0.427	0.642		O2	217.2	0.418	0.572	
	O1	222.9	0.358		O1	223.7	0.350	0.527		O1	224.1	0.347	0.474	
	O5	232.8	0.274		O5	232.5	0.276	0.415		O5	233.2	0.271	0.371	
	O2	296.6	0.049		O2	291.8	0.056	0.084		O2	293.9	0.053	0.072	
	[6] ^b	(216.1)	2.676		[6]	(216.9)	2.604	3.918		[6]	(217.3)	2.580	3.530	
	[7]	(227.6)	2.725		[7]	(227.6)	2.660	4.002		[7]	(228.2)	2.633	3.602	
		Sc2					Sc2					Sc2		
Sc2:	O5	203.8	0.600	Sc2:	O5	203.6	0.603		Sc2:	O5	204.5	0.589		
	O2	208.2	0.533		O2	208.7	0.526			O2	209.4	0.516		
	O4	210.5	0.501		O4	210.8	0.497			O4	211.3	0.490		
	O3	212.9	0.469		O3	212.7	0.472			O3	213.5	0.462		
	O4	215.3	0.440		O4	215.4	0.439			O4	216.3	0.428		
	O5	221.6	0.371		O5	221.5	0.372			O5	222.0	0.367		
	[6]	(212.1)	2.914		[6]	(212.1)	2.909			[6]	(212.8)	2.852		
		Si					Si					Si		
Si:	O4	161.7	1.019	Si:	O3	161.6	1.022		Si:	O4	162.0	1.011		
	O3	162.0	1.011		O4	161.8	1.016			O3	162.4	1.000		
	O1	162.2	1.005		O1	162.1	1.008			O1	162.7	0.992		
	O2	163.3	0.976		O2	163.3	0.976			O2	163.6	0.968		
	[4]	(162.3)	4.011		[4]	(162.2)	4.022			[4]	(162.8)	3.971		

^a BVS; $\text{BV} = e^{(r^0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(\text{Tm}^{\text{III}}-\text{O}) = 2.000$, $r_0(\text{Yb}^{\text{III}}-\text{O}) = 1.965$, $r_0(\text{Sc}^{\text{III}}-\text{O}) = 1.849$ and $r_0(\text{Si}^{\text{IV}}-\text{O}) = 1.624$; ^b the coordination numbers and average distances are given in brackets.

have the higher coordination number and also the longer average Sc–O distance. This is an important prerequisite for the doping experiments, since the ionic radii [21] for Nd^{3+} (104 pm), Tm^{3+} (94 pm), and Yb^{3+} (86 pm) are larger than the one for Sc^{3+} (83 pm). Our structure refinements of the thulium- and ytterbium-doped crystals clearly revealed, that exclusively the Sc1 site is substituted by the larger rare earth element. Only at very high substitution levels (see the solid solution $\text{Lu}_{2-x}\text{Sc}_x\text{SiO}_5$) both sites show mixed occupancies. Thus, the optical properties of these laser materials arise from the doped Sc1O7 site.

As a consequence of the rare earth doping the cell parameters increase, and we observe small differences in the RE–O distances (Table 3). These differences are also reflected in the course of the calculated bond valence sum (BVS) values listed in the same Table. For the Sc2 and Si sites the calculated values are in good agreement with the expected val-

ues for Sc^{3+} and Si^{4+} , respectively [22,23]. Due to the RE/Sc mixing in the thulium- and ytterbium-doped crystals we observe a BVS much larger than 3 if the calculation is carried out solely for Tm^{3+} , respectively Yb^{3+} , and a much smaller BVS when using Sc^{3+} . This drastic over-bonding already for the thulium-doped compound indicates that it is difficult to introduce larger cations. In view of the very large r_0 value of 2.105 Å for $\text{Nd}^{\text{III}}-\text{O}$ [22] it is readily understandable that the neodymium-doped SSO crystal showed no neodymium content within the accuracy of our diffraction experiment.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft. The authors thank the financial support from NSFC (Grant 60908030, 60938001, 61178056), Science and Technology Commission of Shanghai Municipality and (No. 10ZR1434200) and Hundred Talents Project of the Chinese Academy of Sciences.

- [1] N. A. Toropov, V. A. Vasil'eva, *Russ. J. Inorg. Chem.* **1962**, 7, 1001.
- [2] M. D. Alba, P. Chain, T. González-Carrascosa, *J. Am. Ceram. Soc.* **2009**, 92, 487.
- [3] M. D. Alba, P. Chain, P. Florian, D. Massiot, *J. Phys. Chem. C* **2010**, 114, 12125.
- [4] R. Gaume, B. Viana, J. Derouet, D. Vivien, *Opt. Mater.* **2003**, 22, 107.
- [5] S. Campos, A. Denoyer, S. Jandl, B. Viana, D. Vivien, P. Loiseau, B. Ferrand, *J. Phys.: Condens. Matter* **2004**, 16, 4579.
- [6] A. Denoyer, Thèse, Faculté des Sciences, Université de Sherbrooke, Québec, Canada **2007**.
- [7] Yu. D. Zavartsev, A. I. Zagumennyi, Yu. L. Kalachev, S. A. Kutovoi, V. A. Mikhailov, V. V. Podreshetnikov, I. A. Scherbakov, *Quantum Electr.* **2011**, 41, 420.
- [8] K. J. Hubbard, D. G. Schlom, *J. Mater. Res.* **1996**, 11, 2757.
- [9] R. Gaumé, B. Viana, D. Vivien, J.-P. Roger, D. Fournier, *Appl. Phys. Lett.* **2003**, 83, 1355.
- [10] H. Eckert, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2010**, 636, 2232.
- [11] S. Balamurugan, U. Ch. Rodewald, T. Harmening, L. van Wüllen, D. Mohr, H. Eckert, R. Pöttgen, *Z. Naturforsch.* **2010**, 65b, 13.
- [12] S. Balamurugan, U. Ch. Rodewald, T. Harmening, L. van Wüllen, D. Mohr, H. Deters, H. Eckert, R. Pöttgen, *Z. Naturforsch.* **2010**, 65b, 1199.
- [13] H. Ben Yahia, L. van Wüllen, S. Balamurugan, U. Ch. Rodewald, H. Eckert, R. Pöttgen, *Z. Naturforsch.* **2011**, 66b, 14.
- [14] H. Ben Yahia, U. Ch. Rodewald, B. Heying, S. Balamurugan, R. Pöttgen, *Z. Naturforsch.* **2011**, 66b, 1183.
- [15] L. Zheng, J. Xu, G. Zhao, L. Su, F. Wu, X. Liang, *Appl. Phys. B* **2008**, 91, 443.
- [16] L. Zheng, J. Xu, L. Su, H. Li, Q. Wang, W. Ryba-Romanowski, R. Lisiecki, F. Wu, *Opt. Lett.* **2009**, 34, 3481.
- [17] L. Zheng, J. Xu, L. Su, H. Li, W. Ryba-Romanowski, R. Lisiecki, P. Solarz, *Appl. Phys. Lett.* **2010**, 96, 121908.
- [18] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, 10, 73.
- [19] G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112.
- [20] J. Felsche, *Struct. Bond.* **1973**, 13, 99.
- [21] J. Emsley, *The Elements*, Oxford University Press, Oxford **1999**.
- [22] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, B41, 244.
- [23] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, B47, 192.