The Solid Solution $Lu_{2-x}Sc_xSiO_5$

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The monoclinic silicates Lu_2SiO_5 and Sc_2SiO_5 (Y_2SiO_5 type, space group $C2/c$) form a solid solution $Lu_{2-x}Sc_xSiO_5$. Samples with x = 0.5, 0.8, 1.0 were synthesized ceramically from Lu_2O_3, Sc_2O_3, and SiO_2. The structures of three crystals with x = 0.88, 0.77, and 0.50 were refined on the basis of single-crystal X-ray diffraction data. The rare earth (*RE*) atoms occupy two crystallographically different $8f$ sites with oxygen coordination numbers (CN) of 6 (*RE*2) and 7 (*RE*1). Refinements of the occupancy parameters showed Lu/Sc mixing for both sites with a strong preference of the smaller scandium atoms for CN6.

Key words: Crystal Structure, Solid Solution, Silicate

Introduction

Scandium forms the dimorphic silicate $Sc_2Si_2O_7$. Under ambient conditions it crystallizes with its own monoclinic structure type, space group $C2/m$ [1, 2] and transforms to a cubic high-pressure phase with pyrochlore-type structure at 1270 K and 120 kbar [3]. In nature the solid solution $(Sc, Y)_2Si_2O_7$ is one of the rare scandium minerals. Besides $Sc_2Si_2O_7$ the crystal structure of the silicate Sc_2SiO_5 [4 – 6] has recently been reported. It adopts the monoclinic Y_2SiO_5 type, space group $C2/c$. The technical interest in Sc_2SiO_5 relates to its high thermal conductivity and negative refractive index, which makes it an interesting host material for laser optics [7 – 9]. Furthermore, a variety of multinary scandium silicates are known. In several quaternary silicates like $K_3ScSi_2O_7$ [10] or $Ba_9Sc_2(SiO_4)_6$ [11], one observes full ordering of the cations meeting the coordination requirements of Sc^{3+} (octahedral) on one side and the alkali and alkaline earth metal cations with larger coordination number on the other. The situation is different for Sc_2SiO_5 which is doped with 1 – 4 % of another trivalent rare earth cation for optical applications. The Sc_2SiO_5 structure has two crystallographically independent scandium sites on Wyckoff positions $8f$. These two sites have oxygen coordination numbers 6 and 7 for Sc2 and Sc1, respectively. For an understanding of the electronic structure variations and the interpretation of the optical properties it is important to know on which crystallographic site the doping cations are located. Such studies have not yet been reported for the host material Sc_2SiO_5.

During attempts to prepare $Lu_3Ga_3Sc_2O_{12}$ single crystals for systematic ^{45}Sc solid state NMR studies [12 – 14, and refs. therein] we obtained crystals of the solid solution $Lu_{2-x}Sc_xSiO_5$ from side reactions. We have then prepared new samples $Lu_{2-x}Sc_xSiO_5$ (Table 1) and obtained small single crystals for site occupancy refinements. These data are reported herein.

Experimental Section

Synthesis

Crystals of the solid solution $Lu_{2-x}Sc_xSiO_5$ were first obtained as an impurity phase from a K_2WO_4 flux synthesis of $Lu_3Ga_3Sc_2O_{12}$ single crystals. Starting materials for the selective synthesis of $Lu_{2-x}Sc_xSiO_5$ samples were Lu_2O_3 (Chempur, > 99.9 %), Sc_2O_3 (ACROS Organics, > 99.5 %), and SiO_2 (Sigma-Aldrich, > 99.9 %). The three oxides were mixed in the ideal atomic ratios $Lu_{2-x}Sc_xSiO_5$ with x = 0.5, 0.8, 1.0, pressed to pellets and reacted in alumina crucibles at 1670 K for 48 h, followed by quenching.

EDX data

Semiquantitative EDX analyses of several needle-shaped $Lu_{2-x}Sc_xSiO_5$ crystals, including those investigated on the diffractometer, were carried out with a Leica 420i scanning electron microscope with LuF_3, Sc, and SiO_2 as standards. The experimentally observed compositions were close to the ideal ones. No impurity elements were detected.

X-Ray diffraction

The polycrystalline $Lu_{2-x}Sc_xSiO_5$ samples were characterized by Guinier patterns (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. Different $Lu_{2-x}Sc_xSiO_5$ crystals suitable for single-crystal X-ray diffraction were selected on the basis of the size and the sharpness of the diffraction spots by Laue photographs on

Table 1. Lattice parameters for silicates of the solid solution $Lu_{2-x}Sc_xSiO_5$.

Compound	*a* (pm)	*b* (pm)	*c* (pm)	β (deg)	*V* (nm^3)	Ref.
Sc_2SiO_5	1367.3(1)	642.63(9)	996.76(2)	121.09(1)	0.7500	[5]
$Lu_{1.12}Sc_{0.88}SiO_5$ [a]	1403.0(3)	653.30(10)	1009.2(2)	121.97(3)	0.7847	this work
$Lu_{1.23}Sc_{0.77}SiO_5$ [a]	1406.6(1)	655.01(6)	1010.74(9)	122.02(1)	0.7896	this work
$Lu_{1.50}Sc_{0.50}SiO_5$ [a]	1410.8(2)	657.14(6)	1013.8(2)	122.07(1)	0.7965	this work
Lu_2SiO_5	1425.4(9)	664.1(7)	1024.1(8)	122.20(8)	0.8193	[18, 19]
Lu_2SiO_5	1427.74(7)	663.98(4)	1024.65(6)	122.224(1)	0.8217	[15]
Lu_2SiO_5	1433(2)	667.1(6)	1032(2)	122.30(13)	0.8338	[20]

[a] Single-crystal data.

Table 2. Crystal data and structure refinement for $Lu_{2-x}Sc_xSiO_5$, space group $C2/c$, $Z = 8$.

Empirical formula	$Lu_{1.12(1)}Sc_{0.88(1)}SiO_5$	$Lu_{1.23(1)}Sc_{0.77(1)}SiO_5$	$Lu_{1.50(2)}Sc_{0.50(2)}SiO_5$
Formula weight, g mol^{-1}	343.46	358.08	392.37
Unit cell dimensions	Table 1	Table 1	Table 1
Calculated density, g cm^{-3}	5.81	6.03	6.55
Crystal size, μm^3	$60 \times 80 \times 100$	$10 \times 20 \times 20$	$20 \times 40 \times 40$
Transm. ratio (max / min)	0.337 / 0.167	0.771 / 0.484	0.679 / 0.340
Absorption coefficient, mm^{-1}	29.7	32.1	37.9
Detector distance, mm	80	80	70
Exposure time, min	6	8	8
ω range; increment, deg	0 – 180, 1.0	0 – 180, 1.0	0 – 180, 1.0
Integr. param. A; B; EMS	12.6; 2.7; 0.011	12.0; 2.5; 0.012	12.8; 3.0; 0.012
$F(000)$, e	1216	1260	1366
θ range for data collection, deg	2 – 32	2 – 32	2 – 33
Range in *hkl*	$\pm 20, \pm 9, \pm 14$	$\pm 20, \pm 9, \pm 14$	$\pm 21, \pm 10, \pm 15$
Total no. reflections	3955	4628	5466
Independent reflections / R_{int}	1297 / 0.0483	1357 / 0.0861	1537/ 0.1140
Reflections with $I \geq 2\sigma(I)$ / R_σ	1139 / 0.0354	904 / 0.0887	990 / 0.1182
Data / ref. parameters	1297 / 76	1357 / 76	1537 / 76
$R1$ / $wR2$ for $I \geq 2\sigma(I)$	0.0246/ 0.0626	0.0524 / 0.1087	0.0426 / 0.0996
$R1$ / $wR2$ for all data	0.0306/ 0.0643	0.0952 / 0.1203	0.0772 / 0.1066
Goodness-of-fit on F^2	1.012	0.996	0.848
Extinction coefficient	0.0011(1)	0.0016(2)	0.0010(1)
Largest diff. peak / hole, e Å^{-3}	2.39 / −1.43	2.59 / −2.88	5.13 / −3.32

a Buerger camera (using white Mo radiation). The data collections of three crystals with different compositions were carried out in oscillation mode on a Stoe IPDS II diffractometer using MoK_α radiation. Numerical absorption corrections were applied to the data sets. Details about the data collections and crystallographic parameters are summarized in Table 2.

Structure refinements

The three data sets showed *C*-centred monoclinic lattices. The observed extinction conditions agree with the space groups $C2/c$, $C2$ and Cc, of which the centrosymmetric space group $C2/c$ was found to be correct during the structure refinements, in agreement with the structure of isotypic Lu_2SiO_5 [15]. The atomic parameters of the lutetium 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 $F_o{}^2$) [16, 17]. Both $8f$ rare earth sites were refined with mixed Lu/Sc occupancies. The refinements then smoothly converged to the residuals listed in Table 2. The refined atomic positions, equivalent isotropic displacement parameters, and interatomic distances (exemplarily for $Lu_{1.12}Sc_{0.88}SiO_5$ and Lu_2SiO_5) are given in Tables 3 and 4.

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-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-423655 ($Lu_{1.12}$-$Sc_{0.88}SiO_5$), CSD-423656 ($Lu_{1.23}Sc_{0.77}SiO_5$), and CSD-423657 ($Lu_{1.50}Sc_{0.50}SiO_5$).

Discussion

The silicates Sc_2SiO_5 [4 – 6] and Lu_2SiO_5 [15, 18 – 20] are isotypic with Y_2SiO_5 [21], and they form a solid solution $Lu_{2-x}Sc_xSiO_5$. The lattice parameters drastically drop from the lutetium to the scandium compound, but in an almost isotropic manner (Table 1

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for the solid solution $\mathrm{Lu_{2-x}Sc_xSiO_5}$. The three structures were refined with the setting of $\mathrm{Lu_2SiO_5}$ given by Gustafsson *et al.* [15]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms lie on the Wyckoff positions $8f$.

Atom	Occupancy (%)	x	y	z	U_{eq}
$\mathbf{Lu_{1.12(1)}Sc_{0.88(1)}SiO_5}$					
Lu1/Sc1	77.3(7)/22.7(7)	0.53839(2)	0.75515(4)	0.46853(2)	82(1)
Lu2/Sc2	34.6(4)/65.4(4)	0.14085(3)	0.37447(6)	−0.16135(4)	84(1)
Si	100	0.31635(10)	0.5922(2)	0.19241(13)	72(3)
O1	100	0.4131(3)	0.5108(7)	0.3630(4)	163(7)
O2	100	0.3754(3)	0.7929(6)	0.1687(4)	134(7)
O3	100	0.2005(3)	0.6472(6)	0.1821(4)	127(7)
O4	100	0.2969(3)	0.4235(6)	0.0631(4)	154(7)
O5	100	0.0178(3)	0.4024(5)	−0.1048(4)	110(7)
$\mathbf{Lu_{1.23(1)}Sc_{0.77(1)}SiO_5}$					
Lu1/Sc1	82(2)/18(2)	0.53820(6)	0.75559(12)	0.46818(8)	113(2)
Lu2/Sc2	41(1)/59(1)	0.14086(10)	0.37420(18)	−0.16171(13)	111(4)
Si	100	0.3161(3)	0.5916(6)	0.1932(4)	104(10)
O1	100	0.4128(10)	0.510(2)	0.3635(13)	197(24)
O2	100	0.3753(9)	0.7912(17)	0.1701(13)	168(23)
O3	100	0.2008(10)	0.6444(19)	0.1816(13)	183(24)
O4	100	0.298(1)	0.4220(16)	0.0640(14)	175(24)
O5	100	0.0178(9)	0.4035(16)	−0.1058(12)	141(22)
$\mathbf{Lu_{1.50(2)}Sc_{0.50(2)}SiO_5}$					
Lu1/Sc1	93(2)/7(2)	0.53795(5)	0.75586(10)	0.46763(7)	77(2)
Lu2/Sc2	57(1)/43(1)	0.14080(7)	0.37421(13)	−0.1624(1)	83(3)
Si	100	0.3165(3)	0.5924(5)	0.1926(4)	52(9)
O1	100	0.4126(8)	0.5097(16)	0.3632(12)	125(19)
O2	100	0.3774(8)	0.7915(14)	0.1737(12)	96(19)
O3	100	0.2000(8)	0.6471(15)	0.1799(13)	127(19)
O4	100	0.2970(8)	0.4275(16)	0.0614(13)	131(21)
O5	100	0.0167(8)	0.4028(14)	−0.1063(11)	95(18)

Table 4. Interatomic distances (in Å), bond valence (BV) and bond valence sums (BVS) for $\mathrm{Lu_{1.12}Sc_{0.88}SiO_5}$ and $\mathrm{Lu_2SiO_5}$. The coordination numbers and average distances are given in brackets.

		Distance	BV	BV			Distance	BV
$\mathbf{Lu_{1.12}Sc_{0.88}SiO_5}$					$\mathbf{Lu_2SiO_5}$			
			Lu1	Sc1				Lu1
Lu1/Sc1:	O5	214.2	0.630	0.453	Lu1:	O5	216.0	0.600
	O1	218.8	0.556	0.400		O1	225.5	0.464
	O3	224.4	0.478	0.344		O3	227.3	0.442
	O1	226.9	0.447	0.321		O1	229.4	0.418
	O2	228.4	0.429	0.309		O2	233.1	0.378
	O5	232.6	0.383	0.275		O5	234.3	0.366
	O2	266.8	0.152	0.109		O2	261.4	0.176
	[6]	$\langle 224.2\rangle$	2.923^a	2.102^a		[6]	$\langle 227.6\rangle$	2.668^a
	[7]	$\langle 230.3\rangle$	3.075^a	2.211^a		[7]	$\langle 232.4\rangle$	2.844^a
			Lu2	Sc2				Lu2
Lu2/Sc2:	O5	209.4	0.717	0.516	Lu2:	O5	216.6	0.590
	O3	214.9	0.618	0.444		O3	223.5	0.490
	O4	214.9	0.618	0.444		O4	223.5	0.490
	O2	218.2	0.565	0.407		O4	223.5	0.490
	O4	218.5	0.561	0.403		O2	223.6	0.489
	O5	223.5	0.490	0.352		O5	226.2	0.455
	[6]	$\langle 216.6\rangle$	3.569^a	2.566^a		[6]	$\langle 222.8\rangle$	3.004^a
Si:	O3	161.3	1.030		Si:	O3	161.4	1.027
	O4	161.7	1.019			O4	162.1	1.008
	O1	161.7	1.019			O1	162.3	1.003
	O2	163.5	0.971			O2	164.0	0.958
	[4]	$\langle 162.1\rangle$	4.039^a			[4]	$\langle 162.5\rangle$	3.996^a

[a] BVS; BV = $e^{(r0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(\mathrm{Lu^{III}}–\mathrm{O}) = 1.971$, $r_0(\mathrm{Si^{IV}}–\mathrm{O}) = 1.624$ and $r_0(\mathrm{Sc^{III}}–\mathrm{O}) = 1.849$ [22, 23].

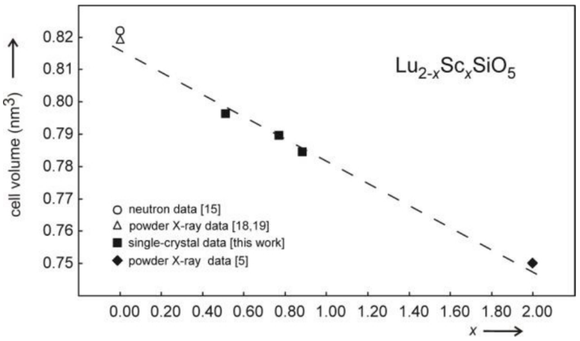

Fig. 1. Plot of the cell volume within the solid solution $Lu_{2-x}Sc_xSiO_5$.

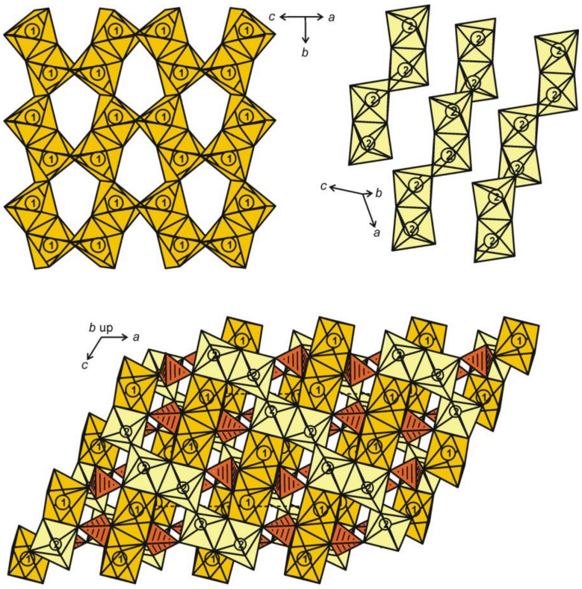

Fig. 2 (color online). (top) Connectivity pattern of the edge- and corner-sharing $Lu1/Sc1O_7$ (left) and $Lu2/Sc2O_6$ (right) polyhedra in the solid solution $Lu_{2-x}Sc_xSiO_5$. (bottom) View of the $Lu_{2-x}Sc_xSiO_5$ structure along the *c* axis, emphasizing the $Lu1/Sc1O_7$, $Lu2/Sc2O_6$, and SiO_4 polyhedra.

and Fig. 1). The RE_2SiO_5 structures have been reported with two different settings in space groups $C2/c$ and $I2/c$. Herein we used the standard $C2/c$ setting previously taken by Gustafsson *et al.* [15] for Lu_2SiO_5. The $Lu_{2-x}Sc_xSiO_5$ structures have two crystallographically independent $8f$ rare earth sites. The Lu1/Sc1 and Lu2/Sc2 atoms have coordination numbers 7 and 6 by oxygen atoms, respectively.

For both mixed occupied rare earth positions we observe a decrease of the *RE*–O distances upon Lu/Sc mixing as compared to Lu_2SiO_5 (Table 4). As expected, the *RE*2 site with the smaller coordination number shows much larger scandium occupancy for all three crystals investigated. As a consequence, the average *RE*–O distance decreases by 2 pm for the *RE*1 and by 6 pm for the *RE*2 site. These differences are also reflected in the course of the calculated bond valence sum (BVS) values listed in Table 4. For Lu_2SiO_5 the calculated values are in good agreement with the expected values for Lu^{3+} and Si^{4+}, respectively [22, 23]. Due to the Lu/Sc mixing in the investigated structures we observe a BVS larger than 3 if the calculation is carried out solely for Lu^{3+} and a much smaller BVS when using Sc^{3+}. In agreement with the course of the occupancy parameters (Table 3), this discrepancy is most pronounced for Sc^{3+} on the *RE*1 site and for Lu^{3+} on the *RE*2 site. These results are an important prerequisite for the doping experiments for optical applications. Sc_2SiO_5 has been used as host matrix for Nd^{3+} [8], Tm^{3+} [9], and Yb^{3+} [7] with concentrations up to 5 at.-%. So far, precise structural studies on the doped materials have not been carried out. Based on the present data we can conclude that the significantly larger RE^{3+} doping cations will preferably occupy the larger *RE*1 site.

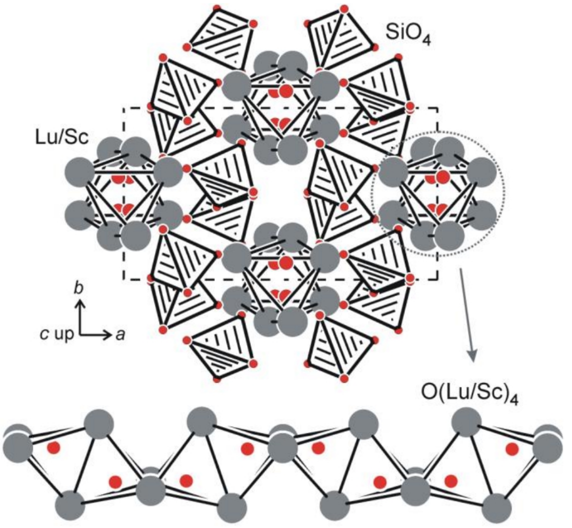

Fig. 3 (color online). (top) View of the $Lu_{2-x}Sc_xSiO_5$ structure along the *c* axis. The $O(Lu/Sc)_4$ and SiO_4 tetrahedra are emphasized. (bottom) Cutout of a chain of *trans*-edge-sharing $O(Lu/Sc)_4$ tetrahedra.

Finally we briefly discuss the connectivity of the metal-oxygen polyhedra. As emphasized in Fig. 2, one can subdivide the $Lu_{2-x}Sc_xSiO_5$ structure into three substructures. The $Lu1/Sc1O_7$ and $Lu2/Sc2O_6$ polyhedra are condensed *via* common edges and corners, leading to two-dimensional subunits. The latter are connected *via* the almost regular SiO_4 tetrahedra, leading to the complex network shown at the bottom of Fig. 2.

The formulations $Sc_2[SiO_4]O$ and $Lu_2[SiO_4]O$ emphasize the oxide-silicate character. While the O1, O2, O3, and O4 atoms connect to the silicon atoms, the O5 atoms are located within rare earth tetrahedra (Fig. 3). These $O5(Lu/Sc)_4$ tetrahedra are trans-edge-sharing, leading to chains which extend in the *c* direction. These chains show the motif of a distorted hexagonal rod packing. These rods are separated by the SiO_4 tetrahedra.

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