ESRF	**Experiment title:** Triclinic type F structure of $Sm_2Si_2O_7$ and $Eu_2Si_2O_7$; geometry of the $Si_2O_7^{6-}$ ion in $La_2Si_2O_7$ at high pressure.	**Experiment number:** CH-88
Beamline: BM 16	**Date of experiment:** from: 22 May 96 to: 24 May 96	**Date of report:** 31 July 1996
Shifts: 6	**Local contact(s):** Eric Dooryhee	*Received at ESRF:*

EXPERIMENTAL TEAM (names and affiliation)

Axel Nørlund Christensen,* Chemistry Department, Aarhus University, DK-8000 Aarhus C, Denmark.
Marie-Agnès Chevallier,* Chemistry Department, Aarhus University, DK-8000 Aarhus C, Denmark.
Anette Frost Jensen,* Chemistry Laboratory IV, H.C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark.
Eric Dooryhee,* ESRF, B.P. 220, F-38042 Grenoble Cedex, France.

Part A. Investigation of the structure of $Sm_2Si_2O_7$.

The rare earth disilicates $RE_2Si_2O_7$ can exist in seven different phases of which four are high temperature phases. $Sm_2Si_2O_7$ exists in a low temperature phase, structure type A, and in a high temperature phase, structure type F, of which only the unit cell and space group is known. $Gd_2Si_2O_7$ exists in a low temperature phase, structure type B, and in a high temperature phase, structure type E. The goal of the present investigation was to obtain more information about the structure type F.

Samples of $Sm_2Si_2O_7$ and $Gd_2Si_2O_7$ were prepared in a solid state synthesis from stoichiometric mixtures of Sm_2O_3 (Auer-Remy) and SiO_2 (Kieselgur, Merck), and of Gd_2O_3 (Research Chemicals) and SiO_2 (Kieselgur, Merck), respectively. Pellets of the reaction mixtures were pressed in moulds of cemented carbide and kept at 1500°C for 75 h.

The synchrotron X-ray powder patterns were recorded with the wave length $\lambda = 0.4276$ Å, which gives a transmission of 62% for a 0.2 mm diameter capillary of the $Sm_2Si_2O_7$ sample, and a transmission of 58% for a 0.2 mm diameter of the $Gd_2Si_2O_7$ sample. The monochromator used was a Si(111) crystal. Each pattern was recorded over 12 h, using a Debye-Scherrer geometry and a 16 bunch machine operation mode with a ring current of 80 to 50 mA. The diffractometer at BM 16 has a continuous scan and readout from a 9 channel detector with Ge (111) analyzer crystals. The data was reduced with a local program (Vaughan 1996). The FWHM of the reflections was typically 0.022° in the 2θ range 3-10° and the signal to background ratio of the strongest reflections was typically within the range 20-33.

The pattern of the $Gd_2Si_2O_7$ sample was used as a test case for profile refinement, using the program FullProf (1) and the reported structure of $Gd_2Si_2O_7$, structure type E (2), and the structure of $Gd_{9.33}[\ ]_{0.67}(SiO_4)_6O_2$ (3). Of the positional parameters only those for Gd and Si were refined. The Gd and Si atoms contribute to 90.7 and 4.3% of the scattering, respectively. The refined positional parameters are in acceptable agreement with the reported values, but have standard deviations one order of magnitude larger than the values arrived at in the single crystal X-ray analysis (2,3).

The pattern of the $Sm_2Si_2O_7$ sample was then used in a profile refinement. The structure of $Sm_2Si_2O_7$, type A, has been reported (4), and the structure of the type F is assumed to be related to that of the type G (5). Using the reported structure of $Ce_2Si_2O_7$, type G (6), starting values for the positional parameters of $Sm_2Si_2O_7$, type F, were calculated. Only the positional parameters of the Sm and Si atoms were refined. The Sm and Si atoms contribute to 90.2 and 4.6% of the scattering, respectively. The refined positional parameters for the type A model were in acceptable agreement with the reported values, but had also standard deviations one order of magnitude larger than the values reported from the single crystal X-ray analysis (4). In the case of the structure type F, the positional parameters of the Sm atoms refined to values close to the values of the model arrived at by packing considerations. However, the Si atoms refined to values which violated the geometry of the disilicate ion. Unit cell parameters for the type F structure and positional parameters for the Sm atoms of $Sm_2Si_2O_7$ are listed below:

$\underline{a}$ = 8.569(2) Å, $\underline{b}$ = 12.837(3) Å, $\underline{c}$ = 5.308(1) Å

$\alpha = 90.30(3)^o$, $\beta = 91.86(2)^o$, $\gamma = 90.25(2)^o$

Space group: P-1.

Atom	x/a	y/b	z/c
Sm1	0.822(2)	0.751(2)	0.715(6)
Sm2	0.680(4)	0.280(2)	0.248(6)
Sm3	0.611(4)	0.587(3)	0.232(5)
Sm4	0.886(3)	0.088(2)	0.728(4)

References.

1. Rodriguez-Carvajal, J. FullProf, Version 3.0.0. April 95-LLB-JRC, Laboratoire Léon Brillouin (CEA-CNRS), Saclay, 1995.

2. Smolin, Yu.I. and Sepelev, Yu. F.: Acta Crystallogr. B26 (1970) 484.

3. Smolin, Yu. I. and Sepelev, Yu. F.: Izv. Akad. Nauk. SSSR Neorg. Mat. 5 (1969) 1823.

4. Smolin, Yu. I., Sepelev, Yu. F. and Butikova, I. K.: Soviet Physics - Crystallogr. 15 (1970) 214.

5. Felsche, J.: J. Less-Common Met. 21 (1970) 1.

6. Christensen, A. N. and Hazell, R. G.: Acta Chem. Scand. 48 (1994) 1012.