JOURNAL OF SOLID STATE CHEMISTRY **91**, 173–175 (1991)

BRIEF COMMUNICATIONS

The Crystal Structure of $Sr_3Y_2Ge_3O_{12}$

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Received July 16, 1990

The crystal structure of the garnet $Sr_3Y_2Ge_3O_{12}$ ($Ia3d$, a = 13.0871(1) Å) has been determined by time-of-flight neutron powder diffraction. © 1991 Academic Press, Inc.

Introduction

Garnets are of considerable practical importance and are also of great interest in crystal chemistry. The reason for the latter is that they have a relatively simple structure (with four parameters completely specifying the structure) and almost half the elements can be a component of a garnet structure. Two observations are of interest to us: (a) Bond valence sums at cations are often significantly different from the expected values whereas the sums at the anion are usually very close to the ideal value (*1*). (b) The two independent bonds to the 8-coordinated atom have unequal lengths, possibly because of nonbonded interactions between atoms (*2*).

Many garnet structures have been refined, but attention has been focused mainly on silicates, aluminates, and ferrites; i.e., on the garnets with smaller unit cell sizes. To investigate the relative importance of anion . . . anion and cation . . . cation nonbonded interactions, it is desirable to have an accurate structure determination of a garnet with a large unit cell. The garnet with the largest unit cell that we have been able to prepare pure is $Sr_3Y_2Ge_3O_{12}$; a composition first reported by Mill' (*3*). The structure of this compound is reported here.

Experimental

Pure $Sr_3Y_2Ge_3O_{12}$ powder was prepared by annealing stoichiometric amounts of intimately mixed $SrCO_3$, GeO_2, and Y_2O_3 at 1250°C. Repeated grindings and firings were found necessary to eliminate contamination by $SrGeO_3$, which forms rather readily. Time-of-flight neutron powder diffrac-

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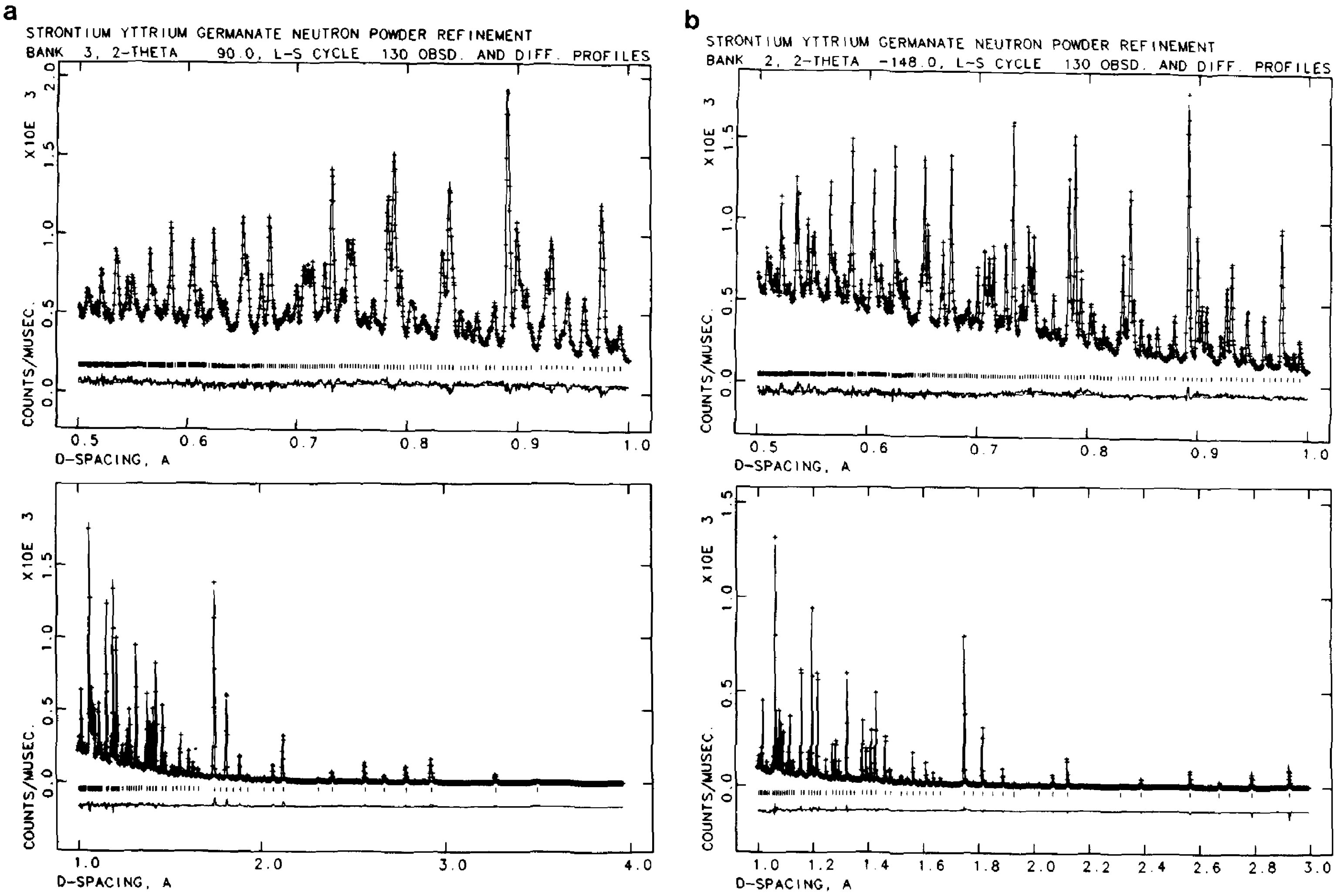

FIG. 1. Neutron diffraction profile fit for $Sr_3Y_2Ge_3O_{12}$; (a) ±90° 2θ; (b) ±148° 2θ. The data are shown as "+" and the calculated profile is the solid line. The difference curve is on the same scale as the data. The tick marks are at Bragg peaks.

TABLE I

POSITIONS AND THERMAL PARAMETERS FOR $Sr_3Y_2Ge_3O_{12}$[a]

	Sr	Y	Ge	O
x	$\frac{1}{8}$	0	$\frac{3}{8}$	−0.03952(4)
y	0	0	0	0.05172(4)
z	$\frac{1}{4}$	0	$\frac{1}{4}$	0.15908(4)
U_{11}	0.65(1)	0.82(1)	0.71(1)	0.98(1)
U_{22}	1.13(2)	$= U_{11}$	0.67(2)	1.10(2)
U_{33}	$= U_{22}$	$= U_{11}$	$= U_{22}$	0.89(2)
U_{12}	0	0.03(2)	0	0.11(2)
U_{13}	0	$= U_{12}$	0	−0.21(2)
U_{23}	0.11(3)	$= U_{12}$	0	0.00(2)

[a] Space group *Ia*3*d*, $a = 13.0871(1)$ Å. Thermal parameters are in units of 10^{-2} Å^2.

TABLE II

BOND LENGTHS AND VALENCE SUMS IN $Sr_3Y_2Ge_3O_{12}$

Bond	Length		Σv
Sr–O	2.5514(5)	4×	1.24
Sr–O	2.6833(5)	4×	0.87
Y–O	2.2494(5)	6×	3.22
Ge–O	1.7679(5)	4×	3.79
O–M		4×	2.01

tion data were collected at 305 K on the neutron powder diffractometer at the Manuel Lujon Neutron Scattering Center at Los Alamos National Laboratories. The crystal structure was refined by the Rietveld method using the generalized structure analysis system (GSAS) (*4*). The final refinement consisted of 806 reflections in the range 0.5 Å $< d <$ 4.0 Å (13,003 profile points). The R_p, R_{wp}, and reduced χ^2 were 3.61, 5.71, and 2.66, respectively, for 49 variables. The variables other than structural parameters are as described earlier (*5*).

Results and Discussion

Figure 1 shows the raw data, calculated profile, and differences. Derived structural parameters are reported in Table I and bond lengths and bond valence sums are reported in Table II. Bond valence sums use the parameters of Brown and Altermatt (*6*).

We call attention to the following features of the structure: (a) The two independent Sr–O bond lengths differ by 0.13 Å. This is in marked contrast to the situation in hydrogarnets such as $Ba_3In_2(OD)_{12}$ in which the two Ba–O bond lengths are very nearly equal (*5*). (b) The bond valence sums at the cations differ from the ideal value, but that at O is almost exactly 2.0. (c) The shortest O . . . O distances (which are in the GeO_4 tetrahedron) are 2.738 and 2.959 Å. (d) The YO_6 octahedron is almost regular—the O–Y–O angles are 89.8° and 90.2° (O . . . O distances of 3.176 and 3.187 Å).

Acknowledgments

This work was supported by the National Science Foundation, Grant DMR-8813524 and has benefited from the use of facilities at the Los Alamos Manual Lujon Neutron Scattering Center, a national user facility funded as such by the Department of Energy/Office of Basic Energy Sciences.

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