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Synthesis and Structural Characterization of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$, a New Compound with the Perrierite Structure

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A new layered germanate $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ has been prepared and its structure was determined from single crystal diffraction data. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.956(2)$ Å, $b = 5.642(1)$ Å, $c = 14.180(3)$ Å, $\beta = 114°09(3)$, and $Z = 2$ formula units by cell. The structure has been refined to residuals of $R = 3.14\%$ for 1380 observations and 152 parameters. $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ is isostructural with perrierite $Ce_4Fe_2Ti_3Si_4O_{22}$, a naturally occurring sorosilicate mineral. The framework consists of rutile-like slabs formed of alternating chains of GeO_6 octahedra and $Mn^{3+}O_6$ distorted octahedra, located between layers of mixed $Ge_{1.2}Si_{0.8}O_7$ disilicates groups that separate the isolated $Mn^{2+}O_6$ octahedra. A structural comparison with $La_4Mn_5Si_4O_{22}$ will be discussed.

INTRODUCTION

The recent study of synthesis of rare-earth manganese silicates and germanates has produced many interesting examples of quasi-low-dimensional systems in which one-dimensional chains or two-dimensional slabs are located between and isolated by silicate or germanate groups: $La_4Mn_5Si_4O_{22}$ and $La_4V_5Si_4O_{22}$ (1), $La_{3.4}Ca_{0.6}V_5Si_4O_{22}$ (2), $La_4Ti_5Si_4O_{22}$ (3), $PrMnGeO_5$ (4), and $GdMnGe_2O_7$ (5). $La_4Mn_5Si_4O_{22}$ displays the unusual characteristic of three oxidation states of manganese: 2+, 3+, and 4+.

For many years, much attention has been devoted to such systems with multivalent transition metals owing to their unusual and anisotropic physical properties (6–16). In this paper we report the synthesis of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ which is isostructural with $La_4Mn_5Si_4O_{22}$ and thus belongs to the perrierite structural type. It contains manganese atoms at two oxidation states: 2+ and 3+. The main structural feature is the presence of rutile slabs built up from alternate chains of MnO_6 and GeO_6 octahedra.

EXPERIMENTAL SECTION

Synthesis and Characterization

$La_4Mn_5Si_4O_{22}$ was prepared at 900°C for a week, from a redox reaction between $LaCl_3$, MnO_2, and SiO_2.

$$4\ LaCl_3 + 7\ MnO_2 + 4\,SiO_2$$
$$\Rightarrow La_4Mn_5Si_4O_{22} + 2\,MnCl_2 + 4\,Cl_2\,(g)$$

$MnCl_2$ was removed by dissolution in alcohol.

Unfortunately, the same reaction with GeO_2 instead of SiO_2 yields a mixture of oxides of different chemical formulations. On the other hand, it is well known that rare earth oxychlorides react easily with transition metal oxides, as TiO_2 and SiO_2 to give oxosilicates (17), SiO_2 generally arising from the silica tubes.

Accordingly, $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ was prepared by a redox reaction between LaOCl, MnO_2, GeO_2, and SiO_2. MnO_2, GeO_2, and SiO_2 starting materials were commercial reagents (Aldrich 99.9% purity). LaOCl was previously prepared by a thermal decomposition in air of $LaCl_3, 7\,H_2O$ at 600°C for one day:

$$LaCl_3,\ 7\,H_2O \Rightarrow LaOCl + 6\,H_2O^{\nearrow} + 2\,HCl^{\nearrow}$$

The reaction mixture was then sealed in an evacuated silica tube and heated at 800°C for 10 days. Quartz tube attack was noted during the reaction, even when tubes were coated with carbon, and X-ray microanalyses indicated the presence of silica in crystal samples.

$$4\,LaOCl + 3\,MnO_2 + 5.2\ GeO_2 + 0.8\ SiO_2$$
$$\Rightarrow La_4Mn_3Ge_{5.2}Si_{0.8}O_{22} + 2\ Cl_2\uparrow$$

This is the stoichiometric reaction; it has been studied with different amounts of SiO_2 without change in the resulting compound. The use of lanthanum oxychloride LaOCl

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instead of $LaCl_3$ which is very hygroscopic makes it possible to avoid the formation of $MnCl_2$. All attempts to prepare a pure germanate compound failed which suggest that the presence of silicon is necessary to stabilize the structure.

The crystals of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ are light red needles. A Philips CM 30 transmission electron microscope equipped with a Gatan multichannel spectrometer was used for X-ray microanalyses in order to analyze the bulk composition of the crystals. To avoid a possible contamination of the surface by silica arising from the tube attack, crystals were cleaned using a mixture of HF, CH_3CO_2H, and HNO_3 during a controlled time. Analyses gave a silica content of 1.8–2.2% in weight, close to the 2% value consistent with the structural determination.

STRUCTURAL DETERMINATION

First, single crystals were analyzed by the Weissenberg technique in order to select a nontwinned crystal suitable for structure determination. The data were collected using a Siemens P4 diffractometer, according to data collection listed in Table 1. The cell parameters reported in Table 1 were determined and refined from a least squares refinement based on 25 reflections with $3^\circ < 2\Theta < 25^\circ$. The space group was determined to be $P2_1/c$. Data were corrected from Lorentz polarization, absorption, and secondary extinction (18). Data reduction, structural solution, and refinement were performed using the SHELXTL plus package of structural software (19). The atomic scattering factors were those of Cromer and Waber (18) and the correction, for anomalous dispersion was made from Cromer and Waber (20).

TABLE 1
Crystallographic Data

Structural type	Perrierite
Empirical formula	$La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$
Formula weight	1472.38
Crystalline system	Monoclinic
Space group	$P2_1/c$
Lattice parameters	
a (Å)	11.956 (2)
b (Å)	5.642 (1)
c (Å)	14.180 (3)
β°	114.09 (3)
Volume (Å^3)	873.21
Z	2
Temperature (K)	293
Color and habit	Light red needle
Crystal dimensions (mm)	$0.01 \times 0.02 \times 0.2$
Density (calc.) (g/cm^3)	5.60
Diffractometer	Siemens p4
Radiation (Å)	Mo$K\alpha$ ($\lambda = 0.71073$)
μ (Mo$K\alpha$) (cm^{-1})	206.1
Scan type	ω
F_{000}	1313
$\Theta_{\max}$	35
Number of reflections measured	3672
Number of observations $I > 3\sigma(I)$	1380
Number of variables	152
Residuals R, R_w	0.0314, 0.0314

$R = \sum \| Fo| - |Fc\| / |\sum Fo|$

$R_w = [[\sum w(|Fo| - |Fc|)^2 / \sum wFo^2]]^{1/2}$ with $w = 1/(\sigma^2(Fo))$

TABLE 2
Atomic Coordinates and U_{eq}

Atom	Wickoff position	X/a	Y/b	Z/c	U_{eq} (Å^2)
La1	4e	0.75759(7)	− 0.0277(2)	0.2365(6)	0.0070(2)
La2	4e	0.2359(7)	0.9735(2)	0.05417(6)	0.0075(2)
Mn1	2d	0	0	0.5	0.0076(8)
Mn2	4e	0.4986(2)	0.0107(4)	0.7276(1)	0.0035(5)
Gel	4e	0.4999(1)	0.7514(2)	0.9962(2)	0.0073(4)
Ge/Si2[a]	4e	0.2366(1)	0.5021(4)	0.9134(1)	0.0049(3)
Ge/Si3[a]	4e	0.0439(1)	0.5090(3)	0.6600(1)	0.0046(3)
O1	4e	0.323(1)	0.754(2)	0.9178(8)	0.005(3)
O11	4e	0.322(1)	0.241(2)	0.9367(8)	0.009(3)
O2	4e	0.381(1)	0.264(2)	0.7105(9)	0.007(3)
O21	4e	0.381(1)	0.760(2)	0.7139(9)	0.008(3)
O3	4e	0.101(1)	0.297(2)	0.6015(9)	0.012(3)
O31	4e	0.097(1)	0.775(2)	0.6356(8)	0.012(3)
O4	4e	0.5113(8)	0.008(2)	0.9149(6)	0.008(2)
O5	4e	0.4187(8)	0.508(2)	0.0813(6)	0.007(2)
O6	4e	0.1786(9)	0.549(2)	0.0026(2)	0.016(3)
O7	4e	0.137(1)	0.432(2)	0.7878(8)	0.019(3)
O8	4e	− 0.11072(8)	0.482(2)	0.6324(7)	0.014(3)

[a] Ge/Si2 and Ge/Si3 = Ge (80%) and Si (20%).

Lanthanum atoms were localized from a Patterson three dimensional map and the remaining atoms by consecutive calculations of difference Fourier maps. The positions and thermal displacement parameters were refined by the full-matrix least squares method. All atoms were anisotropically refined. Positional and thermal displacement parameters are listed in Table 2, while important distances are given in Table 3.

RESULTS AND DISCUSSION

The structure determination of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ shows that it is isotypic with $La_4Mn_5Si_4O_{22}$ and thus belongs to the perrierite structural type, based on rutile-like slabs made of MnO_6 octahedra located between layers of Si_2O_7 disilicates groups. A full description of the structure of $La_4Mn_5Si_4O_{22}$ was given in a previous paper (1). Germanium atoms replace Mn^{4+} in the rutile-like layer and a part of silicon in sorosilicate groups. The structure can be described as a stacking of two types of slabs along the a axis (Fig. 1):

TABLE 3
Main Distances (Å) in Various Polyhedra

La1–O1^a	2.527(10)	La2–O1^e	2.694(13)
La1–O11^b	2.546(11)	La2–O11^d	2.612(13)
La1–O2^b	2.472(14)	La2–O2^d	2.580(11)
La1–O21^a	2.545(14)	La2–O21^d	2.523(14)
La1–O3^b	2.697(1)	La2–O3^d	2.543(14)
La1–O31^a	2.399(10)	La2–O31^d	2.928(14)
La1–O4^c	3.054(8)	La2–O4^b	2.660(10)
La1–O7^c	2.693(13)	La2–O6	2.559(12)
La1–O8^d	2.611(12)	La2–O8^h	2.505(8)
Gel–Gel × 2	2.808(3)	Ge/Si2–O1	1.744(11)
	2.838(3)	Ge/Si2–O6 × 2^j	1.747(1)
			1.693(13)
Gel–O1	1.947(11)	Ge/Si2–O7	1.735(10)
Ge1–O11^h	1.945(12)		
Ge1–O4 × 2^i	1.892(11)	Ge/Si3–O3	1.744(14)
Ge1–O5 × 2	1.875(11)	Ge/Si3–O31	1.722(12)
		Ge/Si3–O7	1.751(10)
		Ge3–O8^k	1.692(10)
Mn1–O3 × 2	2.220(10)	Mn2–O2 × 2	1.933(11)
Mn1–O31 × 2^g	2.198(10)		1.951(12)
Mn1–O6 × 2^g	2.138(12)	Mn2–O21 × 2^g	1.939(11)
			1.947(12)
		Mn2–04	2.598(10)
		Mn2–O5	2.024(10)

Note. Symmetry code: $^a1 + x, 2 + y, 1 + z$; $^b1 + x, 1 + y, 1 + z$; $^c1 + x, y, z$; $^dx, 1 + y, 1 - z$; $^ex, y, 1 - z$; $^f1 + x, y, z$; $^gx, 1 - y, z$; $^h1 + x, 1 + y, 2 + z$; $^ix, 1 + y, z$; $^jx, y, 1 + z$; $^k1 - x, y, z$.

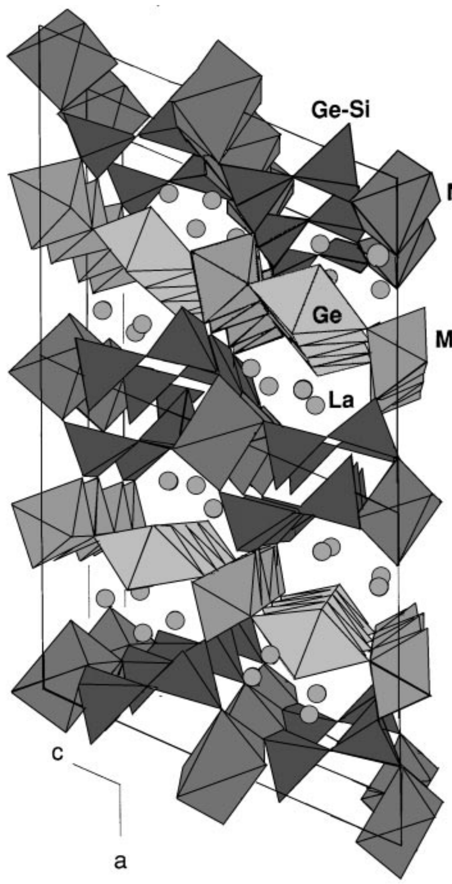

FIG. 1. Projection of the structure of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ along the *b* axis.

— the first one is a rutile-type metal layer built up on alternate chains of MnO_6 and GeO_6 corner-shared octahedra running along the *b* axis.

— the second one is formed of isolated MnO_6 octahedra bonded by each corner to six di-germano–silicate groups M_2O_7 made of two MO_4 tetrahedra, sharing one corner, with the following statistical distribution: $(Ge_{1.6}Si_{0.4})O_7$.

Like in $La_4Mn_5Si_4O_{22}$, lanthanum cations La^{3+} are located in channels, in a tricapped trigonal prism made of nine oxygen atoms (8 + 1). In $La_4Mn_5Si_4O_{22}$ two different coordinations were observed: La1 (7 + 1) and La2 (8 + 2).

Crystalline parameters of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ and $La_4Mn_5Si_4O_{22}$ are compared in Table 4. The substitution of Mn^{4+} and Si^{4+} cations by Ge^{4+} cations results in the lowering of the symmetry from $C2/m$ to $P2_1/c$. Oxygen positions O1, O2, and O3 in the space group $C2/m$ are split in two positions in the space group $P2_1/c$, O1/O11, O2/O21, and O3/O31, respectively.

Apart from MnO_6 octahedra, the geometry and distances observed in the other polyhedra are very similar to $La_4Mn_5Si_4O_{22}$. The distorted coordination of the Mn2 site might be related to the Jahn–Teller nature of the Mn^{3+} ion. The Mn2–O4 distance 2.598 Å is longer than that observed in $La_4Mn_5Si_4O_{22}$, 2.464 Å, while the La1–O4 and La2–O4 distances do not change. The Mn^{3+}–Mn^{3+} distances across shared octahedron edges (2 × 2.889 Å) are slightly longer than the distances seen in the parent compound, 2 × 2.827 Å, and thus farther from the critical value ($Rc = 2.76$ Å) defined by Goodenough (6) which would indicate possible electron delocalization and metal–metal interactions.

TABLE 4
Crystalline Parameters of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ and $La_4Mn_5Si_4O_{22}$

	$La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$	$La_4Mn_5Si_4O_{22}$
Structural type	Perrierite	Perrierite
Molecular weight (g/mol)	1472.38	1294.66
Symmetry	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/m$
Cell parameters (Å)		
a	11.956(2)	14.042(2)
b	5.642(1)	5.571(2)
c	14.180(3)	11.703(2)
β°	114.09(3)	114.34(4)
Volume (Å^3)	873.21	833.06
Z	2	2

TABLE 5
Bond Valence Calculations

La1	La2	Mn1	Mn2	Ge1	Ge2	Ge3
2.95	2.81	2.06	3.00	3.90	4.20[a] 3.96[b]	4.33[a] 4.06[b]

[a] For Ge2 and Ge3, calculations have been made with a site fully occupied by a germanium[a] and with a partial substitution $Ge_{0.8}Si_{0.2}$[b] deduced from the structural determination.

In $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$, manganese atoms appear at two oxidation states, 2+ and 3+, in octahedral sites. These ions occupy the same position as in $La_4Mn_5Si_4O_{22}$, i.e., Mn1 and Mn2 sites, respectively.

Bond valence sum calculations were performed to check the validity of this model through the computation of the total valence at each site, according to the Brese and O'Keefe tables (21). In each case, calculated results are in good agreement with expected values particularly for Ge2 and Ge3, when assuming a partial substitution by Si (Table 5).

It is likely that the magnetic behavior of $La_4Mn_3Ge_{5.2}Si_{0.8}O_{22}$ will be more simple than that of $La_4Mn_5Si_4O_{22}$. Detailed physical measurements have been undertaken to study the evolution of properties versus transition metal and cationic substitutions in this family.

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