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Abstract
Several rare-earth silicates have been synthesized at 10 GPa and 1600–
1700 °C: a La orthosilicate ($La_4Si_3O_{12}$) with a defect $Ba_3(PO_4)_2$-type, a new
structure type (K) for Nd and Gd disilicates ($Nd_2Si_2O_7$ and $Gd_2Si_2O_7$) with
a diorthosilicate structure, and a new structure type (L) for Dy disilicate
($Dy_2Si_2O_7$) with a structure containing linear triple tetrahedral groups [Si_3O_{10}],
but having one in six atoms distributed with 50% occupancy over two tetrahedral
positions.

1. Introduction

The single rare-earth element (REE) disilicates exhibit a complex structural chemistry at
room pressure due largely to the monotonic decrease in size of the REE^{3+} cation through the
lanthanide series, and seven distinct structure types (A–G) have been reported (cf references
in [1]). In six of these structure types (A, C, D, E, F, and G) the SiO_4 tetrahedra are associated
into diorthosilicate [Si_2O_7] groups, and the structures essentially represent different ways
of packing diorthosilicate groups and REE^{3+} cations present in the ratio 1:2. The seventh
structure type (B), which is adopted by the disilicates of Eu, Gd, Tb, Dy, Ho, and Er at
the lowest temperatures investigated, is very unusual in having the SiO_4 tetrahedra in a one-
to-one combination of a single (isolated) tetrahedron and a linear triple tetrahedral group
[Si_3O_{10}] [2, 3]. It was also found that the type B phase was stable at high pressure, and a new
structure type (X) replaced type C at moderate temperature and pressure [4]. In this paper,
we report a La orthosilicate $La_4Si_3O_{12}$ and two new structure types for REE disilicates: type
K for $Nd_2Si_2O_7$ and $Gd_2Si_2O_7$ with a diorthosilicate structure, and type L for $Dy_2Si_2O_7$ with
a structure containing linear triple tetrahedral groups [Si_3O_{10}], but having one in six atoms
distributed with 50% occupancy over two tetrahedral positions.

2. Experimental procedure

Disilicates of Nd, Gd, and Dy were synthesized using the MA6/8 superpress at University of Alberta. All experiments were run in a Pt capsule within a 14M assembly using a $LaCrO_3$ furnace, and monitored with a $W_{95}Re_5$–$W_{74}Re_{26}$ thermocouple. All furnace parts were previously fired at $1000\,°C$ in air. The assembly was stored at $110\,°C$ prior to the experiment. Starting materials were REE^{3+} oxides and amorphous silica (99.999%, Aldrich), which were mixed in stoichiometric proportion and reacted at $950\,°C$ for 2 h in Pt crucibles. The experiments were run at 10 GPa, $1600\,°C$ for 24 h (or $1700\,°C$ for 12 h), and the samples were quenched before the pressure was released.

The rare-earth disilicates were characterized by means of petrographic optical microscopy, powder and single-crystal x-ray diffraction, and electron probe micro-analysis (EPMA). Single-crystal measurements were made at room temperature and pressure with a Nonius Kappa CCD diffractometer and graphite monochromatized Mo $K\alpha$ x-radiation (50 kV, 32 mA, $\lambda = 0.709\,26$ Å). Reflection data were processed with DENZO and SCALEPACK and XDISPLAYF. Structure solution was effected with SHELXTL/PC and all structure refinements were made with LINEX77. Scattering factors for neutral atomic species and values of f' and f'' were taken, respectively, from tables 2.2A and 2.3.1 of the *International Tables for X-ray Crystallography*. Relevant experimental details are given in table 1.

3. Discussion

3.1. La orthosilicate $La_4Si_3O_{12}$

Crystals of a non-stoichiometric La orthosilicate with a defect $Ba_3(PO_4)_2$ structure were grown from a bulk composition of La disilicate. The ideal formula is $La_{2.67}\square_{0.33}(SiO_4)_2$ and the crystal data are $a = 5.463$, $b = 16.382$, $c = 7.429$ Å, $\beta = 115.78°$, space group $C2/m$. The two La positions are 12 coordinated but, interestingly, have inner oxygen shells of high symmetry for La1 (octahedral) and for La2 (tetrahedral). Charge neutrality is maintained by vacancies in La2. Thus high-pressure La orthosilicate is analogous to low-pressure REE orthosilicates with the apatite structure. Ordering of La^{3+} cations and vacancies is indicated by weak superstructure reflections and anomalously high atomic displacement parameters. It appears that La disilicate and melt coexist at high pressure. The $Ba_3(PO_4)_2$ structure is also likely to be adopted by other REE silicates at high pressure.

3.2. Type K structure

The type K structure is a diorthosilicate, and was observed for the disilicates of Sm and Eu as well as Nd and Gd as reported in table 1. The REE^{3+} cations are located at either end of the diorthosilicate group. The X(1) (X = REE^{3+}) cation is in irregular eightfold and the X(2) cation in irregular ninefold coordination with 2.9 Å. The bond valence for X(2) is only 2.82. Hence the X(2) cation is significantly under-bonded, and the mean X(2)–O distance is greater than the mean X(1)–O distance, suggesting that, in the decompressed structure, the nearest-neighbour environment is too big for the REE^{3+} cation, and that the X(2) polyhedra would be more compressible than X(1). The mean REE^{3+}–O bond distances for X(1) and X(2) decrease from $Nd_2Si_2O_7$ to $Gd_2Si_2O_7$ as expected, closely following the trend for variation of effective bond distance at given coordination number through the lanthanide series. For the X(1) position, the individual REE^{3+}–O bond distances decrease in proportion to the decrease in the mean distance, but for X(2) the decrease of individual REE^{3+}–O bond distances is not systematic.

Table 1. Experimental details.

	$Nd_2Si_2O_7$	$Gd_2Si_2O_7$	$Dy_2Si_2O_7$
a (Å)	6.6658(2)	6.5558(4)	6.5971(3)
b (Å)	6.7234(3)	6.6469(3)	6.6504(2)
c (Å)	12.3975(6)	12.2394(6)	18.0582(6)
α (deg)	90	90	83.791(2)
β (deg)	102.147(3)	102.844(3)	88.653(2)
γ (deg)	90	90	88.498(2)
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Formula weight	456.7	482.7	493.18
D_x (g cm^{-3})	5.584	6.166	6.242
Refined parameters	101	101	308
μ (cm^{-1})	193.3	257.3	287.0
R	0.029	0.026	0.0426
R_ω	0.026	0.024	0.0423

In contrast, the dihedral angle in the diorthosilicates of the type K structure is significantly reduced relative to comparable low-pressure structures: 124.4(2)° for $Nd_2Si_2O_7$ and 123.2(3)° for $Gd_2Si_2O_7$. In the low-pressure structures, the dihedral angle varies markedly with the size of the REE^{3+} cation, being about 130–135° in disilicates of the light rare earths and increasing to 180° in the type C phases of $Er_2Si_2O_7$ and $Yb_2Si_2O_7$. It is well known that the energy of an isolated or hydrogen-saturated polymerized silicate group varies with Si–O–Si angle at a given Si–O bond distance, and 140° is the strain-free value for the Si–O–Si bond angle in silicates in general [5]. It is not coincidental that the change in slope of the dihedral bond angle distribution for the low-pressure REE disilicates (near Gd) also occurs at about 140°. Evidently the heavy rare-earth cations (Lu–Er) are too small to interconnect diorthosilicate groups in simple packing models without straightening the dihedral angle. Conversely, the light rare-earth cations (La–Sm) are too large and cause the dihedral angle to be bent to accommodate their large cation polyhedra.

3.3. Type L structure

The type L structure of $Dy_2Si_2O_7$ (table 1) comprises alternating [001] strips of the type B structure and a disordered sheared structure containing structural elements found in the type B structure [3]. The silicate topology of the type B structure of $Dy_2Si_2O_7$ is a one-to-one mixture of linear triple tetrahedral groups $[Si_3O_{10}]$ and single (isolated) tetrahedron $[SiO_4]$. The strip of type B structure in type L is actually visually equivalent to the type B structure of $Dy_2Si_2O_7$ (cf figure 1 of [3]). The geometries of corresponding SiO_4 tetrahedra in type L and B structures are closely comparable, including the characteristic long bond to the bridging oxygen in the one terminal tetrahedron, which is 1.718 Å for Si(5)–O(7) in type L and 1.744 Å for Si(2)–O(4) in type B. Moreover there is striking agreement between the coordination environments of corresponding Dy atoms as viewed in [010] projection.

The [010] strip of sheared structure affords structural continuity with the type B strip very similar to that within the type B structure itself. It also appears to be formed of linear triple tetrahedral groups and isolated SiO_4 tetrahedra interconnected with Dy atoms. However, in the refined type L structure there are two Si positions with half-occupancy (Si(6A) and Si(6B)) which result in all of the SiO_4 tetrahedra being seemingly linked in a single linear six-membered chain of Si(1) corner-linked to Si(6B) face-linked to Si(6A) edge-linked to Si(6A) face-linked to Si(6B) corner-linked to Si(1). The silicate chains are cross-linked by Dy(5) and Dy(6).

Recognizing that the Si(6A) and Si(6B) are disordered and that face-shared SiO_4 tetrahedra are an unstable combination in the pressure range investigated, this six-membered chain is readily reduced to the two ordered combinations of linear triple tetrahedral group and isolated SiO_4 tetrahedra.

Overall, there are two non-equivalent linear triple tetrahedral groups $[Si_3O_{10}]$ and two non-equivalent isolated SiO_4 tetrahedra in the structure of type L $Dy_2Si_2O_7$. The Dy atoms are accommodated in irregular polyhedra: five in eightfold and one in sevenfold coordination to 3.0 Å.

Interestingly, the type L structure does not have high-pressure characteristics, being similar to the type B structure of $Dy_2Si_2O_7$ in respect to coordination of Si and Dy, size of SiO_4 tetrahedra and large cation polyhedra, bridging oxygen (Si–O–Si) bond angles, and packing density. The increase in density calculated with room pressure measurements from type B to L $Dy_2Si_2O_7$ is only 1.4% and significantly less than the increase of 12–14% from type G $Nd_2Si_2O_7$ and $Sm_2Si_2O_7$, type F $Eu_2Si_2O_7$, and type E $Gd_2Si_2O_7$ to the type K structure for these REE disilicates [1]. We therefore propose that the type L structure of $Dy_2Si_2O_7$ formed during quenching the high-pressure experiment from a high-pressure precursor phase which we label $Dy_2Si_2O_7$ type M. This hypothesized high-pressure polymorph of $Dy_2Si_2O_7$ essentially differs from the type L phase only in that Si(6) is now in fivefold trigonal bipyramidal coordination with unit occupancy, and the trigonal bipyramids are edge-shared within a four-membered chain terminated by SiO_4 tetrahedra.

4. Conclusions

At high pressure the stable phase of La silicate is La orthosilicate ($La_4Si_3O_{12}$) with a defect $Ba_3(PO_4)_2$-type structure.

Disilicates of Nd and Gd at 10 GPa and 1600–1700 °C have a new structure type (K), which is a high-pressure modification because the diorthosilicate group is compressed along its long axis by closure of the dihedral angle and the average coordination number of the REE^{3+} cations is increased to 8.

The type L $Dy_2Si_2O_7$ is analogous to the type B structure, having linear triple tetrahedral groups $[Si_3O_{10}]$, but has one in six Si atoms distributed with 50% occupancy over two tetrahedral positions. It appears to have formed from a non-quenchable 10 GPa polymorph which we label type M.

References

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