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Structure of a new form of silicon phosphate (SiP_2O_7) synthesized at high pressures and temperatures

Kurt Leinenweber *, Linda A. Stearns [1], Jacob M. Nite, Péter Németh [2], Thomas L. Groy

Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604, USA

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ABSTRACT

A new high-pressure phase of SiP_2O_7 has been found and its crystal structure solved and refined from a single crystal grown at a condition of 16 GPa and 2000 °C and recovered to ambient conditions. The material is monoclinic, with the space group $P2_1/c$ and lattice parameters $a=4.3042(7)$ Å, $b=7.1505(12)$ Å, $c=6.2897(11)$ Å, $\beta=103.805(2)$. The structure contains SiO_6 octahedra in a corner-sharing arrangement with P_2O_7 dimers, the same structural elements and vertex-sharing present in all the low-pressure forms of SiP_2O_7. However, the network is more condensed: the topology of the packing of SiO_6 octahedra and P_2O_7 dimers (represented by Si and the bridging oxygen that both lie on centers of symmetry) is that of the CsCl structure, with some distortion. The resulting phase is 11.2% to 22.3% denser than the various low-pressure forms of SiP_2O_7. The structural data indicates that the P_2O_7 dimers are linear (P–O–P angle=180°), an unusual feature for phosphates.

1. Introduction

SiP_2O_7 is interesting from a crystal chemical point of view, because it is one of the few oxides stable at ambient pressure that has silicon in six coordination, and is used in a variety of applications such as as a component in fuel cells and as source wafers for *N*-type (phosphorus) diffusion into silicon wafers. SiP_2O_7 has a variety of modifications crystallizing at one atmosphere [1–8] (Table 1). Not all of the modifications are fully characterized in terms of structure; in particular only four of them have had structures reported from powder or single-crystal x-ray diffraction. These structures are all based on SiO_6 octahedral units that share corners with P_2O_7 groups, groups which are in turn composed of two PO_4 tetrahedra sharing one corner. It is likely that the other polymorphs are also composed of such groups.

Additional polymorphism is often found at high pressure for many materials, with the thermodynamic requirement that the stable high pressure phases are denser than the low-pressure ones. In crystalline materials that can be represented by a polyhedral model, this densification can occur through changes in the packing of a polyhedral network, changes in how the polyhedra are linked (by corners, edges or faces) or through increases in the coordination numbers of the atoms. It is interesting to ask the question of what are the densification mechanisms in phosphates. In this study it was undertaken to look for dense high pressure polymorphs of SiP_2O_7. The structural chemistry of phosphates is still relatively less understood than that of silicates, another group that is based on a high-valency tetrahedral cation and in which there is a great deal of polymorphism. In the silicates, the coordination of the silicon eventually changes from four to six. SiP_2O_7 is often noted for having six-coordinated silicon even at ambient pressure. Sixfold coordination of phosphorus, on the other hand, is very rare, although it is expected to occur at some pressure, possibly very high, in any phosphate, and has been seen in two recent examples [9,10]; likewise, seven-coordination of silicon, another option for coordination increase, is only indicated in one example, a monoclinic zirconia-type polymorph from a meteorite [11]. However, it is also possible for the packing to become denser even when the coordinations remain the same. Several recent papers have found this type of behavior, packing changes with pressure, for other tetravalent-cation phosphates [12,13].

In this study, samples of silicon phosphate were subjected to high pressures and temperatures. At a pressure of 8 GPa and temperature of 1000 °C, the low pressure form (SiP_2O_7–AIV) was still stable, but at pressures of 16 GPa to 21 GPa and temperatures ranging from 1300 °C to 2000 °C, a new high pressure form was found. This new form may be designated SiP_2O_7-hp. The structure of this new material has been solved from single-crystal x-ray diffraction and is found to be a unique structure with very dense

* Corresponding author. Fax: +1 480 965 2747.
E-mail address: kurtl@asu.edu (K. Leinenweber).
[1] Current address: The Biodesign Institute, Evolutionary Medicine and Informatics, Arizona State University, Tempe, AZ 85287-5001, USA.
[2] Current address: Chemical Research Center of the Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri út 59-67, Hungary.

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Table 1
List of several previously reported phases of SiP_2O_7, along with the new phase described here.

Name	Space group	Unit cell parameters	Synthesis	Structural description	Density
SiP_2O_7-AI	*Pa*-3	A=22.42 Å	[1]	[1,2]	3.21
SiP_2O_7-AII	*Tetragonal*	A=22.36, c=14.91	[1]	[1]	
SiP_2O_7-AIII	$P2_1/c$	A=4.73 Å, b=6.33 Å, c=14.71 Å, β=90.1	[1,3]	[4]	3.05
SiP_2O_7-AIV	$P2_1/n$	A=4.71 Å, b=11.98 Å, c=7.62 Å, β=91.2	[1,3]	[4–6]	3.11
SiP_2O_7-BI	*Hexagonal*	A=8.18, c=11.85	[1]		
SiP_2O_7 Form I	$P6_3$	A=4.72, c=11.82	[7]	[8]	2.92
SiP_2O_7 Form II	*Same as AIV (acc. to Poojary table)*		[7]		
SiP_2O_7 Form III	*Tetragonal*	A=14.20, c=7.39	[7]		
Form IV	*Cubic* (*same as* AI?)	A=7.47	[7]		
SiP_2O_7-hp (current study)	$P2_1/c$	a=4.30, b=7.15, c=6.29, β=103.8	This study	This study	3.57

Table 2
List of high pressure experiments and run products relevant to this study.

Run Number	Pressure (GPa)	Temperature (°C)	Duration (h)	Capsule	Run products
R-430[a]	8	1000	5.75	Welded Pt	SiP_2O_7-AIV+$SiPO_4$(OH)
R-434[b]	8	1000	50	Welded Pt	SiP_2O_7-AIV+$SiPO_4$(OH) (xtals)+SiO_2 (coesite)
R-439[c]	8	1000	9	Welded Pt	$SiPO_4$(OH)
BB-278[a]	21	1500	2	Graphite	SiP_2O_7 (hp)+SiO_2 (stishovite)
BB-357[a]	17.5	1300	2	Welded Au	SiP_2O_7 (hp)+$SiPO_4$(OH)
BB-695[a]	16.5	1525	1.5	Welded Pt	SiP_2O_7 (hp)+$SiPO_4$(OH)
BB-711[a]	16	2000	1	Welded Pt	SiP_2O_7 (hp, xtals)+melt
T1072[d]	18.8	1500	0.4	BN	SiP_2O_7 (hp)+SiO_2 (stishovite)

[a] Starting material $Si_5O(PO4)_6$ with 4–5% naturally adsorbed H_2O.
[b] Starting material $SiO_2+Si_5O(PO_4)_6$ with 4–5% naturally adsorbed H_2O.
[c] Starting material $Si_5O(PO_4)_6$ with 4–5% naturally adsorbed H_2O plus additional added H_2O for better mineralization.
[d] In-situ experiment in the large-volume press at GSECARS, Argonne National Laboratories.

packing of the SiO_6 and P_2O_7 units. The structural data and the structural features of the new phase are reported here.

2. Experimental methods

X-ray peaks from an unidentified phase were first found in experimental run products recovered from a pressure of 21 GPa and a temperature of 1500 °C. Lower pressures and higher temperatures were then attempted in order to isolate single crystals of the phase. The record of all the high pressure experiments in the system SiO_2–P_2O_5–H_2O for this study and the study of Stearns et al. [14] are shown in Table 2. These experiments used a multi-anvil high pressure device first introduced by Kawai and Endo [15]; our specific modification of the design was introduced by Walker et al. [16], and details of the multi-anvil cell assemblies used in this study are described in Leinenweber et al. [17]; we used the 14/8, 10/5 and 8/3 assemblies from that paper. The phosphorus source for all experiments was $Si_5O(PO_4)_6$ with a certain amount of physisorbed water, the same material used in [14]. The water content (4–5 wt%) was determined by a weight loss test on the starting material weighed, heated to 800 °C in a Pt crucible, recovered, and re-weighed. For the single crystal synthesis attempts, a welded platinum capsule was used, and the naturally physisorbed water in the starting material acted as a mineralizer for the growth of single crystals. Despite the presence of water in the charge, crystals large enough for single-crystal structure analysis were not obtained in runs at 1300 °C and 1525 °C; finally, a run at 16 GPa and 2000 °C produced crystals, coexisting with a melt, that were suitable for single-crystal x-ray diffraction.

The sample was checked by electron probe microanalysis to verify its stoichiometry and purity. Within the sealed platinum capsule, no elements other than Si, P and O were visible in the EDS spectra of the crystals or the associated melt. Using wavelength dispersive analysis on all three elements, the composition of the crystals was close to the ideal stoichiometry SiP_2O_7. Also, a probe total close to 100% on an oxide basis indicated that hydrogen (from the H_2O mineralizer) did not occupy the phase in significant quantities. The probe results for three points in the sample were: Si 11.1 ± 0.4%, P 19.1 ± 0.4%, O 69.84 ± 0.06%, compared to the theoretical values of 10 atom percent for Si, 20 atom percent for P, and 70 atom percent for O.

The single crystal data collection was performed on a Bruker SMART APEX single crystal diffractometer. Details of the data collection and refinement are shown in Table 3.

Once the structure of the new phase was determined, full powder diffraction experiments combined with Rietveld refinement using GSAS were performed on the six experiments R-430 to BB-695 in Table 2, in order to ascertain the phase assemblages in each run and to check for consistency with the single-crystal results. The resulting phase assemblages are listed in Table 2, and the powder patterns for the new phase were verified to be consistent with the single-crystal structure. Because of the desire to preserve the high-quality single crystals, the sample from BB-711 was not ground up for powder diffraction, but the microprobe and single-crystal data are indicative of a sample with a single phase of SiP_2O_7 plus a melt and it is so indicated in the run table.

3. Results and discussion

The refined structure parameters for the new high pressure form of SiP_2O_7 are shown in Table 4, and the aniosotropic thermal parameters are listed in Table 5. First-neighbor interatomic distances are given in Table 6, and bond angles are listed in Table 7. This structure, shown in Fig. 1, appears to be unique. It has the same basic structural units as the low-pressure phases: SiO_6 groups (octahedra) and P_2O_7 groups (dimers of two tetrahedra