x-Ge(HP04)2·H2O has been hydrothermally prepared and its thermal behavior has been studied by DTA and thermogravimetry. Three pyrophosphates can be obtained on heating at high temperature. x-GeP2O7 crystallizes in a cubic superstructure related to that of the pristine material. x-GeP2O7 transforms to β-GeP2O7 above 950°C and this yields γ-GeP2O7 above 1000°C. However, γ-GeP2O7 could not be prepared as a single phase at high temperature and ambient pressure because P2O5 is partly released leading to a contamination with Ge2O3(P2O7)n, which is the final thermal decomposition product. γ-GeP2O7 has been synthesized as a single phase by heating x-GeP2O7 at 20 kbar and 1000°C. γ-GeP2O7, previously reported as cubic, is monoclinic with a space group C2/c or lower. γ-GeP2O7, with a simple stoichiometry, crystallizes in a very large unit cell with at least 26 Ge, 54 P, and 190 O crystallographically independent atoms. This complex superstructure is caused by the ordered pattern of Ge, P, and O atoms. These high B-values indicate either high thermal expansion materials; superstructure; powder diffraction.

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Key Words: low thermal expansion materials; superstructure; powder diffraction.

INTRODUCTION

There is a recent interest in MIVX7O7 (M = Si, Ge, Sn, Pb, Ti, Zr, Hf, Mo, W, Re, Ce, Th, U; X = P, V, As) compounds and their solid solutions because they may present isotropic negative thermal expansion for some compositions in the appropriate temperature intervals (1). There is also general agreement in that MIVP2O7 crystallizes in a cubic structure with Z = 4, a ~ 8 Å, that was solved (2) for M = Zr from powder X-ray diffraction data in space group Pa3. Studying Weissenberg pictures of a GeP2O7 single crystal (3), a 3 × 3 × 3, Z = 108, supercell was found that was also cubic within experimental error of that time. A careful study of the powder patterns for M = Si, Sn, Pb, Ti, Zr, Hf, and U compounds also showed similar supercells (3, 4); these supercells were confirmed for M = Ge, Zr, and U by indexing of Guinier-Hägg photographs taken with strictly monochromatic CuKα1 radiation (4).

A landmark in the study of these compounds was the 3 × 3 × 3 superstructure determination of SiP2O7 from single crystal data [a = 22.418 Å, Pa3] (5). Similar cubic superstructures have recently been described from Rietveld refinements for MP2O7 (M = Zr, (6) Ti (7)) and from single crystal data for ZrV2O7 (8). However, we are aware that the situation may be more complex as synchrotron X-ray single crystal data for MoP2O7 showed 3 × 3 × 3 superstructure peaks that were indexed in a metrically cubic lattice but with lower symmetry, probably orthorhombic (9). Unfortunately, this huge complex structure could not be solved. The description of the MP2O7 structure in the cubic subcell, a ~ 8 Å, requires all the pyrophosphate, P–O–P, groups to be linear which it is energetically very unfavorable. In the cubic superstructure description, most (89%) P–O–P bonds are bent to angles ranging between 140° and 150°, while the remaining 11% P–O–P are described as linear, due to both P and the bridging oxygen atoms are lying on a threefold axis of rotation. The thermal vibration parameters of the bridging oxygens of linear P–O–P groups have much higher values than those of the remaining bent bridging oxygens. These high B-values indicate either high thermal anisotropic vibration or positional disorder or even a wrong description of the symmetry of the structure. The developing of a cubic 3 × 3 × 3 superstructure partially relaxes the structure but there remains an internal stress as the linear P–O–P groups are not stable. It is interesting to remark that the metrically cubic orthorhombic diffraction pattern observed (9) for MoP2O7 would be compatible with a...
A very stable compound in the GeO$_2$–P$_2$O$_5$ system (10) at high temperature is Ge$_3$O(PO$_4$)$_6$. Its crystal structure was determined from single-crystal data (11). The thermal decomposition pathway for \( \alpha \)-Ge(HPPO$_4$)$_2$·H$_2$O has been reported (12). \( \alpha \)-Ge(HPPO$_4$)$_2$·H$_2$O changes to Ge(HPPO$_4$)$_2$ above 230°C and subsequently to \( \gamma \)-GeP$_2$O$_7$ at 480°C. \( \alpha \)-GeP$_2$O$_7$ transforms to the \( \beta \) polymorph on heating above 930°C and \( \beta \)-GeP$_2$O$_7$ changes to \( \gamma \)-GeP$_2$O$_7$ above 1020°C. Finally, \( \gamma \)-GeP$_2$O$_7$ decomposes near to 1160°C, releasing P$_2$O$_5$. \( \alpha \)-GeP$_2$O$_7$ has very low crystallinity and even its unit cell is not known. \( \beta \)-GeP$_2$O$_7$ is triclinic \( (V = 232.8\,\text{Å}^3, \rho_{\text{cryst}} = 3.52\,\text{g/cc}) \) and the structure was solved from single-crystal data (13). \( \gamma \)-GeP$_2$O$_7$ was reported to be cubic with the early mentioned \( 3 \times 3 \times 3 \) superstructure (3, 4, 10). \( \gamma \)-GeP$_2$O$_7$ has slightly higher density, \( (V = 11946\,\text{Å}^3, \rho_{\text{cryst}} = 3.70\,\text{g/cc}) \) and the atomic positional parameters have not been reported.

Our main interest in studying \( \gamma \)-GeP$_2$O$_7$ is to characterize its thermal behavior and to compare it with those shown by cubic MP$_2$O$_7$. Hence, X-ray powder diffraction and \( ^{31}\text{P} \) MAS-NMR spectroscopy have been used to characterize the crystal structure and X-ray powder thermomicroscopy has been applied to determine the thermal expansion. Strikingly, we will show that the previously reported ‘cubic’ \( \gamma \)-GeP$_2$O$_7$ \( (a \sim 22.86\,\text{Å}) \) displays the \( 3 \times 3 \times 3 \) superstructure but it has much lower symmetry being monoclinic or triclinic.

**EXPERIMENTAL**

**Syntheses**

\( \alpha \)-Ge(HPPO$_4$)$_2$·H$_2$O, which will be hereafter referred to as \( \alpha \)-GeP, was prepared hydrothermally in a Teflon-lined Parr autoclave with a free volume of 45 mL. \( \alpha \)-GeP was obtained by heating a mixture of 0.8472 g GeO$_2$, 18.71 g H$_3$PO$_4$ (85% w/w), and 5.83 g of H$_2$O at 125°C for 7 days. The overall reactive molar ratios, Ge:P:H$_2$O, were 1:20:60. The resulting white solid was centrifuged, washed with water several times, and finally washed with acetone. \( \gamma \)-GeP$_2$O$_7$ was synthesized by heating \( \alpha \)-GeP at 800°C for 6 h.

\( \gamma \)-GeP$_2$O$_7$ was prepared as single phase at high temperature and pressure by using a piston-cylinder press (Rockland Research Co.). To do so, protocrystalline \( \gamma \)-GeP$_2$O$_7$ was put into a gold capsule, sealed, and placed in a graphite heater. The pressure was set to 20 kbar and the temperature was held at 1000°C for 1 h. Then, the sample was quenched to room temperature and finally, pressure was released. \( \gamma \)-GeP$_2$O$_7$ was also prepared at ambient pressure by heating \( \alpha \)-GeP at 1080°C for 1 day but it contains impurity phases. A purer \( \gamma \)-GeP$_2$O$_7$ sample was obtained at ambient pressure as follows. A slurry mixture of GeO$_2$ (1 g) and phosphoric acid (Aldrich 3 g) was heated at 500°C for 2.5 h. The resulting solid was cooled to room temperature, washed with water, dried, and pelletized. The pellet underwent the thermal treatment indicated in Scheme 1. After this treatment, the sample was examined by X-rays and was found to consist of a major phase, \( \gamma \)-GeP$_2$O$_7$, and a minor one, Ge$_3$O(PO$_4$)$_6$. Then, the mixture was pelletized again and the upper surface was covered with a drop of polyphosphoric acid. The same thermal treatment was applied which yielded \( \gamma \)-GeP$_2$O$_7$ \( (~95\%) \).

\( \beta \)-GeP$_2$O$_7$ was obtained as a single phase. To do so, a pellet of \( \alpha \)-GeP$_2$O$_7$ was covered with a drop of polyphosphoric acid to avoid the loss of P$_2$O$_5$. The sample underwent the thermal treatment showed in Scheme 1 but at lower temperature (the maximum temperature was 980°C instead of 1080°C). The quenching was carried out in water which was used to wash the excess of phosphorus. Ge$_3$O(PO$_4$)$_6$ was obtained as a single phase by heating \( \alpha \)-GeP at 1200°C for 1/2 day.

**Techniques**

**Room temperature X-ray powder diffraction.** X-ray powder diffraction patterns for all samples were collected on a Siemens D-5000, automated diffractometer using graphite-monochromated CuK$_{\alpha 1}$ radiation for phase identification and for monitoring of the chemical reactions. The \( 3 \times 3 \times 3 \) superstructure of \( \gamma \)-GeP$_2$O$_7$ was studied using strictly monochromatic CuK$_{\alpha 1}$ radiation, \( \lambda = 1.5405981\,\text{Å} \), obtained from a Ge (111) primary monochromator, in an Philips X'PERT diffractometer. The pattern was scanned over the angular range, 10–120° (20), with a step size of 0.02° and counting for 25 s per step.

**Variable temperature X-ray powder diffraction.** The powder thermomicroscopic studies of \( \alpha \)-GeP and \( \gamma \)-GeP$_2$O$_7$ were carried out in air on a Siemens D-5000 with
a second goniometer permanently equipped with an HTK10 heating chamber. The samples were packed over the Pt strip that acts both as the heating system and the holder. The patterns were scanned over the angular range, 6°–38° (2θ), with a step size of 0.03° and counting for 3 and 10 s per step for α-GeP and γ-GeP2O7, respectively. The appropriate heating temperatures were selected by using the Diffract AT software. A delay of 10 min was applied before collection of any pattern to allow for transformations to take place.

31P MAS-NMR spectra. 31P MAS-NMR spectra were obtained at room temperature in a MSL 400 Bruker spectrometer at 161.96 MHz, γ- and β-GeP2O7 were spun at \( \sim 10 \) kHz and Ge5O(PO4)6 at \( \sim 4 \) kHz and the spectra taken after \( \pi/2 \) pulse irradiation (4 μs). A time interval of 2–90 s between successive scans was chosen and the number of scans was \( \sim 20 \). The 31P chemical shifts are given relative to 85% aq H3PO4.

RESULTS AND DISCUSSION

The thermal behavior of α-GeP, which belongs to the α-Zn(HPO4)2·H2O type structure (14), was studied by DTA-TG and powder thermodiffractometry. The DTA-TG curves agree with those reported early but we detect four endotherms in the water loss region centered at 310, 410, 580, and 650°C, instead of the three endotherms observed by Chernorukov et al. (12). Figure 1 shows the powder thermodiffractometry of α-GeP at selected temperatures, which was carried out under He flow. α-Ge(HPO4)2·H2O is stable up to 250°C and above that temperature loses the hydration water to yield Ge(HPO4)3. This compound is stable up to 500°C. However, Ge(HPO4)3 undergoes a polymorphic transformation at 450°C which is evident in the thermodiffractometric study as new diffraction peaks appear in the 450°C pattern. Above 550°C, the hydrogenophosphate groups condense to yield α-GeP2O7 which is stable up to 900°C. However, its powder diffraction pattern changes slightly with temperature being quasi-amorphous at 650°C and with sharper peaks (larger long-range order) at 950°C. The relationship in the position of some diffraction peaks with those of the parent layered compound suggest that the structures are similar. It has also been suggested that a topotactic dehydration of M(HPO4)2·H2O (M = Ti, Zr) yields protocrystalline layered MP2O7 at low temperatures, \( \sim 600°C \) (15). The peaks due to β-GeP2O7 start to develop in the pattern collected at 1000°C. At 1050°C, the powder pattern contains the peaks characteristic of β-GeP2O7 and γ-GeP2O7. At 1100°C, the main peaks of Ge5O(PO4)6 begin to appear which means that the sample is starting to release P2O5. Ge5O(PO4)6 is isostructural with Si2O(PO4)6 that can be prepared at low temperatures and it is stable up to 1000°C (16).

The powder pattern of α-GeP heated at 980°C in a crucible for 6 h matches that of PDF 82-0829, which corresponds to β-GeP2O7, although the main peak of γ-GeP2O7 was also evident in the pattern. β-GeP2O7, transforms on heating to γ-GeP2O7, although before this transformation is finished, Ge5O(PO4)6 starts to appear. The powder pattern of α-GeP heated at 1200°C in a crucible matches that of PDF 71-0679 [Ge5O(PO4)6]. This final thermal treatment

FIG. 1. X-ray powder patterns for α-Ge(HPO4)2·H2O with temperature (°C) in the z axis. Main peaks for β-GeP2O7 (○), γ-GeP2O7 (*), and Ge5O(PO4)6 (©) are labeled.
was not carried out in the HTK10 heating chamber to avoid possible P$_2$O$_5$ contamination. Prolonged heating of any GeP$_2$O$_7$ sample above 1200°C yields Ge$_5$O(PO$_4$)$_6$. The preparation of γ-GeP$_2$O$_7$ is more difficult than that of many other “cubic” $M^{IV}$P$_2$O$_7$ compounds because this phase is not stable at high temperatures. All attempts to prepare it as a single phase at ambient pressure and different temperatures were unsuccessful as it was contaminated with the low-temperature phase, β-GeP$_2$O$_7$, or with the high-temperature thermal decomposition compound, Ge$_5$O(PO$_4$)$_6$.

As γ-GeP$_2$O$_7$ has higher density than the other well characterized polymorph, β-GeP$_2$O$_7$, high-pressure synthesis appeared suitable to prepare it; moreover, the high pressure also avoids the release of P$_2$O$_5$. The precursor for this procedure was α-GeP$_2$O$_7$. γ-GeP$_2$O$_7$ was reproducibly prepared as a crystalline single phase with tiny, well-faceted single crystals, by heating under pressure. These crystals did not extinguish light as a whole in the polarizing microscope under crossed polaroids, but rather they seemed to contain many small domains, as well as other defects. Attempts to collect a good data set with a CCD-equipped single crystal diffractometer were unsuccessful, as the diffraction spots were not indexable in terms of a unique set of basis vectors. This was likely due to the poor quality of the crystals. γ-GeP$_2$O$_7$ could also be prepared at ambient pressure as indicated above, but it contains impurity phases.

The peaks in the CuK$_{\alpha1,2}$ powder pattern of γ-GeP$_2$O$_7$ have shoulders which cannot be justified with the previously reported cubic $3 \times 3 \times 3$ unit cell. To avoid the errors and correlations arising from the K$_{\alpha1,2}$ doublets, a powder pattern with strictly monochromatic CuK$_{\alpha1}$ radiation was recorded (Fig. 2). The inset to that figure shows the splitting of the (111) substructure reflection, which indicates that the symmetry is monoclinic (or lower). Other substructure peaks are also split. Many small intensity diffraction peaks are also visible that can only be indexed with the $3 \times 3 \times 3$

![FIG. 2. Selected region of Rietveld plot (le Bail’s fit) of the CuK$_{\alpha1}$ powder pattern for γ-GeP$_2$O$_7$. Tics show the allowed Bragg peaks for the monoclinic $\sim 7.6 \times 7.6 \times 7.6$ Å subcell (top) and the $\sim 23 \times 23 \times 23$ Å supercell (bottom). The splitting of the (111) substructure peak is shown in the inset.](image-url)
FIG. 3. $^{31}$P MAS-NMR spectra for $\gamma$-GeP$_2$O$_7$ (top), $\beta$-GeP$_2$O$_7$ (center), and Ge$_5$O(PO$_4$)$_6$ (bottom). ssb denotes spinning side band associated with the rotation of the sample.

supercell. Hence, $\gamma$-GeP$_2$O$_7$ crystallizes in a monoclinic 3 x 3 x 3 cell. Smaller related cells were tested but they did not index all superstructure peaks. The pattern was fitted by the Rietveld method (17) using the GSAS suite of programs (18) but without structural model (Le Bail’s fit (19)). The resulting refinement was very good: $a = 22.8647(4)$ Å, $b = 22.8783(4)$ Å, $c = 22.9429(4)$ Å, $\beta = 90.328(1)$$^\circ$, $V = 12001.3(4)$ Å$^3$, $P2_1/c$, with $R_{wp} = 11.5\%$. No attempts to solve or refine this structure from powder diffraction data were carried out. It should be noted that the description of the structure in $P2_1/c$ requires the following crystallographically independent atoms: 28 Ge (two in special positions), 54 P, and 190 O (two in special positions). This structure is too complex to be studied by powder diffraction methods. Single-crystal data are needed but, so far, we have been unable to grow crystals good enough to yield meaningful data.

The monoclinic 3 x 3 x 3 cell of $\gamma$-GeP$_2$O$_7$ is not the result of the high-pressure synthesis. The ambient pressure preparations of $\gamma$-GeP$_2$O$_7$ also showed the splitting in the patterns. The low symmetry is confirmed by the MAS-NMR spectrum shown in Fig. 3. NMR spectra were collected for both types of preparations, ambient and high-pressure, and they are quite similar. Here, we report the spectrum from single-phase $\gamma$-GeP$_2$O$_7$. This low symmetry is in agreement with previous observations (9) for MoP$_2$O$_7$ and it may explain the problems encountered when trying to describe the structure of some MP$_2$O$_7$ compounds such as $M = \text{Zr}$ (6). In this last case, the reported structure has many unrealistic bond distances, angles, and temperature factors. The structural relationship of the pseudo-cubic MP$_2$O$_7$ ($M = \text{Ge, Sn, Pb}$) and ($M = \text{Ti, Zr, Hf}$) families studied by with CuK$\alpha$ and neutron powder diffraction and $^{31}$P MAS-NMR spectroscopy will be the subject of a forthcoming paper.

In Fig. 3, the $^{31}$P MAS-NMR spectra for Ge$_5$O(PO$_4$)$_6$, $\beta$-GeP$_2$O$_7$, and $\gamma$-GeP$_2$O$_7$ are shown. The profile for Ge$_5$O(PO$_4$)$_6$ contains a single resonance at $-32.9$ ppm, which is in agreement with the structure as there is a unique crystallographically independent phosphate group. The spectrum for $\beta$-GeP$_2$O$_7$ contains two resonances at $-31.3$ and $-36.9$ ppm, which also agrees with the structure as there is a single crystallographically independent pyrophosphate group with two different PO$_4$ tetrahedra. It is worth emphasizing that these values are displaced from the values observed for other pyrophosphate groups in MP$_2$O$_7$ (1, 7). For $\beta$-GeP$_2$O$_7$, the two detected NMR lines are shifted toward the values detected in Ge-orthophosphates ($-32/45$ ppm). This shift may be due to the small P–O–P value of the bridging angle which is 126.5$^\circ$. For $\gamma$-GeP$_2$O$_7$, the
NMR spectrum displays a considerable complexity and NMR lines are spread over the $-42/-62$ ppm range. Many peaks, more than 35, were observed in the profile which indicates the existence of many crystallographically independent phosphorus atoms. More unresolved components can be hidden in this spectrum. This observation is in agreement with the low symmetry measured in the diffraction study.

Three possible monoclinic space groups can be obtained from $Pa\bar{3}$ by removing symmetry elements: $P2_1/c$, $P2_1$, and $Pc$. As noted in Fig. 4 of Ref. (1), the number of independent pyrophosphate groups are 54, 108, and 108, respectively. In $P2_1$ and $Pc$ space groups, no linear $P-O-P$ groups are required but two are needed in $P2_1/c$. Hence, although our powder diffraction data and $^{31}$P MAS-NMR spectrum for $\gamma$-GeP$_2$O$_7$ are compatible with $P2_1/c$, we cannot rule out a lower symmetry. It is remarkable that a compound with such simple stoichiometry, GeP$_2$O$_7$, contains at least 54, maybe even 108, different PO$_4$ groups in its unit cell. Such structure gives very complex X-ray diffraction and $^{31}$P MAS-NMR profiles.

The thermal expansion behavior of $\gamma$-GeP$_2$O$_7$ has been characterized by CuK$\alpha_{1,2}$ laboratory thermodiffractometry. The compounds remains monoclinic with the $3 \times 3 \times 3$ superstructure up to the highest investigated temperature, 750°C. Substructure peaks are split and some diffraction peaks are displaced more than others, on heating, as expected in a noncubic material. However, it should be noted that determining the thermal evolution of $\gamma$-GeP$_2$O$_7$ quantitatively is not straightforward. The unit cell is very complex with many overlapped peaks that led to divergence in the Le Bail’s fits because there are many correlations. The sample alignment is not ensured as the height of the sample layer cannot be properly controlled. This results in a zero shift-

![FIG. 4.](image-url) Thermal expansion for $\gamma$-GeP$_2$O$_7$ expressed as the variation of the volume of the monoclinic subcell with temperature, obtained from CuK$\alpha_{1,2}$ powder diffraction data.

**ACKNOWLEDGMENTS**

This work was supported by the research grants MAT97-326-C4-4 and MAT98-1053-004-05 of the CICYT.

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