

ARTICLES

Investigation of hardness in tetrahedrally bonded nonmolecular CO₂ solids by density-functional theory

Jianjun Dong,* John K. Tomfohr, and Otto F. Sankey

Department of Physics and Astronomy and Materials Research Center, Arizona State University, Tempe, Arizona 85287-1504

Kurt Leinenweber, Maddury Somayazulu, and Paul F. McMillan

Department of Chemistry and Materials Research Center, Arizona State University, Tempe, Arizona 85287-1704

(Received 6 June 2000)

Stability and compressibility of several nonmolecular (polymeric) CO₂ solids in structures analogous to those of SiO₂ have been investigated with *ab initio* density-functional theory. Contrary to the recent experimental reports of a “superhard” high-pressure tridymite form of CO₂, we find that metastable tetrahedrally bonded CO₂ polymorphs, such as tridymite, cristobalite, and quartz, are relatively compressible, with bulk moduli K of only 1/2 to 1/3 of the reported experimental value. In addition, theory finds that the experimentally reported lattice parameters are not stable for CO₂ $P2_12_12_1$ tridymite. Finally, none of the calculated x-ray spectra of the fully relaxed structures of CO₂ polymorphs obtained from theory agrees with the experiments. The significant discrepancy between experiments and density-functional theory suggests that further studies on nonmolecular CO₂ solids are necessary, and that the assumptions that density-functional theory can describe these materials correctly, or that the framework of the new nonmolecular CO₂ solids contains only CO₄ tetrahedra, must be re-examined.

Interesting materials with unconventional structures and properties can be recovered using high-pressure and high-temperature synthesis routes.¹ One example is the recent success of polymerization of carbon dioxide (CO₂).² Carbon and oxygen are known to form strong C=O double bonds, and several *molecular* crystal phases of CO₂ exist over a wide range of pressures and temperatures. A new CO₂ phase, which is significantly different from all the known molecular crystal phases, was recently discovered by Iota *et al.* at high pressure and high temperature, and this phase is nearly recoverable (down to 1 GPa at room temperature). Iota *et al.* suggested that the new phase is a SiO₂-like phase (such as α -quartz or coesite) based on their Raman results. Very recently, this group reported a synchrotron study, and concluded that the new CO₂ phase has the $P2_12_12_1$ tridymite structure.³ They find that the new CO₂ solid has a very low compressibility. The measured bulk modulus K is 365 GPa, close to that of the second hardest material, cubic BN (369 GPa).

“Superhard” materials are highly important to the materials science and engineering communities. Since the hardness of a material is closely related to its compressibility,^{4–6} and the compressibility scales inversely with bond length, solids that contain small elements (such as B, C, N, and O) are regarded as prime candidates for hard materials. Until recently, C-O based solids have not been considered as candidates. However, the C-O bond is short and its ionicity is comparable to that of B-N, suggesting that polymeric CO₂ solids may offer new opportunities for superhard materials. On the other hand, if the new CO₂ solids have SiO₂-analog frameworks (e.g., quartz, cristobalite, and tridymite), the

compressibility is likely to be greatly increased (i.e., hardness decreased) because volume reduction can occur through intertetrahedron (CO₄) rotation instead of bond compression.

Nonmolecular CO₂ solids have recently been theoretically studied.^{3,7–9} Serra *et al.* investigated the phase transition from the usual molecular phase of CO₂ to a nonmolecular (polymeric) α -quartz phase in the range of 35–60 GPa.⁷ Our previous studies were focused on the energetics and Raman spectra of polymeric structures of CO₂ solids.^{8,9} Our results show that the newly synthesized CO₂ solid is unlikely to have a α -quartz-like structure because of the far more rigid intertetrahedron rotational interactions of CO₂ polymeric solids compared to those of SiO₂. This finding is important to the issue of hardness. Our studies find that the energetically favorable framework polymeric CO₂ solid is based on a SiO₂ β -cristobalite analog, with an intertetrahedron C-O-C bond angle of about 125°. Most recently, Yoo *et al.*³ reported a constant pressure molecular-dynamics simulation study jointly with the x-ray report. Their theory confirmed that the molecular phase should transform under pressure to a $P2_12_12_1$ tridymite phase at around 40 GPa. However, no calculated bulk modulus and/or theoretical structural parameters were provided.

In this report, we theoretically study several possible tridymite structures, and compare their structural stability and compressibility with other CO₂ polymeric phases in SiO₂-analogous polymorphs. We find that tridymite, and all the CO₂ structures derived from SiO₂-analogs that we have studied, have significantly smaller bulk moduli than the reported experimental value of 365 GPa. None of the CO₂ tridymite phases has a binding energy lower than

β -cristobalite ($I\bar{4}2d$). Under pressure, the enthalpy of the cristobalite phases (α , β , γ) becomes even more favorable compared to tridymite. Finally, our theoretical $P2_12_12_1$ tridymite lattice parameters have some major discrepancies with the lattice parameters reported in the experiments. The discrepancy between the theory and experiment causes concern, and raises some doubts as to whether any fully tetrahedrally bonded metastable polymeric CO₂ solids can be superhard.

Our calculations are based on density-functional theory (DFT) in the local-density approximation (LDA) implemented with a plane-wave basis and ultrasoft pseudopotentials.¹⁰ Tests using a generalized gradient approximation (GGA) was found to have little effect on the relative energetics of the nonmolecular phases of CO₂.⁹ All the structures we consider are found to be insulators, allowing simple k -point Brillouin-zone sampling techniques to be used. A $4 \times 4 \times 4$ Monkhorst-Pack grid was always found to be adequate. Standard energy cutoffs for a plane-wave basis were used throughout this work (i.e., for β -cristobalite an energy cutoff of 29 Ryd was used). The implementation we adopted has been tested extensively, including studies of SiO₂ polymorphs.¹¹ We can compare our results for quartz and a defective chalcopyrite phase which were computed by Serra *et al.*,⁷ and our results agree with theirs. This consistency between different implementations of DFT is reassuring.

Tridymite is a class of low-pressure and high-temperature SiO₂ polymorphs including several closely related phases, such as $HP(P6_3/mmc)$, $LHP(P6_322)$, $OC(C222_1)$, $OP(P2_12_12_1)$, $MX-1a(Cc)$, and others.^{12,13} The $P2_12_12_1$ structure reported by Yoo *et al.* does not exist in SiO₂,¹⁴ but can be understood as a distorted $OC(C222_1)$ tridymite, where $P2_12_12_1$ is a subgroup of $C222_1$. To study CO₂ tridymite, we first adopt the experimental lattice parameters ($a = 6.216$ Å, $b = 4.352$ Å, and $c = 6.066$ Å, at 48 GPa), but internal coordinates are initially assigned based on the $OC(C222_1)$ structure. We relax the internal coordinates with these fixed unit-cell lattice parameters until an energy minimum is reached. We refer to this internally optimized structure based on experimental structure as S_E . However, with the experimental lattice parameters, the S_E structure contains significantly distorted CO₄ tetrahedra. The variation of the O-C-O bond angle variation is 34°, which produces enormous strain.¹⁵

We next allow the S_E $P2_12_12_1$ -structure to optimize its external lattice parameters (assuming constant volume), the lattice parameters change to $a = 6.7696$ Å, $b = 3.7746$ Å, and $c = 6.4219$ Å. The internal structural parameters are simultaneously optimized. We refer to this resulting structure as S_{Opt} . The energy lowering is 0.637 eV/CO₂, which is an enormous energy reduction, in fact it is larger than the energy difference between the α -quartz and β -cristobalite phases. Upon optimization of the external coordinates, the distortion of the CO₄ tetrahedra is alleviated. The different C-O bond lengths vary over 0.032 Å and O-C-O ‘‘tetrahedral angles’’ vary over 18°. The intertetrahedron bond angles are between 117° and 126°.¹⁶

Both the S_E and S_{Opt} are tridymite $P2_12_12_1$ structures which can be tested against the observed x-ray diffraction

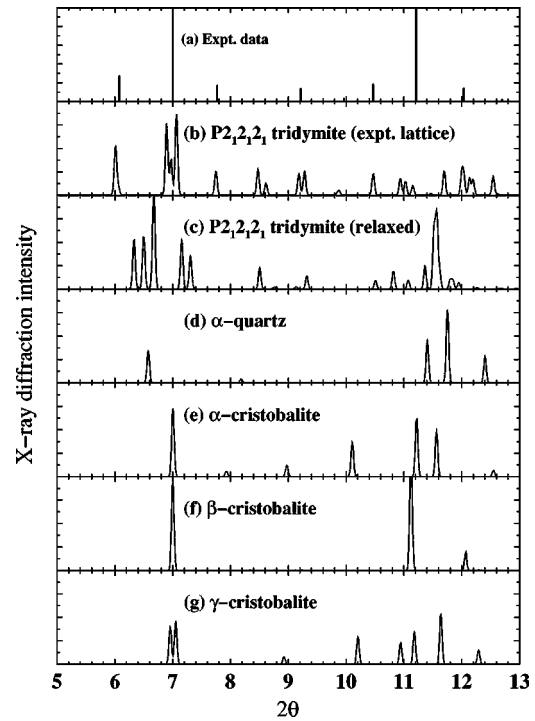


FIG. 1. The calculated x-ray spectra at 48 GPa of different polymeric CO₂ phases. (a) A stick model without widths of the experimental spectrum (Ref. 3). (b) $P2_12_12_1$ -tridymite, structure S_E , using the experimental lattice parameters (Ref. 3), (c) fully LDA relaxed $P2_12_12_1$ -tridymite, structure S_{Opt} , (d) α -quartz, (e) α -cristobalite, (f) β -cristobalite, and (g) γ -cristobalite (Ref. 19).

pattern.³ A schematic x-ray stick spectrum (with no widths) of the experiment³ is shown in Fig. 1(a). The calculated x-ray pattern¹⁷ of the S_E -structure, labeled ‘‘ $P2_12_12_1$ -expt’’ in Fig. 1(b), bears similarity to the observed experimental pattern. The theoretical x-ray pattern we obtain in Fig. 1(b) using the experimental lattice parameters, however, is different than the calculated $P2_12_12_1$ pattern determined by Yoo *et al.*³ (see their Fig. 2). The internal coordinates of Yoo

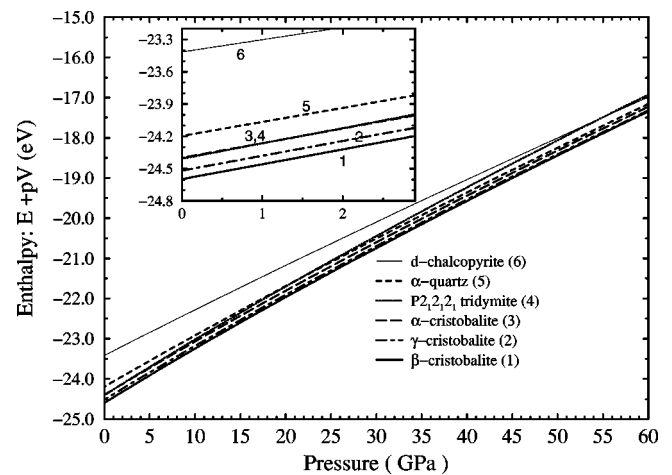


FIG. 2. The enthalpies of several lower-energy, metastable CO₂ phases as a function of pressure. The tetragonal β -cristobalite structure is the minimum enthalpy structure at all pressures shown. The tridymite phase becomes less favorable at high pressure. The inset is a blowup of the curves at low pressure.

TABLE I. The parameters of the Birch-Murnaghan equation for state of several CO₂ tridymite phases obtained from a fit of the LDA energy vs volume curve. The second order EOS contains four parameters: V_0 (minimum-energy/zero pressure volume in the solid structure), E_0 (binding energy relative to separated atoms at V_0), K_0 (bulk modulus at zero pressure), and $K' = dK/dP$ (volume derivative of the bulk modulus). For comparison, previously reported results of three metastable phases (Ref. 9) (α -quartz, α -cristobalite, and β -quartz) are also listed. The numbers given in parentheses are the relative energy and percentage change in volume with respect to the β -cristobalite structure, respectively. The percentage ratio of calculated bulk moduli to the experimental bulk modulus K_0^{exp} (365 GPa) (Ref. 3) is also given in parentheses.

Phase	Symmetry	E_0 (eV/CO ₂)	V_0 (Å ³ /CO ₂)	K_0 (GPa)	K'
<i>HP</i> tridymite	$P6_3/mmc$	-22.77 (+1.83)	30.83 (+38.%)	233.5 (64%)	4.0
<i>LHP</i> tridymite	$P6_322$	-23.87 (+0.73)	25.66 (+15.%)	192.1 (53%)	4.3
<i>OC</i> tridymite	$C222_1$	-24.01 (+0.59)	23.97 (+7.5%)	141.9 (39%)	3.6
<i>OP</i> tridymite	$P2_12_12_1$	-24.28 (+0.32)	23.85 (+7.0%)	134.1 (37%)	3.5
<i>MX-1a</i> tridymite	Cc	-24.33 (+0.27)	23.08 (+3.1%)	158.1 (43%)	4.2
$P2_12_12_1$ tridymite	$P2_12_12_1$	-24.41 (+0.19)	22.91 (+2.7%)	151.5 (42%)	3.9
<i>d</i> -chalcopyrite	$I\bar{4}2d$	-23.42 (+1.18)	18.40 (-17.%)	347.2 (95%)	4.2
α -quartz	$P3_221$	-24.20 (+0.40)	20.93 (-6.3%)	205.7 (56%)	3.9
α -cristobalite	$P4_12_12$	-24.40 (+0.20)	22.01 (-1.3%)	142.8 (39%)	4.2
γ -cristobalite	$Pna2_1$	-24.52 (+0.08)	22.12 (-0.8%)	147.2 (40%)	3.8
β -cristobalite	$I\bar{4}2d$	-24.60 (+0.00)	22.30 (0.00%)	149.1 (41%)	3.6

et al., which are not provided in their paper, are determined by a fitting procedure to the experimental data, while ours were obtained by a density-functional energy optimization. The patterns show significant differences which reflects the differences of the internal structures obtained by the two methods. The x-ray pattern calculated with the fully relaxed S_{Opl} structure, labeled “ $P2_12_12_1$ -relaxed” in Fig. 1(c), is even further different from the experimental pattern. For comparison, we have also calculated the x-ray-diffraction patterns of α -quartz, α -cristobalite, β -cristobalite, and γ -cristobalite at 48 GPa [in Figs. 1(c), (d), (e), and (f), respectively]. None of these spectra fit the experimental data well. A common feature is the lack of the smallest 2θ angle peak at 6° . These results indicate that the structure of the polymeric CO₂ solid is not yet satisfactorily understood. The possible existence of impurities or intergrowth of multiple phases may complicate the interpretation of x-ray data, and further studies are necessary.

To systematically understand the complex CO₂ tridymite structures and their compressibility, we investigate a series of CO₂ tridymite polymorphs which are isostructural to the known SiO₂ tridymite. We compare the results of CO₂ tridymite to its $P2_12_12_1$ structure, as well as to other polymorphs. All CO₂ structures are fully relaxed, and the calculated equations of state (EOS) are fit to the Birch-Murnaghan equation (see Table I for the fitting parameters). Our aim is to find trends in the stability and compressibility of polymeric tetrahedrally bonded CO₂ frameworks.

We begin with the most symmetric tridymite phase, the hexagonal *HP* phase ($P6_3/mmc$), which exists at high temperature in SiO₂. Here CO₄ tetrahedra are arranged to form perfect hexagonal rings within the *ab* plane of the hexagonal cell. This highly symmetric phase has a fixed 180° intertetrahedron bond angle, and was shown to be energetically unfavorable even in SiO₂.¹⁸ Since CO₂ solids prefer an even smaller C-O-C angle than SiO₂,^{8,9} CO₂ *HP* tridymite is an

unrealistic structure. Indeed, it is about 1.83 eV/CO₂ (~ 20000 K in temperature units) higher in binding energy than the β -cristobalite CO₂ structure. Nevertheless, the *HP* structure is of interest because this structure has no adjustable internal coordinates, and its lattice parameter are determined solely by the C-O bond length. This enables us to examine the “intrinsic compressibility” of CO₂ tridymite solids where inter-tetrahedron rotations are forbidden. The calculated bulk modulus of CO₂ *HP* tridymite is 233.5 GPa, and the C-O bond length for the minimum energy structure is about 1.358 Å. A previous LDA study of SiO₂ *HP* tridymite found a bulk modulus of 139.6 GPa and an Si-O bond length of 1.589 Å.¹¹ The ratio of K^{CO_2}/K^{SiO_2} is about 1.67, which fits well with an empirical bulk modulus scaling law with bond length “*d*” of $d^{-3.5}$, which would yield a ratio of 1.73. We find that this ratio for group-IV oxides is also close to the previously calculated bulk modulus ratio for group-IV nitrides, with $K^{C_3N_4}/K^{Si_3N_4}$ close to 1.6.⁵ The calculated bulk modulus of CO₂ *HP* tridymite is only 64% of the reported experimental bulk modulus of CO₂ tridymite, and this difference between theory and experiment is quite significant.

Other known tridymite phases can be derived by rotating the CO₄ tetrahedra in *HP* tridymite and distorting the perfect hexagonal stacking rings in the *ab* planes to ditrigonal (in *LHP* and *MX-1a*) or oval (in *OC*) rings. *OC* tridymite in SiO₂ also has a series of complicated incommensurate superstructures (*OS* tridymite) containing both ditrigonal and oval rings, and *OP* is the only lock-in ($3 \times 1 \times 1$) superstructure.^{12,13} The CO₄ tetrahedral rotation in tridymite relaxes the framework into more energetically preferred structures; this causes fairly minor energy changes in SiO₂, but significantly lowers the binding energies in CO₂ solids. However, none of these tridymite phase has a lower binding energy than β -cristobalite ($I\bar{4}2d$). We have considered *HP*, *LHP*, *OC*, *OP*, *MX-1a*, and $P2_12_12_1$ tridymite, and the

results are listed in Table I. The most energetically stable CO₂ tridymite is indeed the fully relaxed $S_{O_{pt}}$ ($P2_12_12_1$) tridymite, whose binding energy is near that of α -cristobalite. However, it remains 0.19 eV/CO₂ (2300 K in temperature units) higher than that of the β -cristobalite phase.

The reduction of the C-O-C bond angles in HP , LHP , OC , $MX-1a$, and $S_{O_{pt}}$ from 180° (as in HP tridymite) causes a significant reduction in volume. All tridymite phases remain “expanded-volume” phases relative to β -cristobalite. As expected, the bulk modulus decreases (compressibility increases) from that of HP -tridymite in other tridymite phases since the CO₄ tetrahedra are allowed to rotate under compression. The typical bulk moduli of these other CO₂ tridymite phases is comparable to that of cristobalite, which is only about 40% of the reported 365 GPa.

Two other cristobalite-like structures, $C9$ and defective chalcopyrite, have geometries where the CO₄ tetrahedra are not allowed to rotate, as was the case of HP -tridymite. The bulk modulus of $C9$ is 235.5 GPa, while that of d -chalcopyrite is 347.2 GPa. The d -chalcopyrite structure has an intertetrahedral C-O-C bond angle of 109°. Its high bulk modulus is likely a consequence of its very high density ($V_0 = 18.4 \text{ \AA}^3/\text{CO}_2$, about 83% of that of β -cristobalite), which also causes a significant increase in the energetics (1.18 eV/CO₂ higher than that of β -cristobalite).

The enthalpies of some polymeric CO₂ phases are compared as a function of pressure (at zero temperature) in Fig. 2. The tetragonal β -cristobalite phase remains the most favored structure amongst all tridymite and all other phases tested to at least 80 GPa. Next lowest in enthalpy

(at low pressure) is γ -cristobalite, which is a reduced symmetry orthorhombic cristobalitelike phase.¹⁹ The tridymite $S_{O_{pt}}$ - $P2_12_12_1$ and α -cristobalite phases begin at zero pressure with nearly identical enthalpies, but the tridymite phase increases its enthalpy more rapidly because of its larger volume, and becomes energetically less competitive at high pressure.

In conclusion, density-functional calculations of CO₂ $P2_12_12_1$ -tridymite show significant differences with the recent x-ray analysis of new polymeric CO₂ solids. Our calculations find that the experimental lattice parameters are far from an equilibrium structure, and the fully relaxed structure does not agree with the observed x-ray-diffraction pattern. More generally, we find that CO₂ solids built with CO₄ tetrahedra are much more compressible than the reported superhard CO₂ solids. The β -cristobalite phase ($I\bar{4}2d$) remains the lowest energy, or lowest enthalpy, polymeric CO₂ structure. However, none of the SiO₂-like polymorphs of CO₂ studied so far give a satisfactory fit to the reported x-ray spectra. The disagreement between theory and experiment suggests that the structure of the new nonmolecular CO₂ solids remains unsolved, and further detailed studies are necessary. If the new materials are confirmed as superhard, the assumption of SiO₂-like polymorphs must be reconsidered in CO₂ solids. More complex bonding, a mixture of C-O single bonds and C=O double bonds, may exist in such interesting materials.

We thank the the NSF-ASU MRSEC (Grant No. DMR-96-32635) and NSF (Grant No. DMR-99-86706) for support. It is our pleasure to acknowledge several discussions with Professor M. O’Keeffe and Dr. D. M. Teter.

*Present address: Physics Department, Auburn University, Auburn, AL 36849-5311.

¹P.F. McMillan, *Curr. Opin. Solid State Mater. Sci.* **4**, 171 (1999), and references therein.

²V. Iota, C.S. Yoo, and H. Cynn, *Science* **283**, 150 (1999).

³C.S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Häusermann, and C. Mailhot, *Phys. Rev. Lett.* **83**, 5527 (1999).

⁴Compressibility and hardness are different quantities. Other factors, such as structural defects, also influence the hardness of materials.

⁵A.Y. Liu and M.L. Cohen, *Science* **245**, 841 (1989); *Phys. Rev. B* **41**, 10 727 (1990).

⁶D.M. Teter and R.J. Hemley, *Science* **271**, 53 (1996); *D.M. Teter, MRS Bull.* **23**, 22 (1998).

⁷S. Serra, C. Cavazzoni, G.L. Chiarotti, S. Scandolo, and E. Tosatti, *Science* **284**, 788 (1999).

⁸J. Dong, J.K. Tomfohr, and O.F. Sankey, *Science* **287**, 11a (2000).

⁹J. Dong, J.K. Tomfohr, and O.F. Sankey, *Phys. Rev. B* **61**, 5967 (2000).

¹⁰The calculations have been performed using the Vienna *ab initio* Simulation Program (VASP) developed at the Institut für Theoretische Physik of the Technische Universität Wien, G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); G. Kresse and J.J. Furthmüller, *ibid.* **54**, 11 169 (1996).

¹¹D.M. Teter, R.J. Hemley, G. Kresse, and J. Hafner, *Phys. Rev. Lett.* **80**, 2145 (1998); Th. Demuth, Y. Jeanvoine, J. Hafner, and J.G. Angyan, *J. Phys.: Condens. Matter* **11**, 3833 (1999).

¹²P.J. Heaney, *Silica, Physical Behavior, Geochemistry and Materials Applications*, Reviews in Mineralogy Vol. 29, Miner. Soc. of Am., edited by P.J. Heaney, C.T. Prewitt, and G.V. Gibbs (BookCrafters, Inc., Chelsea, Michigan, 1994), pp. 1–40.

¹³D. Cellai, M.A. Carpenter, and R.J. Kirkpatrick, *Phys. Chem. Miner.* **22**, 50 (1995); A.K.A. Pryde and M.T. Dove, *Phys. Chem. Miner.* **26**, 171 (1998).

¹⁴Note that the reported experimental structural model of $P2_12_12_1$ CO₂ tridymite is different from that of SiO₂ OP ($P2_12_12_1$) tridymite. SiO₂ OP -tridymite is a superstructure of OC -tridymite.

¹⁵Using the experimentally reported lattice parameters, the theoretically optimized internal coordinates are $C1$ (0.9277,0.9414,0.7036), $C2$ (0.4337,0.6194,0.6860), $O1$ (0.5492,0.2312,0.0199), $O2$ (0.2281,0.5767,0.2140), $O3$ (0.4685,0.2547,0.3510), and $O4$ (0.8951,0.5968,0.2045).

¹⁶The fully theoretically optimized internal coordinates are $C1$ (0.9130,0.9210,0.6940), $C2$ (0.4179,0.4935,0.6809), $O1$ (0.5889,0.1972,0.9926), $O2$ (0.2468,0.7033,0.2110), $O3$ (0.4278,0.2252,0.2927), and $O4$ (0.9341,0.7578,0.1608).

¹⁷Our theoretical x-ray patterns assume powders and were generated using the “General Structure Analysis System” (GSAS) method of A.C. Larson and R.B. Von Dreele, Los Alamos National Laboratory.

¹⁸G.V. Gibbs, E.P. Meagher, M.D. Newton, and D.K. Swanson, in *Structure and Bonding in Crystals*, edited by M. O'Keeffe and A. Navrotsky (Academic Press, New York, 1981), pp. 195–225.

¹⁹M. O'Keeffe and B.G. Hyde, *Acta Crystallogr.*, Sect. B: Struct.

Crystallogr. Cryst. Chem. **32**, 2923 (1976). The hypothetical orthorhombic γ phase is $Pna2_1$, with $C(1)$, and two inequivalent oxygen atoms $O(1)$ and $O(2)$, all at $4a$ (x, y, z , etc.) sites.