Polymeric Carbon Dioxide

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This article was submitted to Materials Research Society 1999 Fall Meeting, Boston, MA, November 29 – December 3, 1999

November 2, 1999
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ABSTRACT

Synthesis of polymeric carbon dioxide has long been of interest to many chemists and materials scientists. Very recently we discovered the polymeric phase of carbon dioxide (called CO$_2$-V) at high pressures and temperatures. Our optical and x-ray results indicate that CO$_2$-V is optically non-linear, generating the second harmonic of Nd: YLF laser at 527 nm and is also likely superhard similar to cubic-boron nitride or diamond. CO$_2$-V is made of CO$_4$ tetrahedra, analogous to SiO$_2$ polymorphs, and is quenchable at ambient temperature at pressures above 1 GPa. In this paper, we describe the pressure-induced polymerization of carbon dioxide together with the stability, structure, and mechanical and optical properties of polymeric CO$_2$-V. We also present some implications of polymeric CO$_2$ for high-pressure chemistry and new materials synthesis.

INTRODUCTION

Application of high-pressure strongly perturbs the nature of chemical bonding, electronic and crystal structures, thermal, mechanical, and optical properties, and chemical reactivities of solids. These perturbations, which often occur systematically, provide opportunities for synthesizing new novel materials. Discoveries of a wide variety of materials unique to high P, T-conditions support this thesis; these include novel-gas compounds [4], metallic hydrogen [5], symmetric ice [6], superhard materials [7], high energy density polymers [8], and alkali-transition metal alloys [9]. Commonly used guidance suggestive to these discoveries has often been inferred from the electronic configuration, intermolecular interaction, crystal structure, effective close-packing and density, solubility and miscibility, group periodicity, and pressure-induced changes of these properties.

Molecular solids are described in terms of strong covalent bonds within molecules and weak van der Waals interactions between molecules. The strong intramolecular bonds make these molecules extremely stable at ambient conditions; whereas, the weak intermolecular interactions make such crystals very soft, at least initially at relatively low pressures. Because of this reason, many simple molecular solids particularly made of the first and second row elements such as CO$_2$, N$_2$, C, H$_2$O, CH$_4$, other C-N-O-H compounds are often considered as "inert" at relatively low pressures below 10 GPa. In fact, high stabilities of these molecules are often assumed even at very high pressures (10-40 GPa) and temperatures (1000-5000 K), as CO$_2$, N$_2$, H$_2$O, C are considered to be four major detonation products of energetic molecules.

At high pressures, however, the nature of these intermolecular interactions rapidly alters and becomes highly repulsive. Electron kinetic energy dominates, and electrons localized within intramolecular bonds become unstable. It is due to the higher power dependence of kinetic energy on density, $p^2$, than that of potential energy, $p^0$ (see Fig. 1). Therefore, at high pressures, the isolated electrons within intramolecular bonds are any longer stable, which leads to delocalization of the electrons through neighboring molecules. Such a modification of chemical bondings clearly results in soften of the stiff repulsive intermolecular potentials at high pressures and thus in physical and chemical phase transformations to a cross-linked two or three dimensional network structures. This perhaps is the reason for which the unsaturated molecular bonds become unstable above 10 GPa and which the network structures are ubiquitous at high pressures as can be seen in diamond, c-BN, $\beta$-C$_3$N$_4$, polymeric N$_2$, etc. [7,8].
Three mechanisms may occur at high pressures to delocalize electrons and soften repulsive potentials: (i) ionization creating attractive electrostatic energy, (ii) polymerization delocalizing intramolecular electrons between neighboring molecules, and (iii) metallization completely delocalizing electrons through conduction bands. These processes probably occur with increasing pressure as molecular phases \( \rightarrow \) ionic species \( \rightarrow \) polymeric phases \( \rightarrow \) metallic phases. This conjecture is supported by our recent discoveries of the molecular-to-extended ionic and polymeric CO\(_2\) phase transitions, both of which occur prior to the metallization at high pressures and temperatures [1-3]. In this paper we will describe the pressure-induced polymerization of CO\(_2\) together with its stability, structure, and mechanical and optical properties.

**EXPERIMENT**

The transformations of molecular solids to the extended phases often require relatively large positive volume changes (5-20 cm\(^3\)/mol) and, thus, are associated with large kinetic barriers (30-150 KJ/mol) [10]. As a result, these transitions are greatly hindered kinetically despite large thermodynamic stabilities of final products. Nitrogen may be a good example, in which system the polymerization has been suggested theoretically at about 60 GPa [8] but recent experiments indicate nitrogen being molecular even at 120 GPa [11].

In this study, we use a laser-heating technique to overcome the kinetic barrier existing in the molecular-to-extended phase transitions of carbon dioxide. Liquid CO\(_2\) was loaded in a diamond-anvil cell (DAC) contained in a high-pressure vessel by condensing CO\(_2\) gas at -40 °C and 10 atmospheres. The polymeric carbon dioxide was synthesized by heating carbon dioxide to high temperatures (>1800 K) at high pressures (>35 GPa) by using a Nd: YLF laser. However, because of the low absorption of carbon dioxide at the wavelength of Nd:YLF (1.054 µm), carbon dioxide was indirectly heated through ruby particles. Temperature of the sample was determined by fitting the thermal emission from the heated-area to a gray-body radiation formula.

The quenched products of CO\(_2\) polymerization were investigated by using micro-Raman spectroscopy and synchrotron x-ray diffraction at both ESRF (ID-30) and SSRL (BL10-2). The determination of crystal structure of CO\(_2\)-V has been a challenge due to (i) the incomplete transformation resulting in a mixture phase of CO\(_2\)-III and V, (ii) relatively low-Z materials, (iii) complex, low symmetry crystal structure, (iv) highly strained lattice with strongly preferred orientation. Despite these difficulties, we were able to obtain reasonable diffraction patterns of various CO\(_2\) phases including the polymeric phase by using highly intense x-ray beam at the 3\(^{rd}\) generation synchrotron source. With a 10 µm-size focused monochromatic synchrotron x-ray beam and a fast scanning image-plate detector, we were able to obtain the angle-resolved x-ray diffraction selectively from a nearly completely transformed region of the sample.

The transitions and quenched products of CO\(_2\) were also characterized by micro-Raman spectroscopy using an Ar\(^{+}\)-ion laser, a triplemate, and a liq.-N\(_2\) cooled CCD detector. The resolution of this system is within 1 cm\(^{-1}\).
RESULTS AND DISCUSSIONS

Molecular Phases of CO$_2$

Carbon dioxide crystallizes to the cubic Pa3 structure, CO$_2$-I at 1.5 GPa and ambient temperature [12]. It is optically isotropic as shown in Fig. 2(a). Above 11 GPa, CO$_2$-I transforms to the orthorhombic Cmca phase, CO$_2$-III [12], which exists in a wide range of pressures above 70 GPa [3]. The large quadruple moment of linear CO$_2$ molecule is considered to stabilize both CO$_2$-I and III at least at relatively low pressures [13]. However, above 30 GPa, CO$_2$-III develops a very characteristic texture indicative of a highly strained lattice as shown in Fig. 2(b). It also shows an abnormally large pressure gradient exceeding 20% of the maximum pressure of the sample within 100 μm. These observations clearly indicate that CO$_2$-III has high material strength at these pressures, which is rather unusual for a molecular crystal. In fact, the bulk modulus of CO$_2$-III has also been found to be unusually high 87 GPa, similar to that of elemental silicon [3]. For comparison, the bulk moduli of molecular phases are typically less than 15 GPa. The bulk moduli of various CO$_2$ phases will be discussed in details in the later section below.

Polymeric Phase of CO$_2$

Above 35 GPa and 1800 K, highly strained CO$_2$-III transforms into a new phase CO$_2$-V that can be quenched at ambient temperature as shown in Fig. 2(c). It clearly shows that the texture in transformed area is characteristic from that in untransformed area.

The phase transition from CO$_2$-III to CO$_2$-V is also evident from the Raman spectra obtained before and after heating a sample at 40 GPa as shown in Fig. 3. The Raman spectrum of CO$_2$-III is consisted of a few weakly resolved phonons between 250 and 500 cm$^{-1}$, typical for a highly strained molecular phase [14]. In contrast, the Raman spectrum of CO$_2$-V is different from the vibration characteristics of any known molecular polymorph of CO$_2$, suggesting that it has a different structure. We assigned the most dominant vibration feature at 790 cm$^{-1}$ to the symmetric stretch of the C-O-C bonds, ν$_s$(C-O-C). Based on the pressure dependence shown in Fig. 4, this mode should be located at 660 cm$^{-1}$ at ambient conditions of pressure and temperature. This frequency of ν$_s$(C-O-C) is then translated into 398 - 491 cm$^{-1}$ from the ν$_s$(Si-O-Si) mode in SiO$_2$ polymorphs, depending on the approximation used in the reduced-mass calculation [15]. This mass-weighted vibron frequency agrees reasonably well with ν$_s$(Si-
O-Si) frequencies in quartz at 464 cm$^{-1}$ and in coesite at 510 cm$^{-1}$ [15,16]. In contrast, the analogous mode of stishovite, a high-pressure polymorph of SiO$_2$, occurs at 750 cm$^{-1}$ at ambient conditions [16], even a higher frequency than $v_\text{s}$ (C-O-C) at 660 cm$^{-1}$ of CO$_2$-V. The large pressure-dependent shift of $v_\text{s}$(C-O-C) (Fig. 4) also is analogous to that of $v_\text{s}$(Si-O-Si) in the coesite or quartz polymorphs of SiO$_2$. As previously explained for SiO$_2$ [16-18], the strong shift of $v_\text{s}$(C-O-C) implies a high compressibility of CO$_2$-V as a result of a large change of C-O-C angles in this open structure.

**Crystal Structure of CO$_2$-V**

Figure 5 shows the diffraction pattern of CO$_2$-V at ambient temperature during unloading from 48 GPa. CO$_2$-V is clearly metastable at ambient temperatures over a large pressure range including the entire stability field of CO$_2$-III above 10 GPa. Below 10 GPa, CO$_2$-V begins to depolymerize to CO$_2$-I; however, diffraction peaks of CO$_2$-V remain even at 4 GPa. This observation is consistent with the earlier Raman data showing the C-O-C vibration band above 1 GPa.

The diffraction pattern of CO$_2$-V can be fit in terms of an orthorhombic structure with lattice parameters, $a = 6.216$ Å, $b=4.352$ Å, $c = 6.066$ Å at 48 GPa, consistent with 8 molecules per unit cell (Table I).

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![Fig. 3 Raman spectra of CO$_2$ obtained before and after the laser heating at 40 GPa, showing the phase transition from molecular CO$_2$-III to polymeric CO$_2$-V.](image)

![Fig. 4 Raman spectra of CO$_2$-V obtained during unloading at ambient temperatures. It shows that the CO$_2$-V can be metastably quenched at low pressures above 1 GPa.](image)

![Fig. 5 Angle-resolved x-ray diffraction patterns of CO$_2$ V at several high pressures. The numbers indicate the pressures in GPa.](image)
The intensity data and evidence for preferred orientation do not allow rigorous refinement of the structure. Nevertheless, we found a reasonable description of the diffraction pattern in terms of SiO₂-tridymite structures, particularly with an orthorhombic P₂₁₂₁₂₁ structure that represents about 1/3 of a known SiO₂-tridymite unit cell [19,20]. The difference in the measured and calculated diffraction intensities was notable particularly for the 103 reflection, probably due to the preferred orientation and/or disorder in the oxygen sublattice of the tridymite structure [21]. In fact, we have verified that introducing a slight disorder into the oxygen positions increases the intensity of the 103 reflection and makes it the strongest.

All tridymite structures can be derived from a parent hexagonal (P6₃/mmc) structure, a high temperature modification of β-SiO₂ quartz (P6₂₂₂), by appropriate rotations of CO₄ tetrahedra [20,21]. In this “ideal” P₂₁₂₁₂₁ tridymite structure of CO₂-V, each carbon atom is tetrahedrally bound to four oxygen atoms with the carbon-oxygen bond distances between 1.34(0.01) at 60 GPa and 1.40(0.01) Å at 10 GPa. The O-C-O angles are estimated to be 110(10)° (Fig. 6). These CO₄ tetrahedral units share their corner oxygens to form six-fold distorted holohedral rings with alternating tetrahedral apices pointing up and down the ab plane. The apices of tetrahedra are then connected through oxygen atoms along the c-axis. This interconnected layer structure of tetrahedra yields the C-O-C angle 130(10)°, substantially smaller than those of SiO₂-tridymites, 174°-180°.

**Table I.** The crystal structure of CO₂-V (P₂₁₂₁₂₁) at 48 GPa: a=6.216 Å, b=4.352 Å, c=6.066 Å, and ρ = 3.561 g/cm³. The calculation was based on eight molecules per unit cell, and the final structure is analogous to that of SiO₂-tridymite (see the text).

<table>
<thead>
<tr>
<th>hkl</th>
<th>dᵦ (Å)</th>
<th>Iᵦ</th>
<th>dₒ(F) (Å)</th>
<th>Iₒ</th>
<th>Δd (Å)</th>
</tr>
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<tr>
<td>011;110</td>
<td>3.536</td>
<td>20</td>
<td>3.531</td>
<td>27</td>
<td>0.005</td>
</tr>
<tr>
<td>111; 200; 002</td>
<td>3.074</td>
<td>100</td>
<td>3.066</td>
<td>96</td>
<td>0.008</td>
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<tr>
<td>201</td>
<td>2.766</td>
<td>13</td>
<td>2.766</td>
<td>17</td>
<td>0.000</td>
</tr>
<tr>
<td>211; 112</td>
<td>2.335</td>
<td>37</td>
<td>2.334</td>
<td>14</td>
<td>0.001</td>
</tr>
<tr>
<td>202; 020</td>
<td>2.171</td>
<td>14</td>
<td>2.161</td>
<td>3</td>
<td>0.010</td>
</tr>
<tr>
<td>120; 021</td>
<td>2.054</td>
<td>17</td>
<td>2.058</td>
<td>18</td>
<td>0.004</td>
</tr>
<tr>
<td>103; 301; 310</td>
<td>1.923</td>
<td>33</td>
<td>1.923</td>
<td>100</td>
<td>0.001</td>
</tr>
<tr>
<td>311</td>
<td>1.788</td>
<td>20</td>
<td>1.793</td>
<td>14</td>
<td>0.005</td>
</tr>
<tr>
<td>122; 203</td>
<td>1.701</td>
<td>12</td>
<td>1.700</td>
<td>2</td>
<td>0.001</td>
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The EOS's of CO$_2$ phases have been determined as a function of pressures as shown in Fig. 7. CO$_2$-I transforms to CO$_2$-III at 12 GPa with no apparent volume discontinuity. The x-ray diffraction patterns between 10 and 20 GPa can be fit in terms of CO$_2$-I and III; no features are apparent for CO$_2$-IV. This may mean that the structure of CO$_2$-IV is similar to that of CO$_2$-III as suggested by the description, “distorted CO$_2$-III,” used in earlier Raman studies [14]. The volume changes associated with this molecular-to-extended (III-to-V) transition vary between 15.3 % at 40 GPa and 12.6 % at 60 GPa, at ambient temperatures. Extrapolations of CO$_2$-V and III data yield the volumes 0.322 and 0.453 cm$^3$/g, respectively.

CO$_2$-I is soft, but both CO$_2$-III and V are very stiff solids as summarized in Table II. The bulk modulus $B_o$ of CO$_2$-I is 12.4 GPa typical for a molecular solid. In contrast, the $B_o$ of CO$_2$-III is unusually high 87 GPa, nearly in the range of Si (98 GPa) [22]. This result is consistent with the pressure gradient and observed texture in CO$_2$-III (Fig. 2(b)). Furthermore, the nearest neighbor C-O distance collapses to 2.303 Å at 40 GPa, from 3.135 Å at 1.5 GPa. These imply that CO$_2$-III is not entirely molecular; that is, the intermolecular bonding between neighboring CO$_2$ molecules is substantial. Such increased intermolecular bonding in CO$_2$-III at high pressures will certainly increase the strength of this material and act as a precursor for the transition to an extended phase like CO$_2$-V.

Table II. The bulk moduli $B_o$ and their pressure derivatives $B'$ of CO$_2$ phases in comparison with those of other covalently bonded solids [24,25].

<table>
<thead>
<tr>
<th>Solids</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$B_o$ (GPa)</th>
<th>$B'$</th>
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<tbody>
<tr>
<td>Diamond</td>
<td>3.50</td>
<td>450</td>
<td>1.5</td>
</tr>
<tr>
<td>cubic-BN</td>
<td>3.48</td>
<td>369</td>
<td>4.0</td>
</tr>
<tr>
<td>CO$_2$-V</td>
<td>2.90</td>
<td>365</td>
<td>0.8</td>
</tr>
<tr>
<td>SiO$_2$-Stishovite</td>
<td>4.30</td>
<td>310</td>
<td>8.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$-Corundum</td>
<td>4.00</td>
<td>239</td>
<td>0.9</td>
</tr>
<tr>
<td>SiC</td>
<td>3.22</td>
<td>227</td>
<td>4.1</td>
</tr>
<tr>
<td>SiO$_2$-Coesite</td>
<td>2.92</td>
<td>96</td>
<td>8.4</td>
</tr>
<tr>
<td>SiO$_2$-Quartz</td>
<td>2.65</td>
<td>37</td>
<td>6.2</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.33</td>
<td>98</td>
<td>4.2</td>
</tr>
<tr>
<td>CO$_2$-III</td>
<td>2.22</td>
<td>87</td>
<td>3.4</td>
</tr>
<tr>
<td>CO$_2$-I</td>
<td>1.75</td>
<td>12</td>
<td>4.5</td>
</tr>
<tr>
<td>$\delta$-N$_2$</td>
<td>1.03</td>
<td>3</td>
<td>3.9</td>
</tr>
</tbody>
</table>
**Optical Properties**

CO$_2$-V is also an optically nonlinear solid, generating the second harmonic (SH) of Nd:YLF laser at 527 nm as shown in Fig. 8. The intensity of this sharp SH-band at 527 nm depends on how the Nd:YLF output is partitioned between heating and SH generation. The gray-body fit of the broad feature in Fig. 8 indicates that the temperature of the laser-heated area is 1670 K. We estimate the SH conversion efficiency of this new phase to be about 0.1%. The SH radiation was observed in all twenty samples that underwent the transition, indicating that the frequency doubling process is inherent to the new phase and does not rely on trace impurities that may be incorporated in the CO$_2$ lattice during heating. We also consider that the 0.1% conversion efficiency is remarkably large based on the fact that the conversion efficiency is a nonlinear function of the incident laser power. In this study, we only used 10 W of a CW laser. Furthermore, the second harmonic was measured from a highly heterogeneous polycrystalline sample at 1670 K at 45 GPa, certainly not an ideal condition for the frequency conversion.

Symmetry considerations for SH generation processes provide further support that the crystal structure of CO$_2$-V is non-centrosymmetric like SiO$_2$ tridymite. Strong SH generation of light has been observed in solid forms of SiO$_2$, including crystalline, amorphous, and semiconductor-doped glass with a conversion efficiency up to 20% [26,27]. The relatively sharp phonons and vibrons of CO$_2$-V (Fig. 3) imply that CO$_2$-V is not vitreous; SiO$_2$ glass is well known to have extremely broad vibration bands [16]. On the other hand, the SH process is symmetry forbidden in a crystal structure with a center of inversion [28]. This further excludes the possibility of CO$_2$-V being a centrosymmetric crystal like coesite or stishovite of SiO$_2$ [29,30]. Therefore, it is likely that the structure of CO$_2$-V is non-centrosymmetric like those of SiO$_2$ quartz, coesite, or tridymite, supporting the x-ray result.19

![Fig. 8 The emission spectra obtained during Nd:YLF laser-heating of CO2-V, showing strong the second harmonic emission of the laser at 537 nm at 1670 K and 45 GPa.](image)

**CONCLUDING REMARKS**

We discovered an optically non-linear, superhard polymeric CO$_2$-V at high pressures and temperatures. This is the first discovery of polymer made of CO$_2$ tetrahedra, for which synthesis has been of interest to many chemists and material scientists for many decades. This polymer crystallizes into an orthorhombic tridymite structure above 35 GPa and 1800 K and can be quenched at ambient temperature above 1 GPa. The tridymite structure of CO$_2$ is a high temperature modification of β-SiO$_2$ quartz, and there could be other high-pressure modifications of CO$_2$. Those include other four-fold coordinated CO$_2$ phases like cristobalites, quartz and coesites, three-fold carbonates, six-fold stishovite, and even amorphous CO$_2$ glass. The stability of such a wide-range of polymeric CO$_2$ phases if exist is likely strongly dependent on high pressures and temperatures, and the synthesis of such polymorphs in CO$_2$ is clearly a logical step for future studies.

This new extended polymeric phase of CO$_2$ has very important technological implications for developing high-power optical materials, high strength glass, and energetic materials, especially if it
can be recovered metastably at ambient pressure. This stems from high thermal conductivity and high energy density expected for this low-Z material. However, these new future material applications of CO\textsubscript{2} polymer should cope with several key synthetic new developments, which will be in many regards similar to how the first man-made diamond has been evolved to the large volume synthesis, dynamic synthesis, and metastable CVD growth. Therefore, our current studies are focused on the recovery of CO\textsubscript{2}-V at ambient condition and the development of alternative synthetic routes including metastable ones.

Carbon dioxide, together with nitrogen, carbon, and H\textsubscript{2}O\textsubscript{2}, has been considered to be one of the most stable molecules in a wide range of pressures and temperatures, as these molecules are considered to be four major detonation products of high explosives at 10-50 GPa and 2000-5000 K. The molecular-to-extended phase transition discovered in CO\textsubscript{2} is however contradict to the high stability of carbon dioxide and thus provides a new fundamental insight to the stability and structure of many other simple molecules at high pressures and temperatures. In fact, the extended forms of H\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2}O, NH\textsubscript{3}, CO, C\textsubscript{2}N\textsubscript{2}, O\textsubscript{2} have already been experimentally observed and/or theoretically suggested. For example, N\textsubscript{2} has been suggested to transform into a polymeric black-P structure above 65 GPa [8]; C\textsubscript{2}N\textsubscript{2} and CO polymerize below 12 GPa even at room temperature [31,32]. The symmetric H\textsubscript{2}O and NH\textsubscript{3} recently discovered at high pressures are the extended phases [6,33]. The infrared-active H\textsubscript{2}-III [34] and ε-0\textsubscript{2} [35] may indicate the initial charge separation between adjacent molecules (e.g. H\textsubscript{2}\textsuperscript{8}H\textsubscript{2}\textsuperscript{8} and O\textsubscript{2}O\textsubscript{2}), precursors to the extended phases. Thus, it is important to in-situ investigate the structure and stability of simple molecules at high pressures and temperatures.

ACKNOWLEDGMENTS

This work has been done in collaboration with V. Iota, H. Cynn, B. Baer, K. Visbeck, F. Gygi, G. Galli, C. Mailhiot at LLNL; M. Nicol (UNLV); D. Hausermann (HP-CAT), S. Carlson (ESRF). The x-ray work reported here has been done at the ESRF and SSRL. This work has been performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. This study has been benefited from the use of synchrotron x-ray available at ESRF and SSRL. We recognize the programmatic supports of the work from the PDRP- and LDRD-programs.

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15. The correspondence between the mode frequencies for the two structures can be estimated by considering the rations of the reduced vibrational masses for the symmetric stretching modes in singly bonded C-O-C and Si-O-Si structures. The angle between the two X-O single bonds is chosen to match the bond angle in α-quartz (104.6°). The low frequency limit (398 cm⁻¹) results from considering isolated structures (X₂O molecules) while the upper frequency (491 cm⁻¹) results by considering the second order shell of O atoms moving rigidly with the C (Si).


28. In general, the second harmonic of light is generated in non-centrosymmetric crystals; whereas, only odd harmonic are observed in centrosymmetric crystals. This stems from the second order polarization dependence of electromagnetic transitions. In crystals having a center of symmetry, the inversion of all coordinates must leave all relationships between physical quantities unchanged. Because the electric field $\mathbf{E}$ is odd under inversion operations, the polarization field $\mathbf{P}$ must also be odd, and the coefficients of all even powers in the
expansion of the polarization: \( \mathbf{P} = \varepsilon_{1} \mathbf{E} \sin(\omega t) + \varepsilon_{2} \mathbf{E}^{2} \sin^{2}(\omega t) + \varepsilon_{3} \mathbf{E}^{3} \sin^{3}(\omega t) + \ldots \)
must vanish. In such crystals, only odd multiples of the incident frequency can be generated.

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