

# Pb<sub>17</sub>O<sub>8</sub>Cl<sub>18</sub>: A Promising IR Nonlinear Optical Material with Large Laser Damage Threshold Synthesized in an Open System

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## S Supporting Information

**ABSTRACT:** Mid-IR nonlinear optical (NLO) materials are of great importance in modern laser frequency conversion technology and optical parametric oscillator processes. However, the commercially available IR NLO crystals (e.g., AgGaQ<sub>2</sub> (Q = S, Se) and ZnGeP<sub>2</sub>) suffer from two obstacles, low laser damage thresholds (LDTs) and the difficulty of obtaining high-quality crystals, both of which seriously hinder their applications. The introduction of Cl, an element with a large electronegativity, and Pb, a relatively heavy element to promote the optical properties, affords an oxide-based IR NLO material, Pb<sub>17</sub>O<sub>8</sub>Cl<sub>18</sub> (POC). High-quality POC single crystals with sizes of up to 7 mm × 2 mm × 2 mm have been grown in an open system. Additionally, POC exhibits a large LDT of 408 MW/cm<sup>2</sup>, 12.8 times that of AgGaS<sub>2</sub>. POC also exhibits an excellent second harmonic generation response: 2 times that of AgGaS<sub>2</sub>, the benchmark IR NLO crystal at 2090 nm, and 4 times that of KDP, the standard UV NLO crystal at 1064 nm. Thus, we believe that POC is a promising IR NLO material.

Nonlinear optical (NLO) materials, which can expand the wavelength range provided by common laser sources through second harmonic generation (SHG), have been at the forefront of laser science and technology.<sup>1</sup> Many factors are involved in selecting outstanding NLO materials, including phase-matchability, second-order nonlinear susceptibility, thermal stability, wide optical transparency, availability of large single crystals, and environmental stability. Significant progress has been made in the UV and visible regions, as numerous well-known NLO crystals have been discovered in the last few decades,<sup>2–5</sup> including KH<sub>2</sub>PO<sub>4</sub> (KDP),<sup>6</sup> KTiOPO<sub>4</sub> (KTP),<sup>7</sup> LiNbO<sub>3</sub> (LN),<sup>8</sup> β-BaB<sub>2</sub>O<sub>4</sub> (BBO),<sup>9</sup> LiB<sub>3</sub>O<sub>5</sub> (LBO),<sup>10</sup> CsLiB<sub>6</sub>O<sub>10</sub> (CLBO),<sup>11</sup> and KBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub> (KBBF).<sup>12</sup> In contrast, although many chalcogenide- and pnictide-based materials with uncommon structures recently have exhibited promising IR NLO properties,<sup>13,14</sup> only a few NLO crystals (e.g., the benchmark IR NLO materials AgGaQ<sub>2</sub> (Q = S, Se)<sup>15</sup> and ZnGeP<sub>2</sub><sup>16</sup>) are commercially available in the mid-IR region (2.5–25 μm), the fingerprint region for organic and inorganic

molecules that spans two important atmospheric transparent windows (3–5 and 8–14 μm).<sup>17</sup> However, these crystals suffer from two main drawbacks, including low laser damage thresholds (LDTs) and difficulty in growing high-quality crystals,<sup>18</sup> which seriously hinder their applications. Therefore, the search for new IR NLO crystals with both high LDTs and moderate SHG responses that can also be easily grown is still a challenge in this field.

It has been normally accepted that strong optical absorption causes thermal and electronic effects and eventually leads to laser damage. A high LDT in an IR NLO crystal commonly corresponds to a large energy band gap (preferably larger than 3.0 eV).<sup>19</sup> In recent research,<sup>19</sup> Qin, Lin, and co-workers proposed that large band gaps could be attained by introducing highly electronegative halide anions to form strong ionic bonds that would promote the tight bonding of valence electrons around the anions. Several mid-IR NLO halide crystals with large band gaps and high LDTs, such as NaSb<sub>3</sub>F<sub>10</sub>,<sup>20</sup> Cs<sub>2</sub>HgI<sub>2</sub>Cl<sub>2</sub>,<sup>21</sup> NaBa<sub>4</sub>Ge<sub>3</sub>S<sub>10</sub>Cl,<sup>22</sup> and Hg<sub>2</sub>BrI<sub>3</sub>,<sup>23</sup> have been discovered. However, the presence of a large band gap in a material usually conflicts with a large SHG response. To address this question, oxides that contain cations susceptible to second-order Jahn–Teller (SOJT) effects,<sup>24</sup> including octahedrally coordinated d<sup>0</sup> transition metals and lone-pair cations (e.g., Pb<sup>2+</sup>),<sup>25</sup> are often employed.

For growth of high-quality crystals,<sup>26</sup> oxide-based crystals could be excellent candidates as they can be grown in an open system, which alleviates the difficulty of crystal growth in sealed silica tubes by the Bridgman–Stockbarger technique. Almost all oxide-based materials, however, have high optical absorption in the mid-IR (3–5 and 8–12 μm) due to intrinsic vibrations. To compensate for these vibrations, heavy elements<sup>19</sup> such as iodine and lead could be introduced into the oxide system to obtain a wide IR-transparent window since the vibrations of I–O (in [IO<sub>3</sub>]<sup>–</sup>) and Pb–O are usually assigned to 805 cm<sup>–1</sup> (12.5 μm) and 722 cm<sup>–1</sup> (14 μm), respectively. While a series of metal iodates have been reported to date to be promising IR NLO materials,<sup>27</sup> few lead oxochlorides have been reported.

Received: April 23, 2015

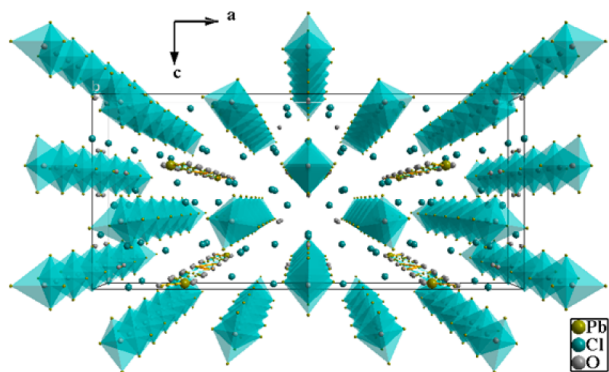
Published: June 29, 2015



Guided by the strategies above, through systematic investigation in the  $\text{PbCl}_2\text{-PbO}$  system, we have found a promising IR NLO crystal,  $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$  (POC). A similar structure and its ionic conductivity were reported by Siidra et al.,<sup>28</sup> but no optical properties were reported. We report the SHG properties of the  $\text{PbCl}_2\text{-PbO}$  system for the first time.

Remarkably, both polycrystalline samples and single crystals of POC have been synthesized in air. The transmittance spectrum measured on a 0.7 mm thick POC crystal plate shows a broad transparent range from 0.34 to 13.9  $\mu\text{m}$ . Additionally, POC exhibits a large LDT of 408  $\text{MW}/\text{cm}^2$  (12.8 times that of  $\text{AgGaS}_2$ ), a large SHG response (4 times that of KDP at 1064 nm and 2 times that of  $\text{AgGaS}_2$  at 2090 nm), and good thermal stability.

POC crystallizes in the space group  $Fmm2$  (No. 42) of the orthorhombic system with the unit cell parameters  $a = 35.4963(14)$   $\text{\AA}$ ,  $b = 5.8320(2)$   $\text{\AA}$ ,  $c = 16.0912(6)$   $\text{\AA}$ ,  $V = 3331.1(2)$   $\text{\AA}^3$ , and  $Z = 3$ . The structure was solved with the SHELXL program package and refined to  $R_1 = 0.0557$  for 1729 reflections with  $F_o > 4\sigma(F_o)$  and  $wR_2 = 0.1321$ . The crystal structure of POC (Figure 1) consists of only the targeted Pb–

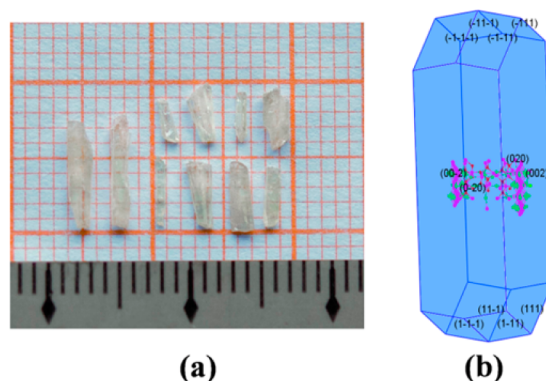


**Figure 1.** Structure of POC viewed along the  $[010]$  direction. The blue units are the  ${}^1_{\infty}[\text{OPb}_2]$  chains formed by edge-sharing  $\text{OPb}_4$  tetrahedra.

O and Pb–Cl bonds, which is beneficial for enlarging its IR and UV cutoff edges, respectively. The  ${}^1_{\infty}[\text{OPb}_2]$  chains formed by edge-sharing  $\text{OPb}_4$  tetrahedra run along the  $[010]$  direction. The Cl atoms and disordered Pb atoms reside between the  ${}^1_{\infty}[\text{OPb}_2]$  chains.

Polycrystalline samples of POC were synthesized by a solid-state reaction in air, and the phase purity was confirmed by powder X-ray diffraction (PXRD). Thermogravimetric analysis (Figure S1 in the Supporting Information (SI)) indicates that POC is thermally stable up to about 550  $^{\circ}\text{C}$ , which is quite high among halide-based IR NLO materials. Meanwhile, single melting (526  $^{\circ}\text{C}$ ) and crystallization (514  $^{\circ}\text{C}$ ) points were reproducibly observed by differential scanning calorimetry (Figure S1). PXRD analysis of the products after melting shows an excellent match between the calculated and experimental patterns (Figure S2), indicative of congruent melting behavior. This, along with the synthesis of POC polycrystalline samples in air, suggested that large crystals for further optical characterization and practical application could be grown from its stoichiometric melt in the open system.

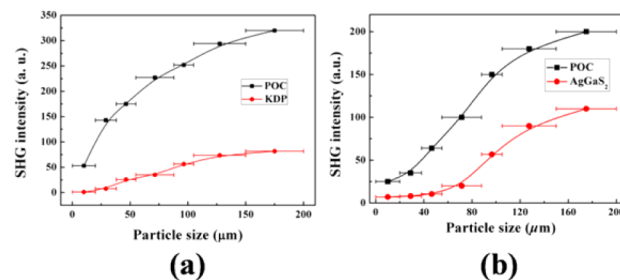
Thus, single crystals of POC were grown from a stoichiometric melt by a modified spontaneous crystallization method in air (see the SI). Transparent POC single crystals with sizes of up to 7 mm  $\times$  2 mm  $\times$  2 mm (Figure 2a) were



**Figure 2.** Crystal growth analysis of POC: (a) photograph of as-grown POC crystals; (b) theoretical morphology of POC.

obtained in the open system. The ability to grow crystals in an open system is a significant development in IR NLO material crystal growth. Current materials are grown in a closed system in sealed silica tubes by the conventional Bridgman–Stockbarger technique. Growth of the POC crystals in an open system allows for more flexible crystal growth conditions that can be more easily regulated to optimize crystal quality. The theoretical morphology of POC (Figure 2b) was studied according to the Bravais–Friedel and Donnay–Harker (BFDH) theory.<sup>29</sup> As shown in Figure 2, the shape of as-grown POC single crystals is rodlike, which is consistent with the theoretical morphology. From the theoretical morphology (Figure 2b), we can find that the distinguishable facets of POC are  $\{111\}$  and  $\{002\}$  planes. In future work, we will explore the growth of larger POC single crystals with seed crystals oriented in different directions.

Because structures of the  $mm2$  crystal class usually exhibit SHG effects, we measured the SHG response of POC by the Kurtz–Perry method using a Q-switched Nd:YAG laser (1064 nm) and an EO-Q-switched Cr:TM:Ho:YAG laser (2090 nm). POC exhibits a large SHG response,  $\sim 4$  times that of KDP, and it is type-I phase-matchable at 1064 nm according to the Kurtz–Perry rule (Figure 3a).<sup>30</sup> On the basis of the



**Figure 3.** Phase-matching curves (i.e., SHG response vs particle size) for POC at (a) 1064 nm and (b) 2090 nm.

nondepleted pump approximation,<sup>31</sup> the second harmonic output conversion efficiency  $\eta$  (eq 1 in the SI) of POC at  $\lambda \sim 1064$  nm is comparable to that of KDP (a standard UV NLO crystal) at  $\lambda \sim 200$  nm, which indicates that POC could exhibit good SHG performance in the IR region. Additionally, the SHG signal intensity of POC with the 2090 nm laser as the fundamental wavelength is about 2 times that of  $\text{AgGaS}_2$  (a benchmark IR NLO crystal) (Figure 3b). The curve of SHG intensity versus particle size (Figure 3b) for POC at 2090 nm

indicates type-I phase-matching behavior. The excellent SHG properties at 1064 and 2090 nm show that POC is a promising NLO material in the IR range. To investigate the relationship between the functional units and the SHG response, the dipole moments of  $\text{PbO}_m\text{Cl}_n$  polyhedra were calculated using the Debye equation.<sup>32</sup> As the stereochemically active lone pair (SCALP) in the Pb polyhedra may affect the macroscopic SHG coefficients, the polyhedral dipoles were evaluated by considering the SCALP of the Pb polyhedra. The detailed calculation results are summarized in Table S4 in the SI. The magnitudes of the dipole moments along the *a*-axis and *b*-axis directions are almost canceled, and their vector sum results in an enhanced net polarization moment in the *c*-axis direction. This direction is consistent with the defined polar direction in crystal class *mm*2.<sup>33</sup> These enhanced arrangements of dipole moment might lead to the excellent SHG response of POC. Meanwhile, as shown in Table S4, the Pb1 and Pb2 polyhedra are the main contributors to the macroscopic polarity, which means that the Pb1 and Pb2 polyhedra might be the main contributors to the SHG response.

The UV–vis–NIR and mid-IR transmittance spectra (Figure 4) were measured on a 0.7 mm thick POC single-crystal plate

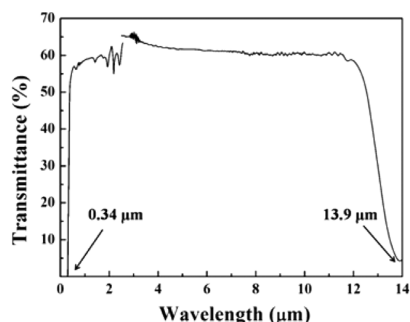


Figure 4. Transmittance spectra of POC.

(Figure S4). As shown in Figure 4, POC is transparent over a broad spectral range from 0.34 to 13.9  $\mu\text{m}$  ( $29\,412$  to  $719\text{ cm}^{-1}$ ), which covers two important atmospheric transparent windows (3–5 and 8–14  $\mu\text{m}$ ) for optical applications. As we mentioned previously, the peak at  $719\text{ cm}^{-1}$  (13.9  $\mu\text{m}$ ) in the mid-IR transmittance spectrum can be assigned to Pb–O vibrations. The diffuse reflectance spectrum of POC powder (Figure S3) indicates that the band gap of POC is about 3.44 eV, which is much higher than that of commercially available IR NLO crystals such as  $\text{AgGaS}_2$ ,  $\text{AgGaSe}_2$ , and  $\text{ZnGeP}_2$  and implies that POC may exhibit a large LDT.

Thus, a preliminary measurement of the LDT was performed on powder samples with powders of  $\text{AgGaS}_2$  as the reference. The results (Table 1) indicate that POC exhibits a large LDT value of  $408\text{ MW/cm}^2$  (1064 nm, 10 ns, 10 Hz).  $\text{AgGaS}_2$  powders show an LDT of  $32\text{ MW/cm}^2$  under the same conditions. The LDT of POC is 12.8 times that of  $\text{AgGaS}_2$ , which implies that POC is an excellent candidate for high-power NLO applications in the IR region.

Table 1. LDT Measurement of POC with  $\text{AgGaS}_2$  as the Reference

compound	damage energy (mJ)	spot diameter (mm)	LDT ( $\text{MW/cm}^2$ )
POC	2.01	0.25	408
$\text{AgGaS}_2$	0.35	0.375	32

In conclusion, we have successfully developed POC as a promising new IR NLO crystal. It is type-I phase-matchable with a large powder SHG efficiency that is about 4 times that of KDP at 1064 nm and 2 times that of  $\text{AgGaS}_2$  at 2090 nm. The introduction of the  $\text{Cl}^-$  anion with a large electronegativity and Pb as a relatively heavy element in POC gives rise to the extension of its UV and IR cutoff edges to 0.34 and 13.9  $\mu\text{m}$ , respectively. POC also exhibits high thermal stability. Remarkably, POC could effectively overcome the two main drawbacks of the commercially available IR NLO materials: (a) it shows a high LDT of  $408\text{ MW/cm}^2$ , which is 12.8 times that of the benchmark IR NLO  $\text{AgGaS}_2$  material, and (b) transparent POC single crystals with sizes of up to 7 mm  $\times$  2 mm  $\times$  2 mm can be obtained in an open system, which can overcome the difficulty of growing high-quality crystals by the conventional Bridgman–Stockbarger technique. The theoretical morphology of POC (Figure 2b) was studied according to the BFDH theory. We therefore believe that POC is a promising IR NLO material, and efforts to grow larger high-quality POC single crystals are in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic data (CIF), experimental methods, and additional tables and figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03986.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 51425206, U1129301, and 51172277), the Western Light of CAS (Grant XBBS201217), the Xinjiang International Science & Technology Cooperation Program (20146001), the 973 Program of China (Grant 2014CB648400), and the Funds for Creative Cross & Cooperation Teams of CAS, Xinjiang Key Laboratory Foundation (Grant 2014KL009). K.R.P. and K.C. acknowledge support from the National Science Foundation (Solid State Chemistry Award DMR-1307698).

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