# Comparison between beryllium and diamond-backing plates in diamond-anvil cells: Application to single-crystal x-ray diffraction high-pressure data

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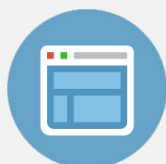
Benedetta Periotto,[1] Fabrizio Nestola,[2,3,a)] Tonci Balic-Zunic,[4] Ross J. Angel,[5] Ronald Miletich,[6] and Lars A. Olsen[1]
[1]*Department of Geography and Geology, University of Copenhagen, 1350 Copenhagen, Denmark*
[2]*Dipartimento di Geoscienze, Università di Padova, 35137 Padova, Italy*
[3]*CNR-IGG, Padova, I-35137, Padova, Italy*
[4]*Danish Natural History Museum, University of Copenhagen, 1350 Copenhagen, Denmark*
[5]*Crystallography Laboratory, Virginia Tech, Blacksburg, Virginia 24060, USA*
[6]*Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrasse 14, 1090 Wien, Austria*

A direct comparison between two complete intensity datasets, collected on the same sample loaded in two identical diamond-anvil pressure cells equipped, respectively, with beryllium and diamond-backing plates was performed. The results clearly demonstrate that the use of diamond-backing plates significantly improves the quality of crystal structure data. There is a decrease in the internal R factor for averaging, structure refinement agreement factors, and in the errors and uncertainties of the atomic coordinates, atomic displacement parameters, and individual bond lengths. © *2011 American Institute of Physics*. [doi:10.1063/1.3590776]

## I. INTRODUCTION

Many recent studies have been focused on the determination of accurate and precise unit-cell parameters as a function of pressure using single-crystal x-ray diffraction. This has allowed results to be obtained that are characterized by extremely low error in the determination of the bulk modulus and its first and second pressure derivatives (e.g., see Refs. 1–5). The simultaneous refinement of unit-cell volume, bulk modulus and its pressure derivatives all characterized by low errors, is possible thanks to a well-established experimental protocol: (1) 8-position centering method proposed by King and Finger,[6] (2) use of SINGLE software,[7] and (3) use of dedicated single-crystal diffractometers equipped with point detectors.[1]

On the other hand a comparable accuracy in the determination of crystal structures (i.e., atomic coordinates) at high pressure is often lacking. Even if a great effort has been made in the last decade to obtain crystal structure data of high quality (e.g., Refs. 8 and 9), we still observe a large scatter of data when various crystal structure parameters are plotted as a function of pressure (e.g., bond lengths, polyhedral volume, distortion parameters). This results from several problems: (1) the access to reciprocal space is limited due to the DAC body, (the effective ratio of reflections to refined parameters is often too low); (2) significant reflection intensity decrease due to the strong absorption by the DAC; (3) general complexity in the background of the diffraction pattern due to the presence of extra reflections from the diamond anvils and diffraction rings from the steel gasket and especially from the beryllium backing plates.

Backing plates play a crucial role not only in supporting the diamond anvils but also in the x-ray absorption, in the opening angle of the windows affecting the x-ray access and in the maximum pressure attainable. It is therefore clear that an improvement in the backing plates could represent an important step towards a general improvement of the structural data collected under high-pressure conditions. In this light, Refs. 10–12 proposed using diamond-backing plates (DBP) instead of the typical Be-backing plates (BBP) for single-crystal diamond-anvil cells (Fig. 1). In general, the advantages of using DBP instead of those made of polycrystalline Be are mainly related to the (a) absence of Be-powder rings (Fig. 2) and to the (b) much higher-pressure generation (e.g., Ref. 11).

In order to definitively prove how DBP can really improve structural data collected with a diamond-anvil cell for single-crystal x-ray diffraction we show in this work a direct comparison between two crystal structure datasets collected for the same single crystal loaded with the same orientation in two identical diamond-anvil cells except that one was equipped with DBP and the second equipped with BBP.

## II. EXPERIMENTAL

The synthetic single crystal of composition $NaInSi_2O_6$ (space group $C2/c$) came from the synthesis batch described in Ohashi *et al.*[13] It is colorless and of about $150 \times 80 \times 50$ $\mu m^3$ in size. The crystal was loaded in an ETH-type DAC equipped with diamond-backing plates (Miletich *et al.*,[10] Fig. 1(a)) and in a second identical DAC but this time equipped with Be-backing plates (Fig. 1(b)). Two stainless steel gaskets preindented to 90 $\mu$m with a spark eroded hole of 200 $\mu$m in diameter were used (diamond culets 600 $\mu$m).

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a)Author to whom correspondence should be addressed. Electronic mail: fabrizio.nestola@unipd.it.
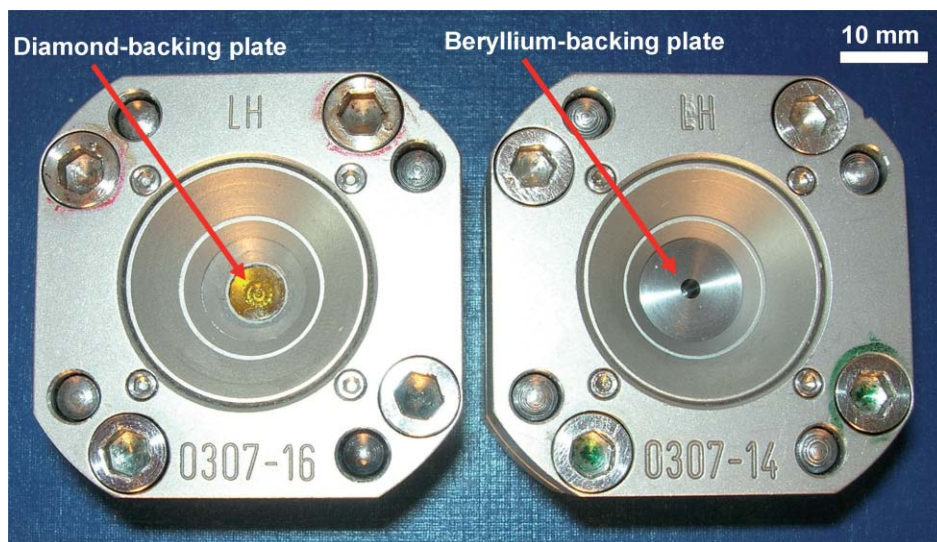
FIG. 1. (Color online) ETH-type diamond-anvil cells equipped with diamond (left side) and beryllium-backing plates (right side).[10]

No pressure transmitting medium was used in order to perform the measurements at an identical pressure (room pressure) and to avoid any experimental differences apart from the backing plates.

Complete intensity data were measured using a Bruker-AXS four-circle diffractometer equipped with a Smart1000 CCD area detector (6.25 × 6.25 cm active area with a resolution of 81.92 pixels cm$^{-1}$) and a flat graphite monochromator, using MoK$\alpha$ radiation and a sample-to-detector distance of 5.5 cm. A total of 1800 exposures (frame width = 0.2°, time = 30 s) were collected. The data collections were made in 16 separate $\omega$-scans covering practically all of the available reciprocal space up to 60° in 2$\theta$. Each scan covered a span of 20° in $\omega$ with the detector (2$\theta$ circle) positioned so as to be parallel to the planes of the gasket and culet faces in the middle of the scan range. This orientation of the detector relative to DAC completely avoids creating blind regions on the detector (parts of the detector surface shaded by the DAC body) at this sample-detector distance. Eight of the scans were performed with the $\phi$ set so that the primary beam was entering

one side of the DAC, the other eight with $\phi$ set 180° away, so that the primary beam entered the other side of DAC first. This allows the crystal displacement from the goniometer center along the beam to be refined. In each group of runs, eight were performed with $\chi$ set to 0°, which makes $\phi$ and $\omega$ axes coincident, summing to a total sweep angle for the primary beam of 80° from both sides of the DAC, covering close to the full opening angle of the beryllium and diamond window. A further four scans were performed with $\chi$ set to 90° and the remaining at various angles to ensure the best coverage of the rest of the unshaded portion of reciprocal space. The data collection strategy, with differences in $\omega$ and 2$\theta$ angles less than 15°, also minimized the potential shadowing effect of the gasket. The SMART software was used for lattice determination and data collection. Data were integrated with SAINT+ (Bruker-AXS) and corrected for absorption (ABSORB (Ref. 14)) leading to a significant improvement in R$_{int}$ for both the dataset here measured.

Weighted structural refinements were done using the SHELX-97 package.[15] The refinements were performed in
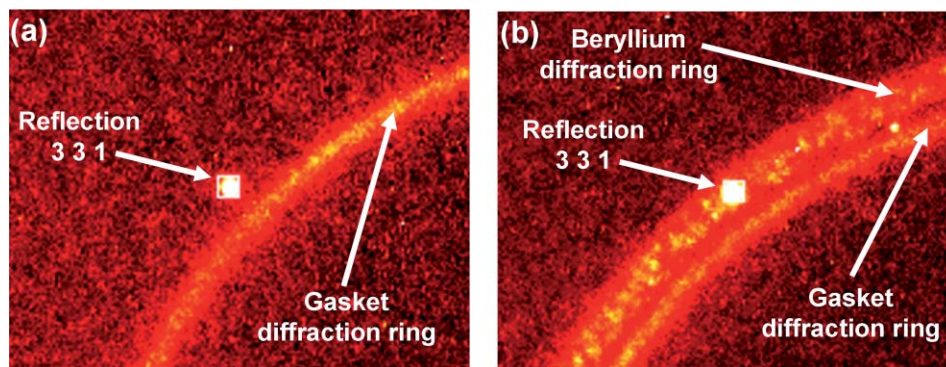


FIG. 2. (Color online) Comparison between measurements obtained with the diamond (a) and beryllium-backing plates (b) in the diamond-anvil cells. In (b) the non-uniform diffraction ring due to the beryllium backing plates overlaps the reflection 3 3 1 while the same reflection collected using the diamond-backing plates (a) is not affected by any experimental problem.

TABLE I. Unit-cell parameters and crystal-structure refinement data for $NaInSi_2O_6$ from the data collections performed in the diamond-anvil cells with the BBP and DBP.

|  | BBP | DBP |
|---|---|---|
| $a$ (Å) | 9.888(1) | 9.904(1) |
| $b$ (Å) | 9.133(1) | 9.136(1) |
| $c$ (Å) | 5.3641(3) | 5.3699(3) |
| $\beta$ (°) | 107.291(6) | 107.247(6) |
| $V$ (Å$^3$) | 462.27(6) | 464.03(5) |
| Unique reflections[a] | 280 | 284 |
| $R_{int}$ (%) | 8.6 | 5.0 |
| Max. $2\theta$ (°) | 56.2 | 56.5 |
| Range of *hkl* | $-11 < h < 11$ | $-10 < h < 11$ |
|  | $-9 < k < 9$ | $-9 < k < 9$ |
|  | $-7 < l < 7$ | $-7 < l < 7$ |
| $R_1$ (%) (l$F_0$l $> 4\sigma$) | 4.9 | 3.2 |
| $wR^2$ (%) | 13.8 | 9.5 |
| GooF | 1.2 | 0.9 |
| Parameters refined | 25 | 25 |

[a]$F_0 > 4\sigma(F_0)$.

space group *C2/c* starting from the atomic coordinates of Ohashi *et al.*[13] The refinements were done using neutral-atom scattering factors for all the atoms. The In site was refined with anisotropic displacement parameters, whereas the other sites were refined isotropically. The unit-cell volumes and the atomic coordinates refined for both loadings were within one standard deviation of those published on the same composition by Ohashi *et al.*[13] indicating that the measurements with the crystal loaded in the two DACs are reliable. Unit-cell parameters, crystal, and refinement data are reported in Table I, atomic coordinates and atomic displacement parameters are in Table II, whereas bond lengths and polyhedral volumes are reported in Table III. In Tables II and III the data for the same $NaInSi_2O_6$ sample studied by Ohashi *et al.*[13] in air are reported for purpose of comparison. For both refinements we adopted the same weighting scheme proposed by SHELX-97 program (a unique weight of 0.079 was used for both the refinements providing the best agreement factor and GooF values, see Table I; this weighting scheme represents the best compromise between the two refinements).

## III. RESULTS AND DISCUSSION

Based on data reported in Table I, it is evident that the unit-cell parameters between the two datasets show differences totally acceptable for data collected on a CCD detector (unit-cell volume within one standard deviation). Using our data collection strategy the number of unique reflections as well as the $2\theta$ range of the measured reflections is nearly

TABLE II. Atomic coordinates and thermal parameters for $NaInSi_2O_6$ obtained using the diamond-anvil cells with the BBP and DBP.

**BBP DAC**

|  | In | Na | Si | O1 | O2 | O3 |
|---|---|---|---|---|---|---|
| x | 0 | 0 | 0.2918(4) | 0.1189(10) | 0.3582(8) | 0.3481(7) |
| y | 0.8945(1) | 0.3026(10) | 0.0864(4) | 0.0806(10) | 0.2453(10) | 0.0125(11) |
| z | 0.25 | 0.25 | 0.2479(5) | 0.1529(14) | 0.3163(12) | 0.0171(11) |
| $U_{11}$ | 0.0084(10) |  |  |  |  |  |
| $U_{22}$ | 0.0086(13) |  |  |  |  |  |
| $U_{33}$ | 0.0075(7) |  |  |  |  |  |
| $U_{23}$ | 0 |  |  |  |  |  |
| $U_{13}$ | 0.0019(5) |  |  |  |  |  |
| $U_{12}$ | 0 |  |  |  |  |  |
| $U_{eq/iso}$ | 0.0083(6) | 0.0192(15) | 0.0086(8) | 0.0105(17) | 0.0126(16) | 0.0084(16) |

**DBP DAC**

|  | In | Na | Si | O1 | O2 | O3 |
|---|---|---|---|---|---|---|
| x | 0 | 0 | 0.2918(3) | 0.1197(6) | 0.3566(6) | 0.3486(5) |
| y | 0.89474(9) | 0.3037(7) | 0.0865(3) | 0.0801(6) | 0.2459(7) | 0.0106(7) |
| z | 0.25 | 0.25 | 0.2474(4) | 0.1522(10) | 0.3174(8) | 0.0176(8) |
| $U_{11}$ | 0.0038(7) |  |  |  |  |  |
| $U_{22}$ | 0.0076(8) |  |  |  |  |  |
| $U_{33}$ | 0.0050(5) |  |  |  |  |  |
| $U_{23}$ | 0 |  |  |  |  |  |
| $U_{13}$ | 0.0013(4) |  |  |  |  |  |
| $U_{12}$ | 0 |  |  |  |  |  |
| $U_{eq/iso}$ | 0.0055(4) | 0.0206(12) | 0.0063(5) | 0.0074(12) | 0.0083(12) | 0.0067(12) |

**Crystal in air[a]**

|  | In | Na | Si | O1 | O2 | O3 |
|---|---|---|---|---|---|---|
| x | 0 | 0 | 0.29172(7) | 0.1190(2) | 0.3568(2) | 0.3488(1) |
| y | 0.89471(2) | 0.3033(2) | 0.08660(6) | 0.0797(2) | 0.2455(2) | 0.0115(2) |
| z | 0.25 | 0.25 | 0.2475(1) | 0.1505(3) | 0.3177(3) | 0.0172(3) |
| $U_{eq}$ | 0.0053(1) | 0.0186(30) | 0.0052(1) | 0.0067(2) | 0.0095(2) | 0.0084(2) |

[a]Crystal in air (Ref. 13), the anisotropic thermal parameters for In was not available.

TABLE III. Bond lengths and polyhedral volumes for $NaInSi_2O_6$ obtained using the diamond-anvil cells with the BBP and DBP compared to literature data. Polyhedral volumes and their standard deviations have been calculated using IVTON program (Ref. 16).

|  | BBP | DBP | Air[a] |
|---|---|---|---|
| Na–O2 (Å) | 2.373(7) | 2.380(5) | 2.375(2) |
| Na–O1 (Å) | 2.475(12) | 2.494(8) | 2.493(2) |
| Na–O3 (Å) | 2.525(11) | 2.503(7) | 2.511(2) |
| Na–O3 (Å) | 2.905(9) | 2.910(6) | 2.903(2) |
| < Na–O> (Å) | 2.570 | 2.572 | 2.570 |
| $V$ (Å$^3$) | 28.05(18) | 28.17(13) | 28.11(4) |
|  |  |  |  |
| In–O2 (Å) | 2.060(9) | 2.074(6) | 2.074(2) |
| In–O1 (Å) | 2.144(7) | 2.146(5) | 2.136(1) |
| In–O1 (Å) | 2.215(7) | 2.217(6) | 2.213(2) |
| < In–O> (Å) | 2.140 | 2.146 | 2.141 |
| $V$ (Å$^3$) | 12.87(9) | 12.98(7) | 12.89(2) |
|  |  |  |  |
| Si–O1 (Å) | 1.590(9) | 1.591(6) | 1.587(2) |
| Si–O2 (Å) | 1.633(9) | 1.629(7) | 1.634(2) |
| Si–O3 (Å) | 1.645(7) | 1.650(5) | 1.652(2) |
| Si–O3 (Å) | 1.653(8) | 1.653(5) | 1.653(2) |
| < Si–O> (Å) | 1.630 | 1.631 | 1.632 |
| $V$ (Å$^3$) | 2.22(2) | 2.22(2) | 2.222(6) |

[a]Crystal in air (Ref. 13).

identical for the two data collections. However, a significant improvement in the data collected using the DBP is indicated by the decrease in $R_{int}$, $R_1$, and $wR^2$ by 42%, 35%, and 31%, respectively (see Table I).

In Table II the refined atomic coordinates and the thermal parameters are reported. The atomic coordinates for both of the datasets measured with the BBP and DBP are within one or two standard deviations of one another, indicating good experimental reproducibility between the two data collections. The only coordinate showing a slight difference between the two datasets is the $y$ of O1 atom. For purpose of comparison the atomic coordinates for the crystal in air performed by Ohashi *et al.*[13] are reported and show an excellent agreement. For O1 the data by Ohashi *et al.*[13] provide a value of 0.0797(2), which is very close (1 $\sigma$) to the data collected using DBP (see Table II). The data collected with the DBP are generally characterized by a strong decrease in the atomic coordinate standard deviation with differences of between 20% and 50%. The atomic displacement parameters are particularly sensitive to the limitations in data obtained under high-pressure conditions. There are significant differences for the two experimental configurations, with a general decrease in values of the displacement parameters from the DBP measurement (between 12% and 55%) and also a general decrease in their standard deviations (between 20% and 38%). Only the parameters of Na show negligible differences.

As a consequence of the general improvement in the atomic coordinates and atomic displacement parameters using the DBP we observe that the errors of bond lengths and polyhedral volumes are also significantly decreased (Table III). In general, Na-O distances show a decrease in the errors between 29% and 36%, In-O distances show a decrease between 29% and 33% and Si-O distances a decrease between

22% and 38%. The Na and In polyhedral volumes show a decrease in the error by 28% and 22%, respectively, whereas the Si tetrahedron is characterized by a similar error in the two datasets.

For this work, we have chosen a crystal structure not experimentally excessively complex to be determined when measured in a pressure cell. The purpose was to load the sample using the same orientation and have all the experimental details equal with fully equivalent datasets in order to obtain a reliable quantitative comparison of the two types of backing plates. To be remarked that using beryllium or diamond-backing plates does not affect the opening angle. It has to pointed out that with respect to the Boehler-Almax-type diamond-anvil cell (not equipped by any backing plates), in general, the ETH cell with diamond-backing plates, even if show similar aperture angle at the same time, is characterized by a lower x-ray transmission and allows to reach lower pressures. However, at present the ETH-type cell remains the most widely used one for single-crystal x-ray diffraction and this is why we performed our work on such diamond-anvil cell.

Our data definitely demonstrate that the use of diamond-backing plates instead of beryllium ones significantly improves the quality of the structure refinement, resulting in a general decrease of all standard deviations associated with atomic coordinates and consequently with the bond lengths. An improved determination of the thermal parameters was also observed and could prove to be crucial for a correct structural analysis in cases of more problematic crystals with large unit cells and/or weaker diffraction intensities. The resulting structural data are more reliable and able to reveal more subtle structural changes under pressure. This strong improvement must be mainly searched in the absence of diffraction rings due to the Be-backing plates: as can be easily noted in Fig. 2, the absence of the Be-backing plates allow to include in the structure refinement also the diffraction intensities of those reflections that usually lye on the Be diffraction rings in a conventional Be-backing plates diamond-anvil cell and which are affected by strong errors due to a non-correct intensity integration.

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