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Trial CAESAR Measurements using MAX80

Kazuhiro FUCHIZAKI[1,*] Akio SUZUKI[2], Hiroki NARUTA[1], Katsumi NAKAMURA[1], and Tomohiro OHUCHI[3]

[1] Department of Physics, Ehime University, Matsuyama 790-8577, Japan

[2] Department of Earth Science, Tohoku University, Sendai 980-8578, Japan

[3]Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

We succeeded in *in situ* combined angle- and energy-dispersive structural analysis and refinement (CAESAR) measurements under high pressure and temperature using MAX80 installed at beamline NE5C, PF-AR, which must be the first successful trial at that beamline to the authors.

1 Introduction

High-pressure experiments were often carried out using a diamond anvil cell (DAC), which allows us to reach a megabar region relatively easily. In addition, the laser heating technique, when combined, can elevate sample temperature beyond several thousand Kelvin. This aspect convinces us why a DAC is used in front-line research on Earth science. However, a very intense, low-emittance beam is required to measure a minimal amount of DAC samples. Because of the limited number of such facilities, the number of accessible researchers is also limited. Non-hydrostaticity realized in a sample space due to uniaxial compression is another problem. We usually need to fill the sample chamber with a suitable pressure-transmitting medium, which should not chemically react with a sample.

A multianvil press (MAP) is another crucial device to generate high pressure. Recently, it can attain beyond 10 GPa, for example, in a 6–6 or 6–8 compression mode. It can still afford to give a sample hole of 1 mm in diameter even when using a truncated edge length (TEL) of 3 mm as the inner side of anvils. A larger sample can facilitate obtaining valuable data even with synchrotron sources of the second generation. The non-hydrostaticity conditions are undoubtedly reduced.

However, a high-pressure vessel with a MAP usually restricts the diffraction geometry to the energy-dispersive diffraction (EDD) mode. EDD data obtained with a fixed scattering angle 2θ can identify a unit cell when treating crystalline materials but cannot provide reliable crystallographic information such as atomic positions, bonding characteristics, and so forth. This unpleasant aspect may be improvable when measurements use an imaging plate in an angle-dispersive diffraction (ADD) mode. However, the pressure vessel mentioned above often limits the 2θ range to 15 degrees at most. Hence, the minimal *d*-spacing remains 0.95 A even for a typical photon energy of 50 keV.

Wang *et al.* overcame this situation by devising a new technique, combined angle- and energy-dispersive structural analysis and refinement (CAESAR) [1]. The technique can be briefly described as follows: For an initially set 2θ, a standard EDD measurement is carried out to obtain the intensity distribution as a function of photon energy E. (In a solid-state detector (SSD) measurement, photons are classified into multichannel bins according to their scattered energies. The relation between channel and energy is usually prescribed separately using characteristic x-rays of multiple substances.) The scattering angle is then changed by an amount $\Delta(2\theta)$ and a measurement is repeated until the final 2θ that can cover the desired range of diffraction. We thus obtain the scattered intensity distribution $I(E,2\theta)$ as a function of both energy and scattering angle. A cross-section at constant E yields the intensity distribution as a function of the scattering angle.

Wang *et al.* [1] demonstrated that the above prescription worked using a MAP installed in synchrotron x-ray sources at APS and SPring-8. Indeed, 'ADD' data tolerable against the Rietveld analysis were obtained from CAESAR measurements for α-Al_2O_3 at ambient conditions and for a mixture of MgO and Au at high pressure.

MAX80, a MAP installed at NE5C in PF-AR, has been operated since the late 1980s. However, to the authors' knowledge, no CAESAR measurements have been tried. Because they are exploring a region of about 15 GPa for SnI_4 to unveil its structural evolution upon pressure-induced amorphization, it is worth challenging CAESAR measurements on this occasion. Because of the relative ease of MAX80's temperature control, the diffraction data could complement the room-temperature measurements of Ohmura et al. using a DAC. The success of measurements would enhance the appeal of MAX80.

2 Experiment

Before carrying out CAESAR measurements, we simulated the distribution of major Bragg peaks of SnI_4 in the ambient crystalline phase (CP-I) to assess the 2θ range with which to obtain meaningful ADD patterns. The upper panel of Fig. 1 depicts the simulated intensity loci of primary Bragg reflections, 222, 400, 440, and 622, on the 2θ–channel plane, where we used the recent calibration result for the relation between the photon energy E and channel number of the multichannel analyzer equipped with an SSD installed in MAX80. For example, if we choose the 600-channel section for the ADD pattern, it is appropriate to adopt an interval between 5 and 12 degrees for the scattering angle. Let us assume it takes at least 2 minutes to measure the minimal scattered intensity at a given angle. Then, if the measurement is made every 0.01 degrees of scattering angle, as was done by Wang *et al.* [1], more than one day is necessary for a whole measurement, including the time required for driving the SSD. Therefore, in our CAESAR measurements, setting the minimum 2θ steps to be 0.1 degrees is practical, considering the usual beamtime given. The interval of 0.1 degrees is too coarse for a diffraction pattern to be analyzed adequately. We hope the intensity interpolation from neighboring channels could equally work, as illustrated by Wang *et al* [1].

Compression was made in a 6–6 mode with an inner set of anvils of a truncated edge length (TEL) of 3 mm. Applying such a TEL of anvils was pioneered by Kawazoe *et al*. [2], and we fully utilized their developed technique to reach a pressure region of about 15 GPa. A fine-powdered sample of high-purity SnI_4 was loaded in a container made of hBN enclosed by a TiB_2 sleeve, to which an electric current was applied to heat the sample. The relationship between the power supplied and the temperature generated was well-calibrated to read the temperature at the sample position.

3 Results and Discussion

A CAESAR measurement conducted at ambient conditions is presented here as a preliminary report; a total result, including measurements at elevated temperatures under ~15 GPa, will be reported shortly.

The lower panel of Fig. 1 shows a contour map of the raw intensity distribution *I*(2θq, channel) measured with the magnitude of intensity illustrated as a heat map on the right. The spectra below 500 channels, consisting of characteristic lines of Sn and I, were unavailable for transforming to an ADD pattern and were removed from the map. Comparing the map thus measured with the one simulated (the upper panel), it is apparent that the brighter loci originate from the primary peaks.

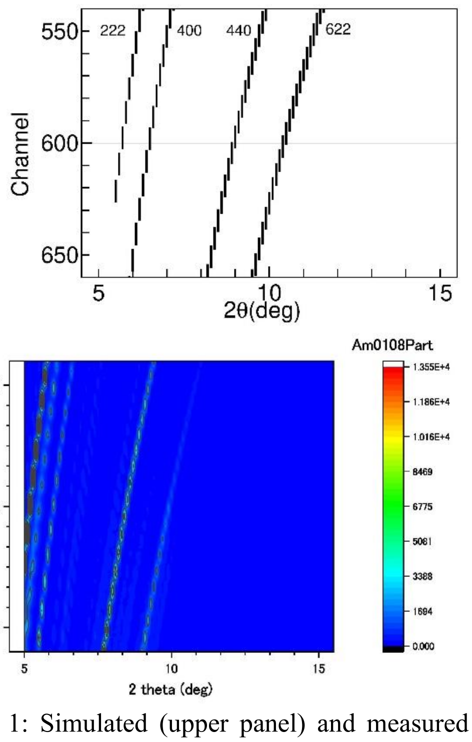

Fig. 1: Simulated (upper panel) and measured (lower panel) loci of the primary Bragg peaks for SnI4's CP-I.

We chose the 600-channel data to obtain an ADD pattern in which the data on the adjacent channels complement intervening intensities. Figure 2 shows the pattern thus obtained after making intensity corrections regarding diffracting volume. Although we measured the intensities every 0.1 degrees, the complement works well as judged from the close resemblance to the ADD intensity distribution resulting from a DAC experiment. Indeed, the intensity distribution, representing an extra bump between 320 and 321 due to diffraction from a container, depicted in the inset proves the perfection of the interpolation. Although the background intensity is nonuniform and relatively high, the pattern may allow us to analyze with the Rietveld method. The result will be included in the full report mentioned above.

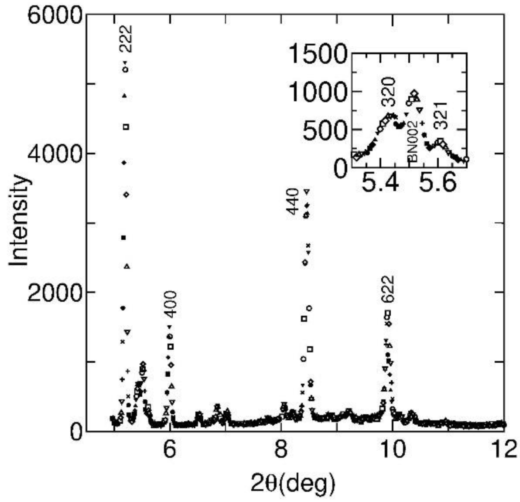

Fig. 2: An ADD pattern converted from the present CAESAR measurement for SnI_4 at ambient conditions.

We could perform four CAESAR measurements in a single compression–decompression cycle. However, each CAESAR measurement was done entirely manually; we changed the scattering angle as one measurement at an angle was over by issuing instructions through a PC controlling the measuring system. We could have been freed from the restriction for more than 12 hours if the process had been automated.

3 Conclusion

We could thus prove that EDD data obtained through MAX80 can be transformed into ADD patterns. Beamline NE5C, in which MAX80 is installed, can use white and monochromatized x-rays, whose switching can be performed in a moment. The facility thus allows simultaneous diffraction and XAFS measurements. MAX80, set up in PF-AR, a synchrotron radiation facility of the second generation, appeals to last a long time. This aspect encourages researchers in high-pressure communities. They must welcome the measurement automation mentioned in the last paragraph.

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* fuchizak@phys.sci.ehime-u.ac.jp