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Feasibility studies for high pressure neutron powder diffraction experiments

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ABSTRACT

We recently performed two neutron powder diffraction experiments on very small samples on the High Intensity Powder Diffractometer (HIPD). These were done to determine the feasibility of performing *in situ* high pressure/high temperature neutron diffraction experiments on HIPD at pressures which would exceed the previous limit of ~50kbar achievable in a neutron diffraction experiment. The first experiment consisted of examining the product from a high pressure preparation done at Stony Brook. The sample, which had been prepared at 65kbar and 1000°C, consisted of a small platinum capsule (3x3x3 mm) filled with $CaGeO_3$ perovskite . The weights of the capsule included 225mg of platinum and 49mg of the germanate. A diffraction experiment taking ~8.6hrs at a LANSCE proton beam current of ~53μA gave peaks of good intensity from both Pt and $CaGeO_3$; we could begin to see them after only 20min of beam time. The second experiment was to test the possibility of diffraction from a high pressure apparatus. We placed in the HIPD sample position the central assembly from a 100kbar octahedral press. Four tungsten carbide anvils and a copper block previously pressed to 65kbar were held in an aluminum frame. The sample consisted of a small bit of nickel foil (175mg) placed in a 3mm hole in the copper block. The active sample volume (~1mm^3) is defined by the gap (~0.7mm) between the anvils and the length of the sample (~4mm). A small portion of the copper block is also seen in this arrangement. This is viewed at 90° 2Θ through a similar gap between the anvils by 4 1/2"x12" ^{3}He counter tubes. This arrangement simulates the operating conditions of a high pressure run at 100kbar and takes advantage of the fixed instrument geometry possible in time-of-flight neutron diffraction experiments. We obtained a diffraction pattern in ~7.1hrs and ~57μA beam current which clearly showed peaks from both copper and nickel with no evidence of diffraction from the anvils or any other part of the assembly. These two experiments clearly demonstrate the feasibility of performing high pressure *in situ* diffraction experiments in excess of 100kbar on HIPD at LANSCE.

I. INTRODUCTION

Due to its very short incident flight path (9m), the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) provides a very intense incident neutron beam so that typical "little finger" sized samples frequently scatter sufficiently strongly so that data collection times are often much less than one hour. Thus it was possible to consider obtaining diffraction patterns from considerably smaller samples and in the very

restricted geometry of a high pressure apparatus. To explore these possibilities two experiments were envisioned; one on material obtained from a high pressure/temperature synthesis run and one on a dummy sample inside a mockup of a pressure apparatus.

II. EXPERIMENTAL

A high pressure/temperature synthesis of $CaGeO_3$ was performed at the High Pressure Laboratory, SUNY, Stony Brook, NY. A stoichiometric mixture of CaO and GeO_2 was placed in a 3mm Pt capsule which was inserted in a 6x6x6mm Cu block. The Cu block was subjected to 65kb pressure and 1000°C temperature in the Kobe Steel D1A-6 octahedral press to effect the synthesis.

For the first diffraction experiment, the Pt capsule containing the synthesized $CaGeO_3$ was supported in a LANSCE standard 1/4"x1-3/4" vanadium can by a small piece of Ta foil so that the capsule would be centered in the HIPD beam. A diffraction data set was taken over 8.7hrs with the LANSCE source operating at ~53μA. After the diffraction experiment, the $CaGeO_3$ was extracted from the Pt capsule and weighed. There was 49mg of $CaGeO_3$ and 225mg of Pt in the sample. The Ta foil was not weighed. The part of data set with $4.8Å \geq d \geq 0.4Å$ obtained from the four 1/2"x12" 10atm ^3He counter tubes positioned 1.25m from the sample at ~153°2Θ were subjected to a 3 phase ($CaGeO_3$, Pt and Ta) Rietveld refinement using the software GSAS[1] to give the residuals $R_{wp}=4.78\%$, $R_p=3.12\%$ and $\chi^2=1.76$. The results of this refinement are given in Table 1.

Table 1. Results of refinement of $CaGeO_3$

CaGeO3 - orthorhombic, Pbnm

a = 5.258(3)Å, b = 5.271(3)Å, c = 7.448(4)Å at 300K

Atom parameters

atom	x	y	z
Ca	0.026(5)	-0.18(7)	1/4
Ge	1/2	0	0
O(1)	0.038(6)	0.426(7)	1/4
O(2)	-0.266(4)	0.282(5)	0.040(2)

$U_{iso} = 0.0038(9)Å^2$

The fit to the data from the final refinement is displayed in Figure 1 in three ways to emphasize different aspects of its quality. The orthorhombic $CaGeO_3$ structure is that of one of the most common distortions of perovskite[2] and results from a twisting of the GeO_6 octahedra as shown in Figure 2. The lattice parameters for the other two phases present in the sample (Pt, a=3.92261(6)Å and Ta, a=3.3035(4)Å) obtained in the refinement agree quite well with the commonly accepted values[3].

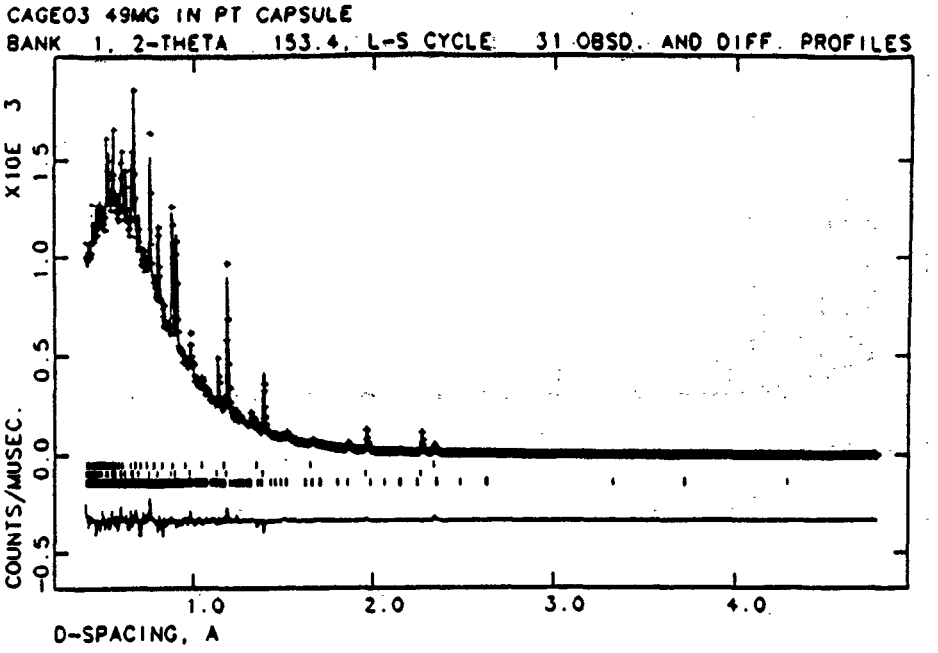

Figure 1a. Observed and calculated profile for the $CaGeO_3$ in Pt capsule for data from 153°2Θ bank on HIPD. The reflection markers are for $CaGeO_3$ at bottom, Pt in middle and Ta at top. The difference (I_{obs}-I_{calc}) curve is also shown. The intensities are shown as counts/μsec.

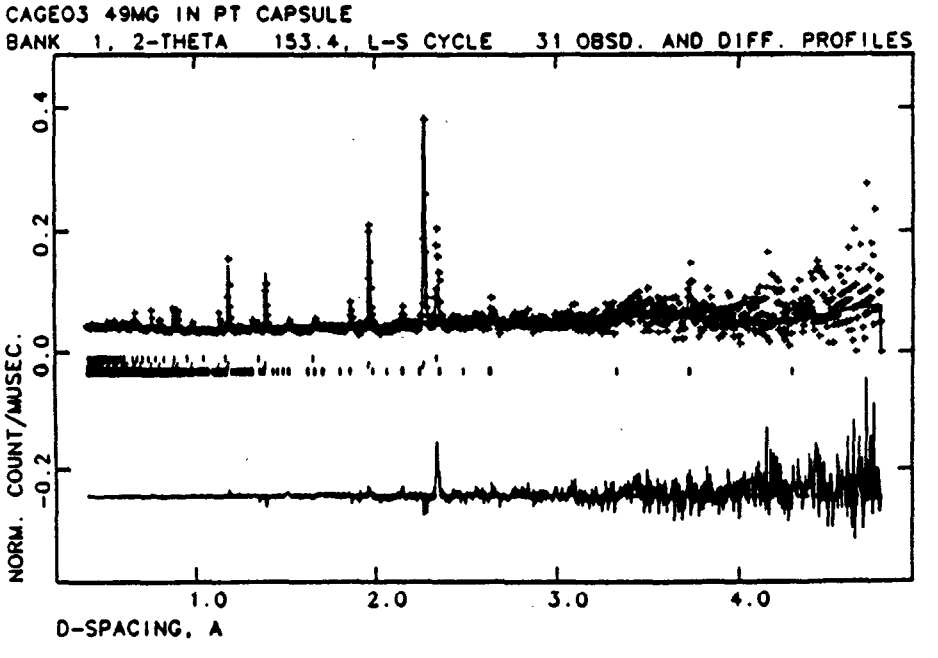

Figure 1b. The same data as shown in Figure 1a except that the intensities are normalized by an incident spectrum measured by the counter bank from a V/Nb alloy rod. The flatness of the background is evident in this figure.

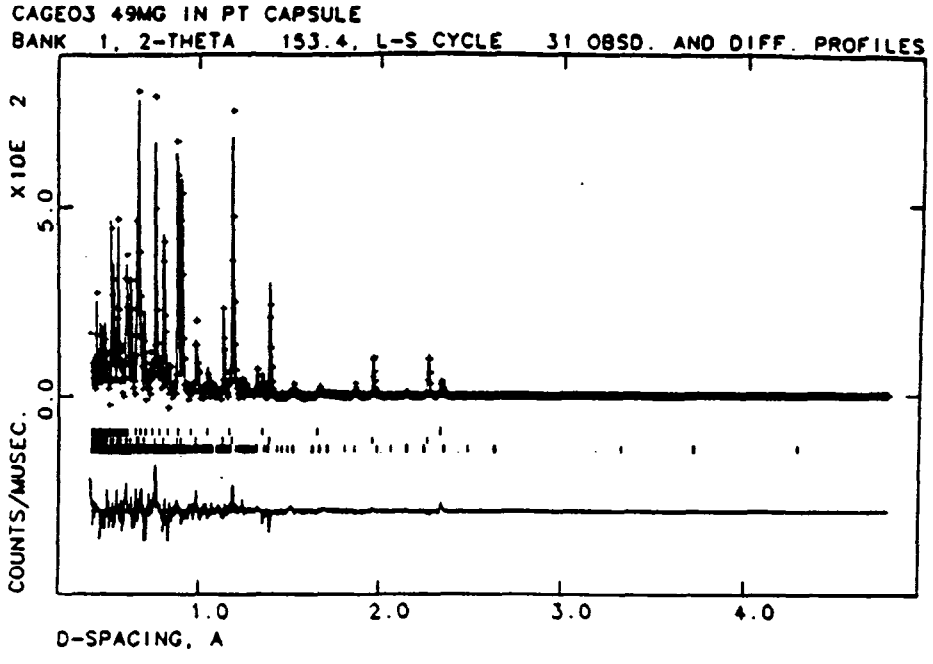

Figure 1c. The same data as shown in Figure 1a except that the calculated background from the Rietveld refinement is subtracted from both the observed intensities and the calculated curve. This shows the fit to the Bragg peaks.

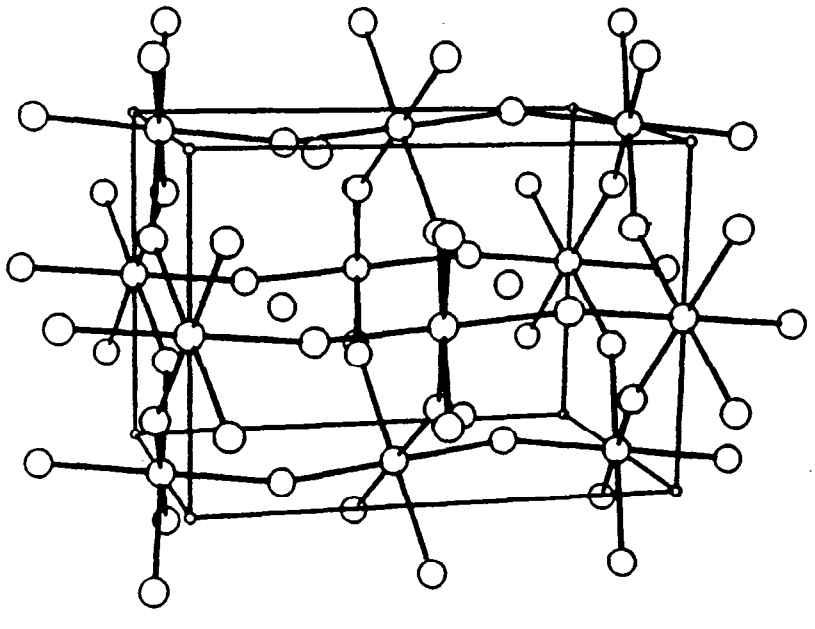

Figure 2. A sketch of the structure of CaGeO3. in this view the a axis is into the paper, the b axis is vertical and the c axis is horizontal. Bonds are shown between the Ge and O atoms.

For the second diffraction experiment, four of the six WC anvils and the previously pressed Cu block from the D1A-6 press were assembled (Figure 3) in a specially constructed Al frame so that the anvils were positioned to simulate the arrangement at 65kb.

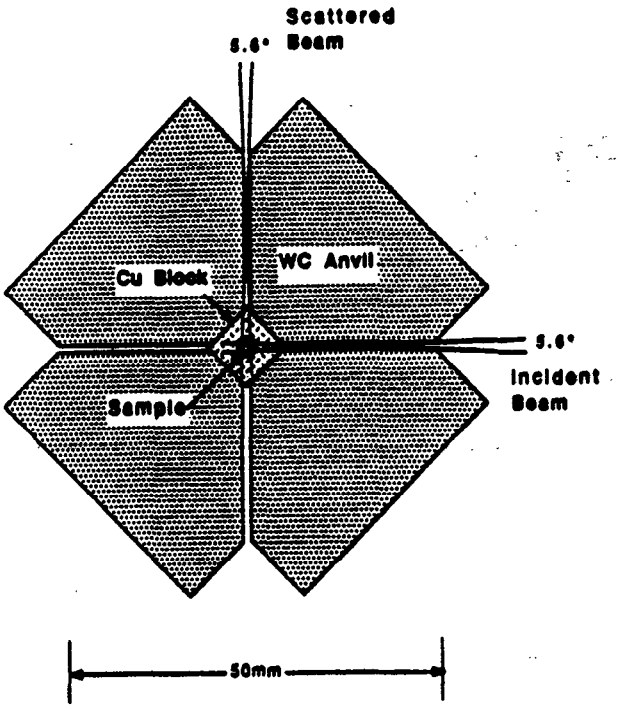

Figure 3. A sketch of the mockup of the arrangement of four WC anvils in an octahedral high pressure apparatus. The incident beam enters between a gap in the anvils and the scattered beam at 90°2Θ exits between a similar gap. The simultaneously illuminated and viewed volume is confined to the sample and does not include any part of an anvil.

The openings between the WC anvils were ~0.7mm giving angular apertures of 5.6°. A small bit of Ni sheet (175mg) was placed in the sample hole in the Cu block. Sheet Cd was affixed to outside of this apparatus to provide crude shielding leaving apertures for the incident and 90°2Θ scattered beams. This assembly was placed in the HIPD and a diffraction data set was taken for 7.1hrs with the LANSCE source operating at ~57μA. The part of data set with 2.75Å≥d≥0.4Å obtained from the four 1/2"x12" 10atm ^{3}He counter tubes positioned 1.0m from the sample at ~90°2Θ were subjected to a 2 phase (Ni and Cu) Rietveld refinement using the software GSAS to give the residuals R_{wp}=5.22%, R_p=3.21% and χ^2=3.10. The fit to the data from the final refinement is displayed in Figure 4 in three ways to emphasize different aspects of its quality. The lattice parameter for Ni (a=3.5235(2)Å) agrees very well with the accepted value[3] but the value obtained for Cu (a=3.6129(3)Å)is 0.057% smaller than expected because of residual stress after relaxation from the 65kb synthesis run. Both phases showed substantial preferred orientation and the unmodeled component was the major error in the least squares fit. In addition, there was an extra background contribution at short d-spacings above the flat background found in the first experiment (compare Figs. 1b and 4b) and in patterns from typical large samples. It probably arose from scattering by the anvils and the Al frame because the incident beam was not collimated to match the extremely small acceptance of the high pressure assembly.

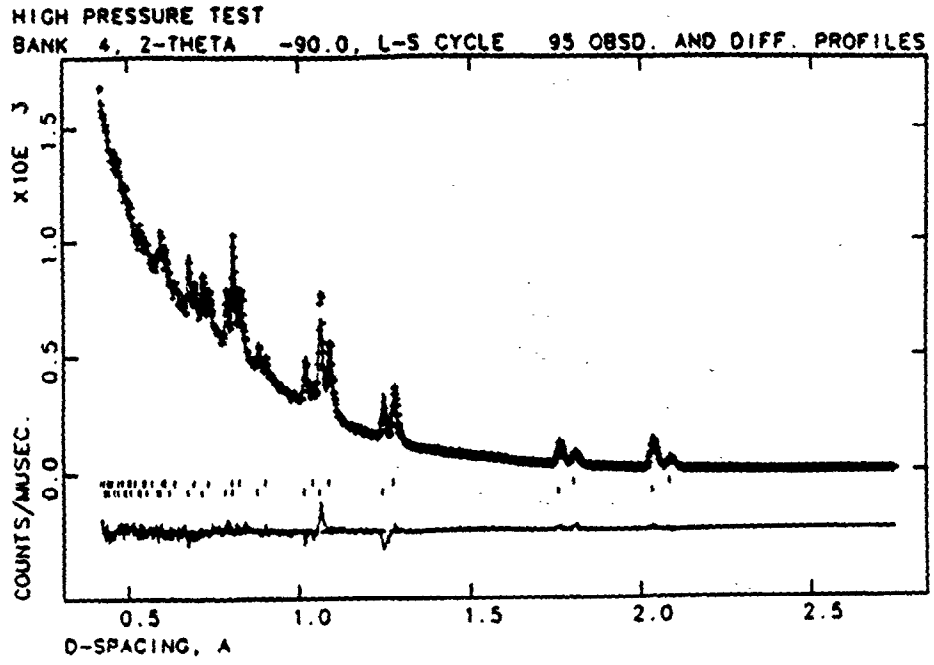

Figure 4a. Observed and calculated profile for the high pressure mockup for data from 90°2Θ bank on HIPD. The reflection markers are for Ni at bottom and Cu at top. The difference (I_{obs}-I_{calc}) curve is also shown. The intensities are shown as counts/μsec.

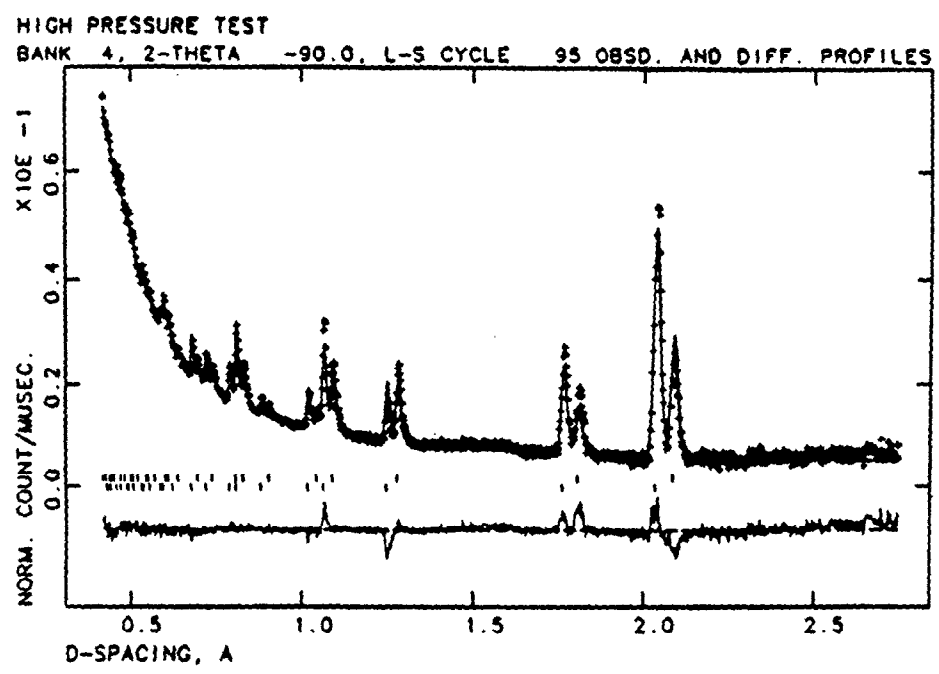

Figure 4b. The same data as shown in Figure 4a except that the intensities are normalized by an incident spectrum measured by the counter bank from a V/Nb alloy rod. The extra background at short d-spacings is evident.

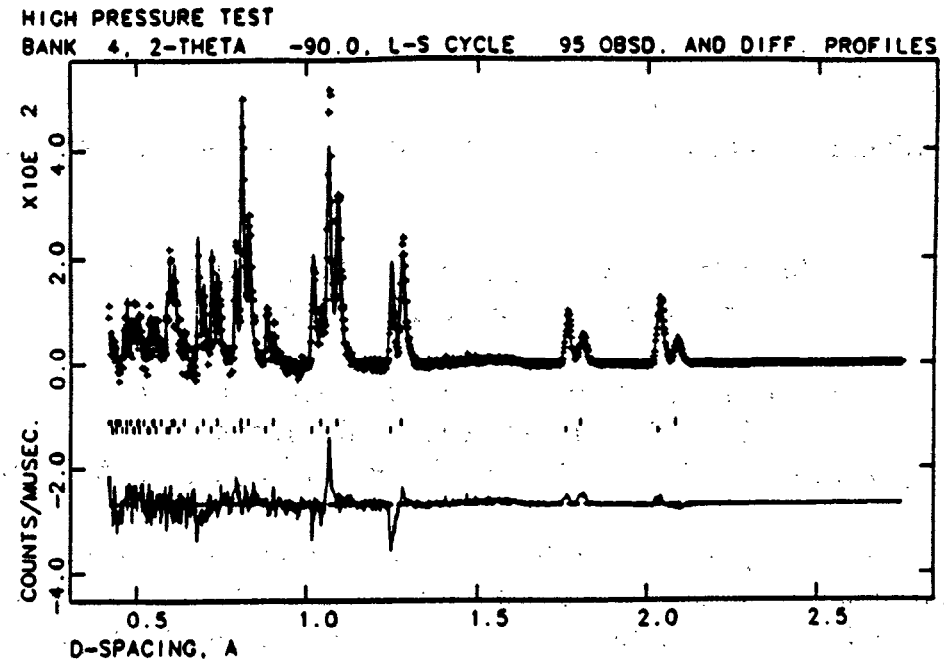

Figure 4c. The same data as shown in Figure 4a except that the calculated background from the Rietveld refinement is subtracted from both the observed intensities and the calculated curve. The error in the fit to the Bragg peaks from preferred orientation is evident.

III. CONCLUSION

Clearly diffraction data can be obtained from small samples on HIPD that when subjected to Rietveld refinement can give useful crystal structure information. This result was sufficiently encouraging that we have performed a number of diffraction experiments on a variety of small (20-300mg) samples with generally good results. In addition, it is feasible to perform diffraction experiments in a high pressure apparatus despite its extremely restrictive aperatures.

References

[1]Larson, A.C. and Von Dreele, R.B., "GSAS - Generalized Crystal Structure Analysis System", Los Alamos National Laboratory Report No. LA-UR-86-748 (1986).

[2]Wycoff, R.W.G., "Crystal Structures, Vol. 1", 2nd ed., Wiley Interscience, New York, pp. 10,16 (1963).

[3]Wycoff, R.W.G., "Crystal Structures, Vol. 2", 2nd ed., Wiley Interscience, New York, pp. 407-410 (1964).