



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Sodiumoxidnitrite and Sodiumoxidarsenate under high pressure	<b>Experiment number:</b> CH 1201
<b>Beamline:</b> ID 9	<b>Date of experiment:</b> from: 19 Sept. 2001 to: 22 Sept. 2001	<b>Date of report:</b> 6 July 2002
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Alessandra Sani	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Dr. Haozhe Liu*, Max Planck Institut für Festkörperforschung, Stuttgart, Germany Dr. Wilhelm Klein*, Max Planck Institut für Festkörperforschung, Stuttgart, Germany Dr. Helmut Haas, Max Planck Institut für Festkörperforschung, Stuttgart, Germany Prof. Dr. Martin Jansen, Max Planck Institut für Festkörperforschung, Stuttgart, Germany		

## Report:

Although  $\text{Na}_3\text{ONO}_2$  was first synthesized in 1937, and called as sodium orthonitrite, it was addressed as sodium oxide nitrite and re-determined as anti-perovskite type cubic structure at ambient conditions by single crystal X-ray diffraction until 1977 [1]. Its low temperature phases were systematically studied by neutron scattering data recently [2]. The compound displays two continue order processes and one discontinue phase transition in which orientational disorder of the nitrite ions is reduced upon the cooling process. However, the high pressure behavior of the compound is unknown up to now. Especially the possibility of pressure induced synthesis of the still unknown orthonitrite  $\text{Na}_3\text{NO}_3$  with the  $\text{NO}_3^-$  ion is worth of investigation. Here we report the results of pressure induced phase transition and amorphization behavior of  $\text{Na}_3\text{ONO}_2$  using *in situ* high pressure techniques within 18 GPa at room temperature and 573 K, respectively.

The crystal structure of  $\text{Na}_3\text{ONO}_2$ , prepared by solid state reaction of sodium oxide ( $\text{Na}_2\text{O}$ ) and sodium nitrite ( $\text{NaNO}_2$ ), has been determined at ambient conditions using X-ray and neutron diffraction data. The high pressure experiments were carried out in a diamond anvil cell (DAC) apparatus. The sample was loaded in a hole of steel gasket in a glove box and no pressure transmitting medium was used due to the severely hygroscopic character of the sample. Several ruby chips were added as pressure marker by its fluorescence pressure calibration method. The angle-dispersive X-ray powder diffraction experiments ( $\lambda=0.41537$  Å) were performed at the beamline ID9 of ESRF. Diffraction patterns were recorded on an

image plate and then converted to the intensity versus  $2\theta$  diffraction angle by using the program FIT2D.

Fig. 1 shows the typical XRD patterns of the sample under various pressures during the compressing processes. The results reveal  $\text{Na}_3\text{ONO}_2$  loses its cubic (space group  $Pm\bar{3}m$ ) symmetry and transforms to a rhombohedral (space group  $R\bar{3}m$ ) high pressure phase (R- $\text{Na}_3\text{ONO}_2$ ) at about 0.7 GPa. The main structural feature of the anti-perovskite structure remains unchanged during the pressure induced phase transition process due to the similarities of the diffraction patterns to the cubic structure. Fig. 2 shows the lattice parameters of R- $\text{Na}_3\text{ONO}_2$  as a function of pressure. As a result of the pressure induced distortion the perfect cubic framework of  $(\text{Na}_3\text{O})^+$  transforms to rhombohedral symmetry, the unit cell angle from  $90^\circ$  at ambient condition to  $90.92^\circ$  at 0.7 GPa, and then gradually to  $94.68^\circ$  at 10.1 GPa. The equation of state of R- $\text{Na}_3\text{ONO}_2$  could be fitted into the second order Birch equation, and its zero pressure bulk modulus was estimated as 47.5 GPa. It indicates that R- $\text{Na}_3\text{ONO}_2$  is a soft high pressure phase, which could work well as pressure transmitting medium itself in DAC during high pressure experiments.

When the pressure was increased up to 11.9 GPa, the ratio between intensities of reflections and background in the diffraction pattern decreases. After 14.5 GPa the crystalline structure of  $\text{Na}_3\text{ONO}_2$  destabilizes and an X-ray diffraction amorphous state achieved. The sample stays in its amorphous state when the pressure was increased up to 18 GPa. In decompressing process, the amorphous state keeps until down to 0.5 GPa. The quenchable behavior of pressure induced amorphization is in agreement with the high pressure Raman results, which is more sensitive than X-ray diffraction to remaining traces of crystallinity. The intensity of the  $\delta$  mode and  $\nu_{as}$  mode of the  $\text{NO}_2$  ion decreases with increasing pressure, and are observed up to 12.4 GPa, then completely disappears as to 14.1 GPa. These Raman peaks do not recover and no Raman active peak, i. e. neither Raman modes of  $\text{NO}_2^-$  or the hypothetical  $\text{NO}_3^{3-}$ , which are possible reaction products, could be observed during the decompressing process to 0.2 GPa. These results indicate that the bond between N-O in the sample disjoints under high pressure, and imply the pressure induced

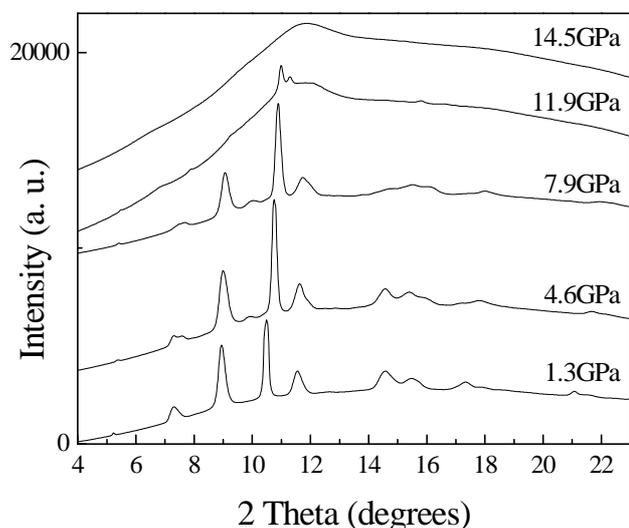


Fig. 1

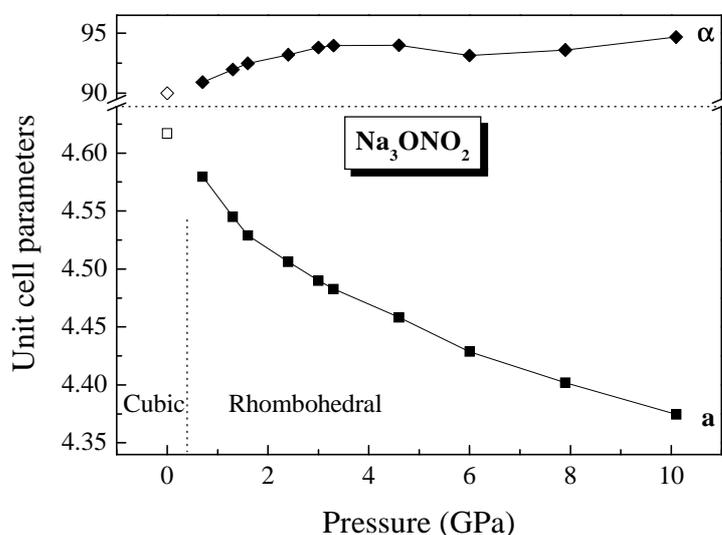


Fig. 2

structural conversion is an irreversible process. These indicates the product, maybe a complicated mixture of high density amorphous phase, do not crystallize again during decompressing maybe inhibited by its topological features because of the lack of activation energy which is necessary for the rearrangement in the solid state.

The pressure induced amorphization has attracted intensive attention from a fundamental viewpoint over the years, and different mechanisms were proposed pertaining on special compounds. One mechanism suggested the pressure dependence of the melting temperature is negative, thus the metastable extension of the melting curve would pass through the amorphization pressure at room temperature, which were observed in ice-I,  $\text{SiO}_2$ , and  $\text{Ca}(\text{OH})_2$  cases. In  $\text{Na}_3\text{ONO}_2$  case, the slowly decomposition instead of melting occurs as heating up to 623 K at ambient conditions, this encourage us to perform high temperature high pressure experiments in order to check the possible negative pressure dependence of decomposition temperature. Using an internal heating DAC device, the high pressure X-ray diffraction experiments at 573 K were carried out to compare with room temperature results. The peaks of little amounts of  $\text{Na}_2\text{O}$  and  $\text{NaNO}_2$ , which are products of decomposition, are observed together with those of R- $\text{Na}_3\text{ONO}_2$  in the patterns measured under a pressure range of 5-12 GPa. Thus the relative lower decomposition temperature under high pressure condition reveals the characteristic of pressure induced structural destabilization of  $\text{Na}_3\text{ONO}_2$ . The x-ray diffraction amorphization happens after pressure beyond 13 GPa at 573 K, this is almost same as the results of room temperature under pressure.

In addition to some general interest in the high pressure behavior of  $\text{Na}_3\text{ONO}_2$ , the orientational disorder of nitrite ion inside the sodium oxide framework is of special interest. The orientational disorder is expected to be reduced under high pressure while the sodium oxide framework transforms its cubic symmetry to lower symmetric structure, then completely frozen at amorphous state after compressing up about 14 GPa. However, the diffraction methods could not really distinguish dynamic disorder phenomena due to the measured patterns are averaged over space and time. The relative poor quality of the high pressure diffraction data, due to stress distribution in the high pressure cell without pressure transmitting medium as well as texture phenomena of the sample, hampered us from obtaining clear information on the evolution of orientational disorder of  $\text{NO}_2^-$  upon pressing. Therefore the role of the orientational disorder change, if any, in the pressure induced decomposition remains unclear.

Sodiumoxidarsenate ( $\text{Na}_5\text{AsO}_5$ ) under high pressure also were studied via *in situ* Raman and X-ray diffraction techniques at room temperature, its structure kept stable and pressure induced amorphization around 20 GPa were observed.

#### References:

1. M. Jansen, Neue Untersuchungen an  $\text{Na}_3\text{NO}_3$ , Z. Anorg. Allg. Chem. 435, 13-20, 1977.
2. G. Klösters, M. Jansen, Neutron Diffraction Study of the Low Temperature Phases of Sodium Oxide Nitrite,  $\text{Na}_3\text{ONO}_2$ , J. Solid State Chem. 145, 267-75, 1999.
3. H. Hass, M. Jansen, Synthese und Charakterisierung von  $\text{Na}_5\text{AsO}_5$ , Z. Anorg. Allg. Chem. 627, 1013-16, 2001.
4. H. Liu, W. Klein, M. Jansen, Pressure Induced Phase Transition and Amorphization of  $\text{Na}_3\text{ONO}_2$ , Submitted, 2002.