Metastable Bi under Extreme Conditions Investigated by Combined XAS and XRD

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Abstract. We report the results of a detailed experimental study carried out at the European Synchrotron Radiation Facility (ESRF) providing an unprecedented insight into the metastable phase diagram of Bi. In particular we focus the attention on a novel metastable crystalline structure of Bi compatible with the β-tin structure. It is reasonable to identify the new structure with the unknown stable Bi-II' structure. These findings have been achieved using the single energy x-ray absorption detection (SEXAD) technique and angular dispersive x-ray diffraction (ADXD) both combined with a "Paris-Edinburgh" V5 large volume press at the BM29 beamline. The results obtained show that the combination of SEXAD and ADXD is a unique and reliable tool for detecting subtle structural modifications in condensed matter.

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INTRODUCTION

Bi is a typical "ice-type" element characterized by a very complex phase diagram (see fig. 1). Since the Bridgman's times several Bi polymorphs have been revealed and studied mainly using x-ray diffraction [1, 2, 3, 4, 5, 6, 7, 8] but, despite these efforts, still today the determination of the atomic structure of some Bi polymorphs is controversial. Recently the raising attention on the structural anomalies of "ice-type" substances has renewed interest in their local atomic structure under extreme conditions. In this paper we report of an experiment carried out at the European Synchrotron Radiation Facility (ESRF) aimed to shed light on the Bi structural properties in a broad region of pressures and temperatures ($25 \div 500\,^{\circ}C$, $0 \div 6\,GPa$). To achieve this ambitious aim a new experimental approach has been used which allows for a reliable and accurate study of subtle phase transitions both in stable and metastable condensed matter [9]. The approach consists in combining single energy x-ray absorption detection (SEXAD) and angular dispersive x-ray diffraction (ADXD). The SEXAD technique, mainly sensitive to the atomic local structure, is particularly sensitive to tiny structural changes. The ADXD technique is suitable for characterizing the crystalline structures and obtaining their lattice parameters. In the following sections we summarize the technical aspects of the experiment and describe some valuable results obtained.

EXPERIMENTAL

The experiment was carried out at the BM29 beamline (ESRF) which makes available a fully automated environment and an experimental setup specialized in high quality x-ray absorption spectroscopy (XAS) measurements [10, 11]. A sketch of the experimental setup used in this work is drawn in figure 2. A similar setup has been shown to be highly efficient to perform reliable and fast structural characterizations by XRD combined with energy dispersive XAS measurements.[12]

The beamline is equipped with a powerful double crystal Si(311) Kohzu monochromator which has an energy resolution $\Delta E/E \approx 10^{-5}$ at $E \simeq 15 KeV$. The x-ray energy was tuned around Bi L_3-edge (13419 eV) for single energy x-ray absorption detection (SEXAD) and at 15 KeV for angular dispersive x-ray diffraction (ADXD). ADXD images has been recorded using an imaging plate detector (MAR345) mounted in off-axis position with respect to the beam at about 50 cm after the sample. The setup has been found to be particularly flexible allowing for changing from SEXAD to ADXD in few seconds without moving the sample.

A "Paris-Edinburgh" (PE) large volume (V5) press [13, 14] positioned over a *xyz* translation stage has been used as pressure device. It can reach sample pressures up to about 10 GPa with standard WC anvils and it can heat the sample up to about 2000°C by means of a 200 A power supply. During the recording operation of the imaging plate (600 seconds) the press rotated continuously of $\pm$ 2.5 degrees around its symmetry axes orthogonal to the x-ray beam. This oscillation improves

the powder statistics limited by the small dimensions of the sample and x-ray spot. [11]

The sample inside the PE press gasket (diameter: 7 mm) is composed by a mixture of Bi, NaCl and BN made in a weight ratio Bi:NaCl:BN 1:2:30 where NaCl and BN have been used respectively as pressure marker and as inert low-absorbing matrix. Details on the sample preparation are available elsewhere. [9] This mixture has been found, by scanning electron microscopy, to be a dispersion of micrometric grains of the Bi powder into the matrix allowing achievement of appreciable undercooling ranges still retaining the behavior of bulk samples due to the relatively large dimensions.[15]

TECHNIQUES AND RESULTS

The measurements were carried out combining SEXAD and ADXD at different constant pressures. The basic principle of the SEXAD technique is based on the occurrence of discontinuous changes of the shape of the x-ray absorption spectra upon a first order phase transition [16]. By monitoring the sample absorption at fixed energy and pressure as a function of temperature the occurrence of a transition can be detected with high accuracy both raising and decreasing the temperature, collecting a set of reproducible SEXAD "hysteresis" loops (see fig. 3). A crucial parameter of this technique is the energy value which should be tuned in order to maximize the absorption changes and enhance the sensitivity to the observed phase transitions. The information provided by SEXAD can be complemented by an accurate analysis of the x-ray diffraction patterns collected by the imaging plate. X-ray diffraction is very important for validating the SEXAD information in presence of complex structural modifications. Moreover x-ray diffraction is necessary for estimating the sample pressure following the lattice contraction of internal pressure markers. Typically few minutes are needed for collecting a SEXAD loop and an ADXD image allowing for a fast and accurate study of a broad region of the sample phase diagram.

In figure 1 the regions of the Bi phase diagram probed by SEXAD are represented by dotted lines. The phase transitions revealed by SEXAD upon raising the temperature are represented by empty circles, while full circles indicate a phase transition upon cooling. These data have been used for determining the metastable phase diagram of Bi. [9] In what follows, we focus on a particular SEXAD loop, indicated by the vertical arrow in fig. 1, collected at about 1.8 GPa with a beam energy of 14465 eV. The loop under consideration is presented in fig. 3. Following the absorption level upon raising the temperature a drop of absorbance is noticeable at the Bi-I–Bi-II phase transition. The region of stability of Bi-II is small as the Bi-II melting occurs after about $20^{\circ}C$. The cooling part of the loop starts around $230^{\circ}C$. Almost any undercooling is observable as liquid Bi rapidly crystallized in a phase which differs evidently from Bi-II. We call this phase β-Bi. Around $100^{\circ}C$ β-Bi changes to Bi-II which turns to Bi-I close to the room temperature.

ADXD patterns obtained by radial integration of the digital images recorded on the image plate confirm the information provided by the above described SEXAD profile. The ADXD images were collected at about 1.8 GPa upon cooling at the following temperatures (see fig.3.): $220^{\circ}C$ (liquid Bi), $180\,^{\circ}C$ (first plateau), $110^{\circ}C$ (second plateau), and room temperature (solid Bi-I). A selected region ($14^{\circ} < 2\theta < 17^{\circ}$) of the whole diffraction patterns has been shown in figure 3 pointing out that three different Bi crystal structures have been obtained below $180\,^{\circ}C$. The main Bragg peaks detected have been found to be compatible with the crystalline structures of Bi-II and Bi-I respectively at $110\,^{\circ}C$ and room temperature. At $180\,^{\circ}C$ the Bragg peaks are compatible with a β-tin structure.

To our knowledge this is the first experimental evidence of a β-tin structure for solid Bi. A tentative interpretation is that β-Bi could be the structure of the so called Bi-II' phase which has been so far revealed only by the differential thermal analysis (DTA) technique [17]. Both β-Bi and Bi-II have the same number of atoms in the unit cell ($Z = 4$) and similar coordination numbers ($N_{\beta} \simeq 6$, $N_{II} \simeq 7$) suggesting a similar local atomic arrangement. The stability region of Bi-II' is restricted to a small region of the phase diagram at about 1.9 GPa and 190°C, but the results provided by this experiment points out that a larger metastable region of Bi-II' could exist at lower pressures and temperatures.

CONCLUSIONS

In this paper we present an original experimental approach which has been found to very be suitable for investigating metastable condensed matter under extreme conditions. We have shown that modern x-ray spectrometers, such as BM29 at ESRF, can be successfully used for simultaneous SEXAD and ADXD measurements. We have reported novel results on the Bi metastable phase diagram obtained using these techniques, focusing on the presence of a novel Bi structure obtained upon cooling from the liquid phase at 1.8 GPa. We conclude that the combination of SEXAD and ADXD is a valuable experimental tool for shedding new light on metastable matter structure and its subtle anomalies.

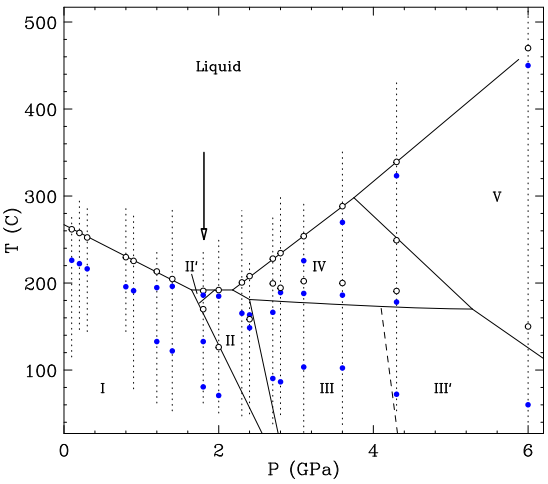

FIGURE 1. Phase diagram of Bi (adapted from Cheng et al.[7]). The different phases are labeled following Cannon [18]. The vertical dotted lines, which joins circles, represent the range of temperatures covered by the SEXAD loops carried out at fixed pressure. The vertical arrow indicates the pressure of SEXAD loop shown in fig. 3.

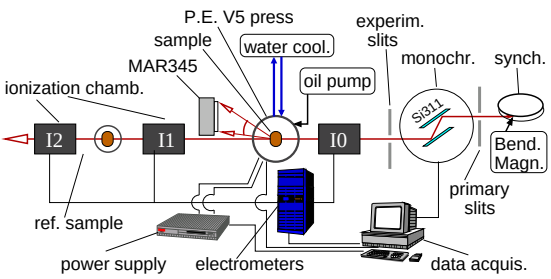

FIGURE 2. Layout of the advanced experimental setup available at BM29 (ESRF) improved for simultaneous SEXAD and ADXD measurements at high pressures and temperatures.

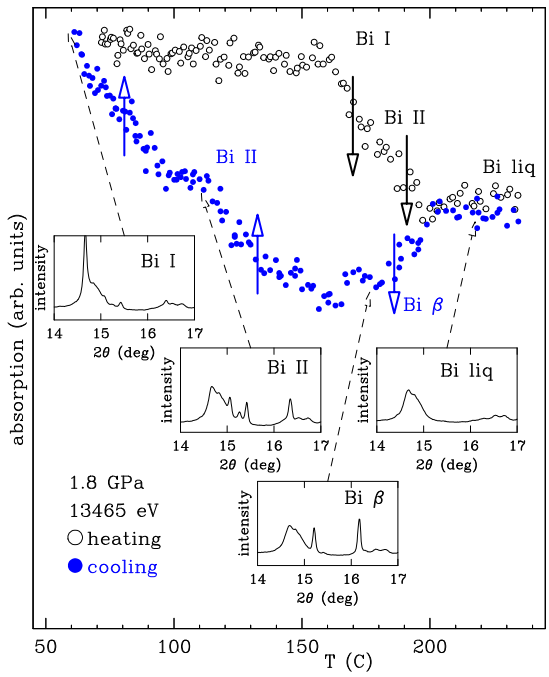

FIGURE 3. SEXAD of micrometric Bi droplets at fixed energy and pressure. The solid arrows indicate the temperature of the phase transitions, associated with the temperature value of the circles in fig. 1. The four insets presents the ADXD patterns of the mixture Bi:NaCl:BN collected upon cooling at suitable temperatures suggested by SEXAD.

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