Title: HIGH PRESSURE METALLIZATION AND AMORPHIZATION OF THE MOLECULAR CRYSTAL Sn(IBr)₂

Author(s): G. Uy Machavariani  
G. Kh Rozenberg  
M. P. Pasternak  
O. Naaman  
R. D. Taylor

Submitted to: XXXVI Meeting of the European High-Pressure Research Group on "Molecular and Low Dimensional Systems Under Pressure"  
Catania, Italy  
September 7-11, 1998

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
High pressure metallization and amorphization of the molecular crystal Sn(IBr)₂.


School of Physics and Astronomy, Tel-Aviv University, 69978 Tel Aviv, Israel

MST10, Los Alamos National Laboratory, Los Alamos, New Mexico NM 87545, USA.

ABSTRACT

An insulator-to-metal transition concurring with amorphization is found in the cubic (Pa₃) molecular crystal Sn(IBr)₂ at P ≈ 20 GPa. Measurements were carried out with diamond-anvil cells at pressures up to ~30 GPa using resistance measurements, X-ray diffraction (XRD), and ¹¹⁹Sn Mössbauer spectroscopy (MS). With increasing pressure a new crystalline phase is observed in the 10 - 23 GPa range; at P ≈ 16 GPa a gradual onset of structural disorder is first observed, and full amorphization takes place at P ≥ 21 GPa. Both electronic properties as measured by R(P,T) and MS data are consistent with a gradual growth of disordered (SnL₂Br₂)ₙ polymeric chains, formed by intermolecular I - I bonding allowing for electronic delocalization to occur. Upon decompression both XRD and ¹¹⁹Sn MS show a significant pressure hysteresis.

Keywords: insulator-metal transition, pressure-induced amorphization, pentatomic molecular crystals.

Galina Yu. Machavariani,
R.&B. Sackler School of Physics and Astronomy,
Tel-Aviv University, 69978 Tel Aviv, Israel
Fax 972-3-642 29 79; E-mail galmach@ccsg.tau.ac.il
INTRODUCTION

The concurrence of pressure-induced (PI) amorphization and insulator-metal (IM) transition in the pentatomic molecular crystals GeI₄ and SnI₄ had been the subject of various studies [1,2,3]. However in the case of the SnBr₄ molecular crystal, both optical [4] and ⁱ¹⁹Sn Mössbauer studies [5] definitely showed that this phenomenon does not occur; to \( P > 25 \) GPa the bromide which becomes amorphous at \( \sim 12 \) GPa, remains a large-gap insulator. From this it was concluded [5] that the mechanism for amorphization in the iodides must be of a different nature; the enhanced intermolecular I - I overlap at high pressure proposed as the mechanism for the onset of both structural disorder and gap closure [1,2] may not take place in SnBr₄. To test the proposed mechanism, we carried out X-ray diffraction (XRD), resistance measurements, \( R(P,T) \), and Mössbauer spectroscopy (MS) measurements of the mixed-halides molecular crystal Sn(IBr)₂ to pressures of \( \sim 30 \) GPa using diamond anvil cells. As will be shown, the combination of these methods provide unique information about the crystalline and disordered metallic states.

EXPERIMENTAL

Polycrystalline and single crystal samples of Sn(IBr)₂ were synthesized by direct vapor-solid reaction of spectroscopical pure IBr and Sn metal in an evacuated glass tube at 230 °C. At ambient pressure Sn(IBr)₂ is an orange-red crystal whose structure was unknown. Its structure was determined using single-crystal XRD studies and was found to be cubic (space group \( P a \bar{3} \)), with eight molecules per unit cell, and lattice parameter: \( a = 12.022(1) \) Å. The structure is identical to that of SnI₄ but with \( a \)-value smaller by about 0.250 Å. Details about ambient pressure structure of Sn(IBr)₂ will be published elsewhere.

TAU diamond anvil cells (DACs) of the miniature type [6], with anvil culets in the 0.4 - 0.5 mm range were used in conjunction with ruby fluorescence for manometry. Powder XRD was carried out at CHESS using the energy dispersive mode, and data were collected at 300 K with \( 2 \theta = 8^\circ \). Resistance measurements were carried out using the four- probe method in the 5 - 300 K temperature range. For the Mössbauer experiments a
5 mCi Ca\textsuperscript{119m}SnO\textsubscript{3} commercial source was used and measurements were carried out at 75 K.

RESULTS AND DISCUSSION

With pressure increase a new crystalline phase was detected at \sim 10 GPa and having an unknown structure. This phase coexists with the original low pressure phase in the range 10-21 GPa. It is noteworthy that at \sim 8 GPa a structural phase transition was also observed in the isostructural SnI\textsubscript{4} [7]. At P \approx 16 GPa a broad diffraction peak typical of a diffraction halo in glasses starts to appear. The relative intensity of this halo increases with pressure, and at P \geq 23 GPa no remnants of crystalline phases are observed. Upon decompression the original crystalline phase reappears between 4.7 and 0.15 GPa, coexisting with remnants of the amorphous phase (see Fig. 1).

The onset of the metallic state is determined from R(P,T) measurements. Figure 2 shows the resistance variation with temperature for several pressures close to the IM transition. The metallic state is determined by the change in sign of dR/dT, from negative to positive. And indeed the first R(T) curve showing a positive slope at T > 65 K is found for P = 22.7 GPa, and at P = 24 GPa metallization takes place in the full 5 - 300 K temperature range. The inset in Fig.2 shows the resistance variation with pressure at 300 K. Definite change in the R(P) slope is observed at \sim 11 GPa, probably related to the crystallographic phase transition as observed with XRD. At \sim 20 GPa the slope is further reduced, coinciding with the onset of an IM transition.

Representative Mossbauer spectra of \textsuperscript{119}Sn(IBr)\textsubscript{2} at various pressures during compression are shown in Fig.3. The spectra obtained in the 0 -8 GPa range show a single line with an isomer shift (IS) of about 1.6 mm/sec relative to CaSnO\textsubscript{3} (Fig 3a). This value of IS is typical of covalently bound four-coordinated Sn\textsuperscript{4+} [8]. Despite the mixed halides forming the pentatomic molecule, the lack of a detectable quadrupole splitting suggests a rather symmetric tetrahedron. At P \geq 8 GPa a second unsplit component with IS = 3.9 mm/sec appears (Fig. 3b). We suppose that this large value of IS is due to the onset of a six-fold coordination and is attributed to a new configuration of 5s5p-4p4d hybridization, which results in an increase of the 5s electron density.
The pressure dependence of the relative abundance of the amorphous phase is shown in Fig. 4. This was obtained from the relative area under the absorption peaks of the MS spectra. The pressure hysteresis is clearly observed, which qualitatively agrees with the XRD data.

CONCLUSIONS

The present results with the mixed halide Sn(IBr)2 molecular crystal confirms the model proposed by Pasternak, Taylor, and co-workers in their studies of SnI4 and GeI4 [1,3], namely, the high pressure phase with its six-coordinated Sn^4+ is in the form of a structurally disordered polymeric (Sn(IHa)2)n (Ha = Br, I) clusters. This structure could be formed due to the enhanced intermolecular I-I overlap. For each molecule, two iodides serve as bridging atoms to form the intermolecular chain. This polymerization process can account for the metallic behavior of Sn(IBr)2 by providing a pathway of electron delocalization along the -Sn-I-I-Sn- linkage of the chains. The cluster’s size increases with pressure culminating into a full concurrent amorphous and metallic phase. It is noteworthy that in analogous SnI4 the metallization onset appears at approximately the same pressure of 19.8 GPa [2]. The amorphization process of the iodide and halide-mixed pentatomic crystals is in contrast to that of the tin bromide case [5] where at ~9 GPa (SnBr4)2 dimers are formed, an amorphous phase is created, yet, the material remains a bona-fide insulator to pressures above 25 GPa.

We thank I. Goldberg and U. Shmueli for their help in the Sn(IBr)2 structure determination. This work was partially supported by grants from the USA-Israel Binational Science Foundation, Grant BSF #95-00012 and the German-Israel Science Foundation, Grant GIF #I-086.401.

References.


[9] The closure of the Sn$^{4+}$ intra 5s5p-4p4d gap could be the reason for the intra-molecular electron delocalization which by virtue of I-I intermolecular bridging results in the pressure-induced metallization.

Figures captions:

Fig.1. X-ray diffraction patterns of the crystalline (a) and amorphous (b) phases of Sn(IBr)$_2$ upon compression. The upper part (c) shows the pattern of the crystalline phase following decompression. Indices of major reflections from the $Pa\bar{3}$ structure are given in (a) and (c). Peak letters denote the atomic excitations of I-K, I-K$_{\beta_1}$; Sn-K, Sn-K$_{\beta_1}$; Sn-K$_{\alpha_1}$, Sn-K$_{\alpha_2}$ edges.

Fig.2. Temperature dependence of the resistance of Sn(IBr)$_2$ for various pressure values close to the IM transition. Incipient metallic behavior is first observed at 22.7 GPa. The inset shows log(R) versus pressure recorded at 300 K. Note the changes in slope at ~12 GPa and ~20 GPa where a structural transition and an IM transition are observed, respectively.

Fig.3. Mössbauer spectra of $^{119}$Sn(IBr)$_2$ at 75 K with increasing pressure. Characteristic IS for the low pressure crystalline phase, where the tetravalent Sn is four-fold coordinated, is ~1.6 mm/s. The IS for the amorphous phase, where Sn is six-fold
coordinated, is ~3.9 mm/s. Values of IS are with respect to the calcium stannate source at the same T.. Solid lines are theoretical fits to the data.

Fig. 4. The pressure dependence of the relative abundance of the high pressure amorphous phase as recorded by MS studies. The solid and open symbols correspond to abundance upon compression and decompression, respectively.
Fig. 1

(c) 0.15 GPa decompression

(b) 30.8 GPa compression

(a) 3.4 GPa compression
Fig. 2
Fig. 3
Fig. 4