7 High Pressure Science

7-1 Pressure-Induced Structural Changes in Liquid III-V Compounds

Liquids of tetrahedrally bonded materials such as liquid Si, Ge, and III-V compounds have attracted much attention because they retain a covalent bonding character with related anisotropic local structure even after metallization on melting. Generally, pressurization reduces the covalent character and causes a decreased anisotropy of the local structure. Due to the structural fluctuation of the liquid, this behavior is expected to differ from that of the crystalline counterpart. To reveal this behavior and the nature of different pressure-induced structural changes, we have studied the structure of three liquid III-V compounds, GaSb, InSb, InAs.

The experiment was performed using an energy-dispersive X-ray diffraction method combined with a multianvil high-pressure apparatus. The structures of the liquids were investigated at pressures of up to about 20 GPa at along each liquid's melting curve. Data at pressures below about 10 GPa was recorded using a MAX80 hydraulic press installed at beamline NE5C of the PF-AR and a MAX-III installed at beamline BL-14C2 of the PF. Data at pressures above about 10 GPa was recorded using a SPEED1500 double-stage high-pressure apparatus installed at BL04B1 at SPring-8. Diffraction profiles were recorded at several detector angles to obtain the structure factor *S(Q)* over a wide *Q* region. The *S(Q)* was obtained by normalizing the diffraction profiles and connecting them to each other. The pair distribution function, *g(r)*, was obtained by Fourier transformation of *S(Q)*. The detailed procedure is described in [1].

Figure 1 shows a typical result of the pressure dependence of *S(Q)* [1]. With increasing pressure, the height of the first peak increases and that of the shoulder on the high *Q* side of the first peak decreases. Simultaneously, the ratio of the position of the second peak to that of the first peak, Q_2/Q_1, which reflects the anisotropy of the local structure, becomes smaller [1-3]. These findings suggest that the structures of the liquids approach those of simple liquid metals as the pressure increases. However, even at the highest pressure experimentally accessible, the hump still exists and the Q_2/Q_1 ratio differs from the value for simple liquid metals (~1.86). These observations suggest that the liquids retain an anisotropic local structure even upon compression to 20 GPa.

To reveal the local structure of the liquids, we show in Fig. 2 the pressure dependence of the coordination number (CN) of the three liquids [1-4]. The CN, which is much smaller than that for simple liquid metals at ambient pressure, significantly increases upon compression, indicating that the local structure of the liquids changes from a relatively open structure to a more closely packed one. An analysis of the *g(r)* profiles using a distorted crystalline model combined with a two-species model [1] reveals that the local structure can be explained by a mixture of a β-tin-like structure and a bcc-like one (Fig. 3) [1-3]. The fraction of the denser local structure (bcc-like local structure) increases with rising pressure (Fig. 4) [1-3]. Surprisingly, the liquids consist of a significant fraction of the β-tin-like local structure, reflecting the existence of covalent bonding character at pressures of up to 20 GPa. In the crystalline states, the β-tin and related phases completely disappear in that pressure region. These findings suggest that compared to the crystalline counterparts the liquid states preserve the covalent chemical bonding character at higher pressures, although the liquid phases already show metallic electric properties even at ambient pressure.

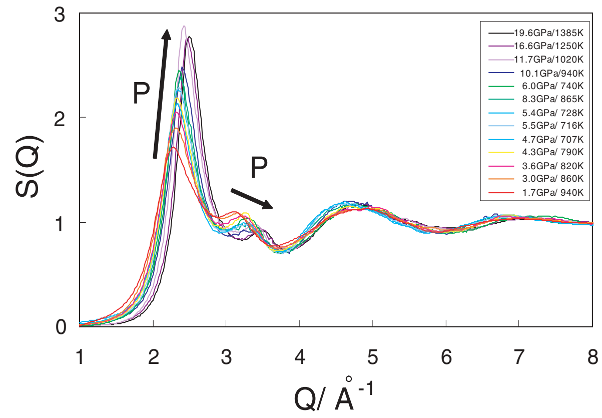

Figure 1
Pressure dependence of *S*(*Q*) for liquid GaSb.

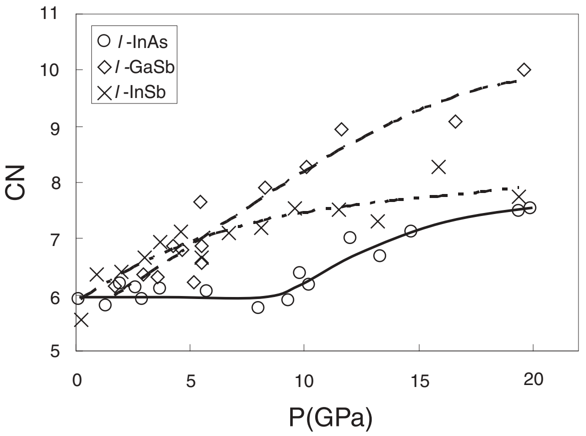

Figure 2
Pressure dependence of CN for liquid GaSb, liquid InSb, and liquid InAs. The solid lines are to guide the eye only.

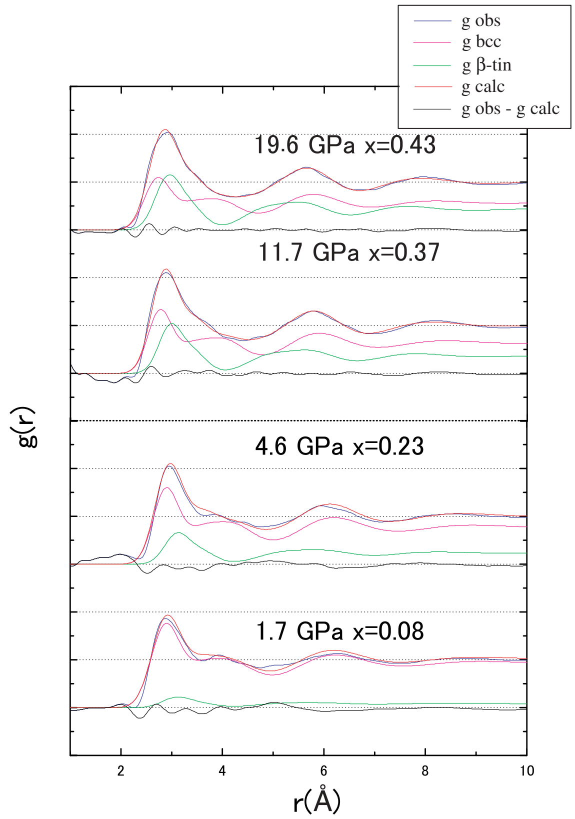

Figure 3
Typical fitting results of *g(r)* for liquid GaSb using a distorted crystalline model coupled with a two-species model. The profile of *g(r)* is simulated by combining two *g(r)* for the β-tin-like and bcc-like structures, where *g(r)* for each structure is weighted by the fractional ratio. x represents the fraction of the bcc-like local structure.

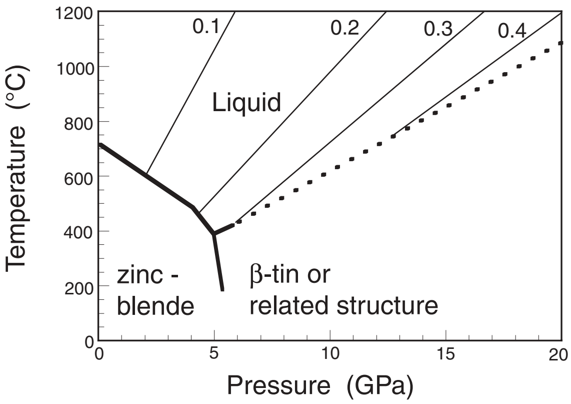

Figure 4
Isofraction lines in the *PT* plane calculated for the bcc-like local structure for liquid GaSb.

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7-2 A New High Pressure Polymorph of $FeAlO_3$

A synchrotron X-ray diffraction pattern recorded at BL-13A has shown a new polymorph of $FeAlO_3$ with an orthorhombic cell to be stable at pressures above 72 GPa and temperatures above 1800 K [1]. The orthorhombic phase transforms to a trigonal form upon release of the pressure (Fig. 5). Although it was not possible to uniquely identify the new orthorhombic phase, we have proposed a candidate structure by considering the identification of the recovered trigonal phase.

(i) $LiNbO_3$ ($R3c$), (ii) corundum ($R\bar{3}c$), and (iii) ilmenite ($R\bar{3}$) can be considered as candidate structures of the trigonal phase with ABO_3 composition. It is already known that it is difficult to distinguish between these phases from powder-diffraction data alone. However, it is also known that the tendency of the *c/a* ratio of these structures is useful for structure identification. The *c/a* ratio of 2.71 for the observed trigonal phase is closer to that of the corundum structure than those of $LiNbO_3$ (2.63) or ilmenite (2.8). The observation that the unit-cell parameters are almost intermediate between those of corundum and hematite also supports a corundum type for $FeAlO_3$. Importantly, the Fe^{3+} and Al^{3+} ions would be expected to occupy a single cation site in the corundum structure of $FeAlO_3$ in a disordered manner, because there is a single cation site in the corundum structure. However, this disorder is not evident by considering their similar ionic radii (0.63 Å for Fe^{3+} and 0.61 Å for Al^{3+} in an octahedral site).

It has recently been reported that corundum and hematite transform to the Rh_2O_3(II) structure (Fig. 6) at high pressure and high temperature [2,3]. It is well known that the powder-diffraction pattern for the Rh_2O_3(II) structure is quite similar to that for the $GdFeO_3$-type orthorhombic perovskite structure. However, neither the Rh_2O_3(II) structures of Al_2O_3 nor Fe_2O_3 could be quenched and recovered as the corundum structure on release of pressure. On the other hand, some oxides with $GdFeO_3$-type orthorhombic perovskite structures, which are stabilized at high pressure and high temperature, transform to the $LiNbO_3$ structure during decompression [4]. This observation indicates that the cation order-disorder-type transition should not occur during decompression at room temperature, since there is a single cation site in the corundum and Rh_2O_3(II) structures, and two cation sites in the perovskite and $LiNbO_3$ structures. Therefore, we conclude that the recovered trigonal phase may have a corundum structure, suggesting that the high-pressure orthorhombic phase is likely to be a Rh_2O_3(II) structure rather than a $GdFeO_3$-type orthorhombic perovskite structure.

Recent experimental studies of the incorporation of Fe^{3+} into Al^{3+} bearing $MgSiO_3$-perovskite have pointed out that an $FeAlO_3$-$MgSiO_3$ type substitution would be a favorable mechanism in the earth's lower mantle [5].

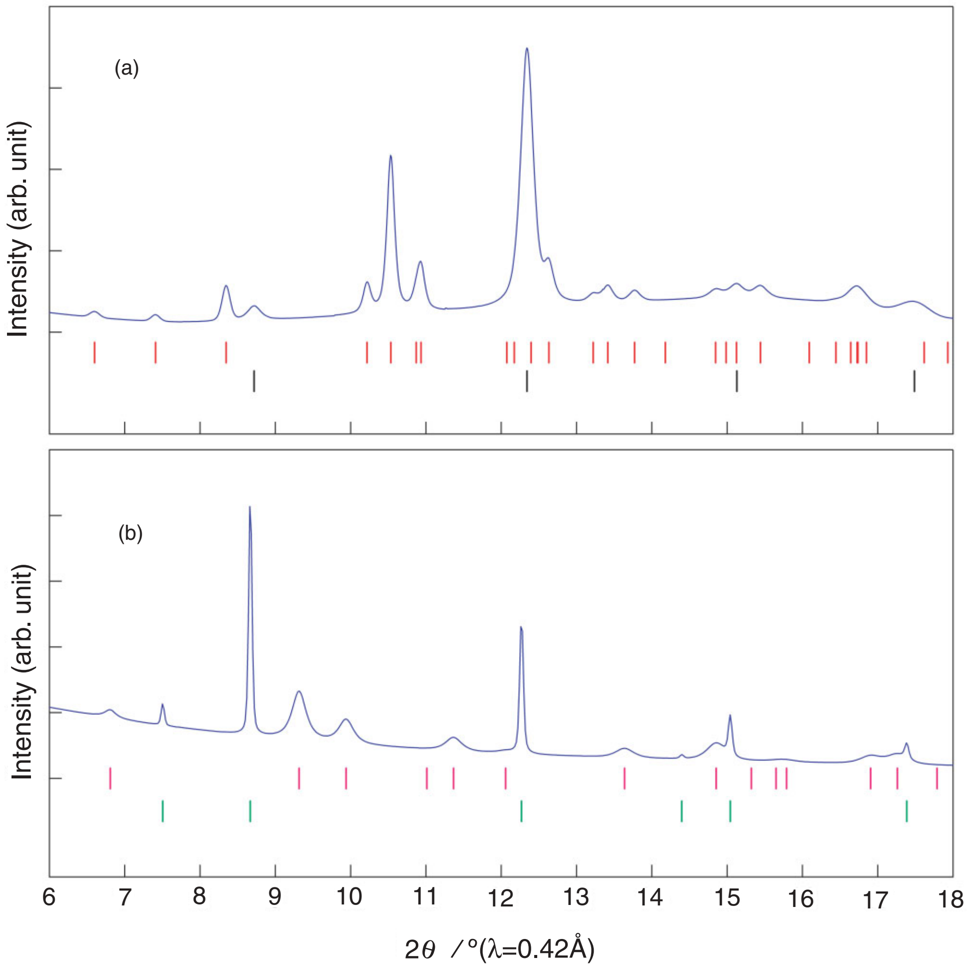

Figure 5
Synchrotron X-ray diffraction pattern generated at (a) 72 GPa and 300 K after heating and at (b) ambient conditions following decompression. (a) Red bars represent the position of the reflections calculated on the basis of the Rh_2O_3(II) structure (a=4.785 Å, b=6.535 Å, c=4.482 Å) and black bars those of the B2 phase of NaCl. (b) Purple bars represent reflections calculated on the basis of the corundum structure (a=4.915 Å, c=13.34 Å) and green bars those of the B1 phase of NaCl.

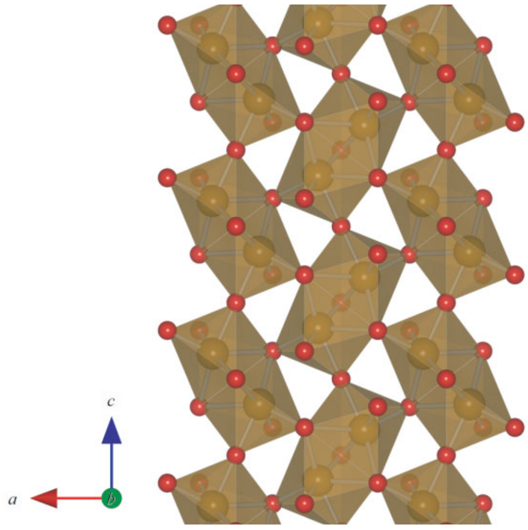

Figure 6
Polyhedral representation of the Rh_2O_3(II) structure.

However, we have little knowledge about the phase relation of $FeAlO_3$ at high pressures. Our result indicates that the $FeAlO_3$ component would be stabilized with an Rh_2O_3(II) structure rather than a $MgSiO_3$ perovskite structure at the bottom of the lower mantle. It is reasonable to speculate that there is a maximum solubility of the $FeAlO_3$ component into $MgSiO_3$ perovskite under lower mantle conditions [6].

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