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Al_2O_3 as a metallic glass at 300 GPa

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Based on published experiments and theory, we predict that strong covalent single-crystal Al_2O_3 with a 10 eV band gap becomes a metallic glass at ~300 GPa under shock and static compression. The insulator-metal transition is probably entropy driven, i.e., compressive energy is absorbed by breaking bonds. Resulting Al and O atom densities are sufficiently high for hybridization into a metal. Alternatively, if Al and O phase separate, electrical conduction occurs through Al filaments whether or not O conducts. If Al_2O_3 metallizes, other strong insulators are expected to do so as well.

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Pressure is a useful tool to probe oxides with unusual physical properties. NiO, for example, is the prototypical Mott insulator. Based on its band structure, it is expected to be a metal; because of electron correlations it is a transparent antiferromagnetic insulator. Mott predicted that NiO will become a metal at some high pressure,[1] not yet reported experimentally. Oxides have the highest superconducting critical temperatures T_c, many of which can be tuned by application of pressure.[2] The interaction causing superconductivity in those oxides is yet to be identified. Pressure-induced amorphization has been observed experimentally in many electrically insulating materials, including oxides.[3,4] In none of those cases has pressure-induced amorphization been accompanied by metallic conduction. Recently, amorphous insulating SiO at ambient has been reported to undergo an insulator to metal transition at ~12 GPa.[5] While it is not unusual that oxides are amorphous at high pressures, the fact that an amorphous oxide can also be a metal was unanticipated prior to Ref. 5.

In this Brief Report we predict, based on a significant body of published experimental and theoretical results, that strong covalent single-crystal Al_2O_3 at ambient becomes a metallic glass at ~300 GPa (3 Mbar) achieved by both shock and static compression. Since Al_2O_3 is one of the strongest known covalent materials and has a band gap of ~10 eV at ambient, it is surprising that Al_2O_3 might turn into a metallic glass at pressures achievable in a laboratory. Even more surprising is the fact that the mechanism of metallic conduction in disordered, strong Al_2O_3 at 300 GPa is expected to be the one that causes minimum metallic conductivity in fluid hydrogen at 140 GPa,[6] namely, a Mott transition.[7] Predicted metallization of Al_2O_3 and observed metallization in fluid hydrogen depend on entropy generation and not simply on band-gap closure.

Shocked materials at 100 GPa pressures are generally thought to be at substantially higher temperature and pressure than materials under static compression at the same density. This is not the case for single-crystal Al_2O_3.[8–10] Implications of this observation lead to the prediction herein.

This prediction for Al_2O_3 has broader implications that warrant experiments to determine if it is true. (1) If Al_2O_3 becomes a metallic glass at 300 GPa, then it is probable that other strong oxide crystals achieve the glassy metallic state at sufficiently high pressures as well. In this case, amorphization and metallization of insulating phases at 100 GPa pressures would open up a field for scientific investigations. It is even conceivable that the ground states of all strong electrical insulators are metallic glasses at ultrahigh pressures. (2) Diffuse x-ray scattering and measurements of O-O, Al-Al, and Al-O pair correlations are needed to characterize this relatively low-Z material above 100 GPa in a diamond-anvil cell (DAC). Such experiments are challenging, time consuming, and yet to be done. Determining that the structure of Al_2O_3 is amorphous at 300 GPa in a DAC will stretch current technology to its limits and possibly lead to improved diagnostics that will enable strong solid insulators to be studied systematically at 100 GPa pressures. (3) Since Al superconducts at $T_c = 1.14$ K and O superconducts above 95 GPa at $T_c = 0.6$ K,[11] metallic glassy Al_2O_3 might superconduct as well. Other strong insulators, such as NiO, might also superconduct in the glassy metallic state at 100 GPa pressures. In this case, under pressure NiO would transition from an antiferromagnetic insulator to a superconductor without any chemical additions. (4) Since most minerals are oxides, results for Al_2O_3 are relevant to the natures of the deep rocky mantle of earth and interiors of extrasolar rocky planets now being discovered.

Sapphire disorders substantially under shock[9,10] and static[8] compression, and has phase transitions at 300 K and 100 GPa pressures[12,13] that are probably frustrated. Remarkably, the shock-compression curve (Hugoniot) (Refs. 14 and 15) and theoretical isotherm of Al_2O_3 (Ref. 16) are nearly coincident up to ~400 GPa. This implies that thermal pressures are small because shock temperatures are small. In most materials, irreversible shock heating causes the Hugoniot to deviate significantly from the isotherm at substantially lower pressures. In Ar, for example, Hugoniot and isotherm differ substantially by only 5 GPa.[17]

These observations imply that below ~400 GPa, shock dissipation is absorbed primarily by entropy of bending and breaking strong, covalent bonds (approximately electron volt), which leaves relatively little dissipation to go into shock heating. Once all bonds in the crystal are broken at ~400 GPa, additional dissipation must then go into temperature, which is observed as a rapid increase in thermal pressure on the Hugoniot.[18] Above 100 GPa additional entropy is generated by frustrated phase transitions. The purpose of this Brief Report is to examine possible conse-

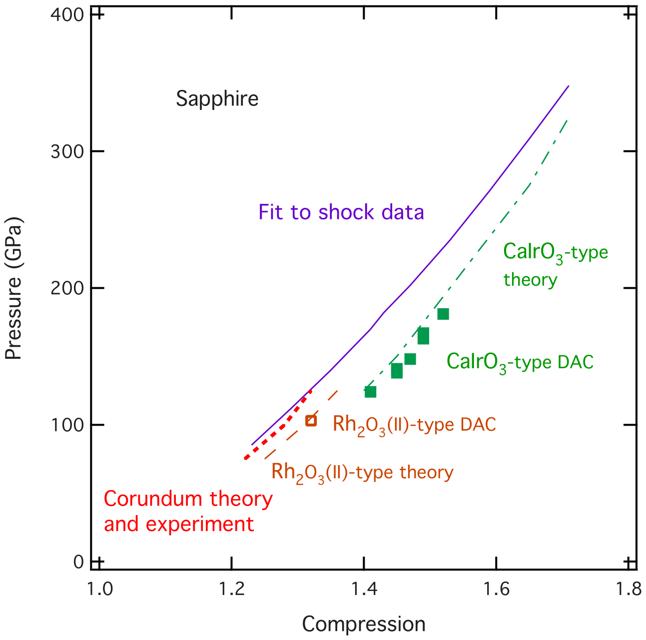

FIG. 1. (Color online) Pressure versus compression (ρ/ρ_0) for Al_2O_3: solid curve—fit to experimental sapphire Hugoniot data (Ref. 14); open and solid squares, Rh_2O_3(II) type and $CaIrO_3$ type, respectively, laser heated and thermally quenched at high pressures in DAC (Ref. 8); dotted, dashed, and dashed-dotted curves theory for corundum, Rh_2O_3(II) type, and $CaIrO_3$ type, respectively (Ref. 16).

quences of pressure-induced disorder on the electrical conductivity of Al_2O_3 in the range 100–400 GPa.

The fit to Hugoniot data from 80 to 340 GPa,[14] experimental data obtained in a laser-heated DAC from 103 to 180 GPa,[8] and theory for three equilibrium phases at 300 K in various pressure ranges[16] are plotted in Fig. 1, which has an expanded scale relative to previous plots.[9,16] The fit to this Hugoniot data is $u_s = C + S u_p$, where u_s is shock velocity, u_p is particle velocity, $C = 0.874$ cm/μs, and slope $S = 0.957$.[14] Slope $S < 1.0$ implies a continuous phase transition under shock from 20 to 340 GPa. More recent sapphire Hugoniot data[19] indicate a phase transition at 79 GPa. Calculated bulk shock temperatures at 100 GPa are only ~ 1000 K.[20]

Theory and DAC data indicate three equilibrium phases: corundum (α phase), Rh_2O_3(II) type, and $CaIrO_3$ type. The phase transition on the Hugoniot at 79 GPa might correspond to the one observed at 103 GPa in a DAC. The Hugoniot fit shows no indication of phase transitions observed in a laser-heated DAC at 103 and 124 GPa. Under shock compression the onset of opacity[21] and decrease in electrical resistivity of sapphire[22] at 130 GPa correlate with the predicted transition to $CaIrO_3$ type observed in a DAC. Because of the relatively low bulk temperatures, strong (approximately electron volt) interatomic bonds, and short experimental lifetimes (100 ns), shock dissipation in Al_2O_3 is dominated by entropy generation, shocked sapphire is probably not in thermal equilibrium, and shocked Al_2O_3 probably never enters the Rh_2O_3(II)-type phase. Above a shock pressure of 100 GPa Al_2O_3 probably undergoes one continuous transition in short-range order from corundum toward $CaIrO_3$ type. This is the likely mechanism for a continuous phase transition implied by $S < 1$ in the u_s-u_p data over such an enormous pressure range.

Static compression of corundum in a DAC at 300 K produces *only* disordered corundum at all high pressures investigated.[8] Only with laser heating and thermal quenching at high pressures were Rh_2O_3(II) type and $CaIrO_3$ type synthesized at 103 GPa and from 124 GPa to 200 GPa, respectively. X-ray spectra of laser-heated and thermally quenched samples consist of relatively broad individual diffraction peaks, indicative of disordered structures with short-range order and with long-range order that probably decreases with increasing static pressure. In fact, no lattice parameters were given for the sample compressed to 200 GPa, presumably because the sample was too disordered. Entropy is substantial in a DAC, as well as under shock. Given that experimental lifetimes of DAC experiments are about a factor of 10^8 longer than lifetimes of shock experiments and since statically compressed and laser-heated corundum transforms to phases that are not well ordered, it is reasonable to assume that Al_2O_3 is highly disordered under shock compression.

Agreement between theory and laser-heated DAC data in Fig. 1 is excellent up to 180 GPa. At higher pressures the calculated 300 K isotherm for $CaIrO_3$ type anomalously curves upward *toward* the Hugoniot, which is essentially linear from 180 to 340 GPa. The Hugoniot generally curves upward away from the isotherm because of increasing thermal pressure on the Hugoniot.[18] Figure 1 suggests that theory for $CaIrO_3$ type intersects the measured Hugoniot somewhat below 400 GPa. Although Umemoto and Wentzcovitch predict a phase transition from $CaIrO_3$ type to U_2S_3 type at 380 GPa, given disorder in this system it is problematical if this prediction will be tested in the near future. In short, Al_2O_3 is disordered and amorphous above 200 GPa in both the DAC and on the Hugoniot.

Since metallic liquids and glasses are both strong scattering systems, electrical conductivity of a metallic glass is comparable to minimum metallic conductivity (MMC) ~ 2000 $(\Omega\ \mathrm{cm})^{-1}$, the value for metallic fluid hydrogen.[6] Alternatively, since resistivity is conductivity^{-1}, minimum metallic conductivity is equivalent to maximum metallic resistivity (500 $\mu\Omega$ cm in this case). Electrical conductivities of dense fluid hydrogen were measured under dynamic pressures of 90–180 GPa achieved by a shock wave reverberating in liquid hydrogen contained between two *c*-cut sapphire disks. Metal electrodes passed through one of the disks to measure electrical resistance of the hydrogen. Electrical resistivities of *c*-cut sapphire measured from 80 to 220 GPa shock pressures[22] are plotted in Fig. 2. In the range 80–180 GPa the resistivity of shocked sapphire is four to five orders of magnitude larger than that of metallic fluid hydrogen. Thus, the electrical resistivities of shocked sapphire have negligible affect on those hydrogen resistivity measurements.

However, extrapolation of sapphire resistivity data to higher shock pressures shows that maximum metallic resistivity, indicated in Fig. 2 by its equivalent MMC, is achieved at about 280 GPa. Because of disorder in both shock-compressed and static-compressed sapphire, and because MMC is dominated by strong scattering and weakly dependent on material,[7] MMC is also expected in sapphire com-

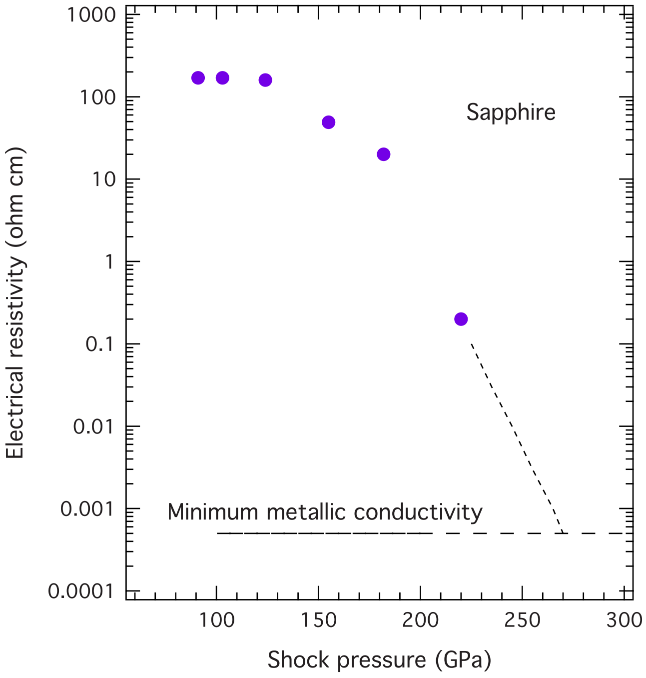

FIG. 2. (Color online) Electrical resistivities of *c*-cut sapphire: solid circles—experimental data at shock pressures from 80 to 220 GPa (Ref. 22); short dashes—extrapolation of experimental data to 280 GPa, pressure of maximum metallic resistivity (500 $\mu\Omega$ cm), indicated by its common equivalent-minimum metallic conductivity along long dashes.

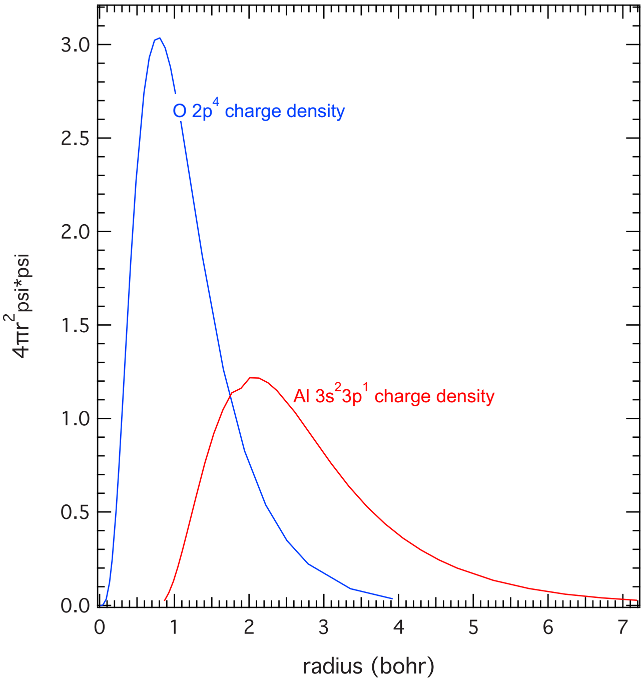

FIG. 3. (Color online) Spherically averaged atomic electron densities versus radius for O $2p^4$ and Al $3s^2 3p^1$ electrons calculated with Hartree-Fock-Slater method (Ref. 25). At 300 GPa average separation between all Al and O atoms in disordered Al_2O_3 is $3.3a_0$, where a_0 is Bohr radius.

pressed in a DAC to ~300 GPa. Experiments in a DAC have the added advantage that material structure can be determined by x-ray scattering and electrical resistivity and optical reflectivity are readily measured.

If compressed sapphire does achieve MMC, the question arises as to the mechanism of electrical conduction. The fact that most covalent bonds in sapphire must be broken before metallic conduction is achieved suggests a phenomenon similar to that in metallic fluid hydrogen. Ashcroft pointed out that in order for dense fluid H to reach MMC, it is first necessary for the bonds in H_2 molecules to break.[23] In this case H can be treated as spherically symmetric; this idea works successfully for H, N, and O.[7] Thus, we assume that if bonds in crystalline Al_2O_3 break, Al and O atoms can also be treated as spherically symmetric. At a compression of 1.6 of initial density of sapphire (4.0 g/cm^3), the densities of Al and O are $7.6\times10^{22}/\text{cm}^3$ and $1.1\times10^{23}/\text{cm}^3$, respectively. This density of Al is 25% greater than the density of Al metal at ambient. The density of O is 73% of the metallization density of pure fluid O.[24] If Al and O phase separate at 300 GPa, the Al would be metallic, disordered, and compose 40% of the mixture. Since the Al composition would exceed the percolation limit for electrical conduction, the Al-O glass would have a conductivity comparable to MMC, whether or not O is metallic.

The more interesting question is whether it is possible for Al and O atoms at a sapphire compression of 1.6 to form a miscible alloy. To begin to answer this question, it is necessary to determine the radial extents of Al and O atoms relative to the space into which they must fit. The total density of Al and O atoms is $1.9\times10^{23}/\text{cm}^3$, which means on average each Al and O must fit into a cube with an edge length of $3.3a_0$, where a_0 is the Bohr radius. The radial extents of the outermost electrons of Al and O atoms were calculated in the Hartree-Fock-Slater approximation using integrals computed by Herman and Skillman.[25] The radial extents of $3s^2 3p^1$ and $2p^4$ electrons of Al and O atoms are $7a_0$ and $4a_0$, respectively, as shown in Fig. 3. Since one or the other of the curves in Fig. 3 would originate from adjacent atoms only $3.3a_0$ apart, the overlap would be substantial. Thus, it is spatially possible for Al and O to form hybridized energy bands of a metal in such a glass. These simple considerations indicate that densities of Al and O atoms in sapphire are so large, that simply breaking bonds in sapphire plus a modest compression, considering the 100 GPa pressures involved, are sufficient to turn strong covalent Al_2O_3 into a metallic glass.

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