Pressure-Induced Amorphization and Reduction of T-Nb$_2$O$_5$

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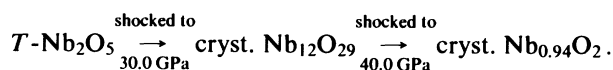*Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213-3890*

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Energy dispersive x-ray diffraction measurements show that the T phase of Nb$_2$O$_5$ becomes x-ray amorphous at a pressure of 19.2 GPa at 300 K. This pressure-induced amorphization is novel since the oxide is simultaneously reduced as it becomes amorphous. The amorphization occurs because the pressure-induced reduction T-Nb$_2$O$_5 \rightarrow$ crystalline Nb$_{12}$O$_{29}$ is kinetically impeded. A consideration of the ambient pressure atomic mechanism of the oxidation of NbO$_x$ compounds ($x < 2.5$) suggests that the pressure-induced amorphous state is formed by oxygen defects in the T-Nb$_2$O$_5$ lattice.

Ziman begins his book *Models of Disorder* with the following sentence: "Disorder is not mere chaos: it implies defective order" [1]. How defective this order can be is just beginning to be quantified: Kruger and Jeanloz discovered that AlPO$_4$ becomes amorphous when compressed, yet when the pressure is released the crystalline state returns with its initial crystalline orientation [2,3]. This indicates a close structural relationship between the ambient pressure crystalline state and the high-pressure amorphous state. Pressure-induced amorphization has been observed for several classes of materials; e.g., α-quartz, berlinite, Ca(NO$_3$)$_2$/NaNO$_3$, SnI$_4$, anorthite, and Ca(OH)$_2$ [2,4,5]. Pressure-amorphized materials can have properties different from those of their melt-quenched counterparts; a recent example is the anisotropicity of pressure-amorphized α-quartz [6]. Understanding the mechanism and driving force behind these pressure-induced transformations is seminal in revealing the "order" in amorphous solids. Several possibilities, not necessarily mutually exclusive, have been suggested as the driving force for solid-state amorphizations. These include melting, mechanical instabilities, a kinetically impeded phase transition, and the generation of many defects or dislocations [2,4,7–11].

Kikuchi et al. studied the effect of shock compression on the T phase of pentavalent niobium oxide (T-Nb$_2$O$_5$) [12]. They found that T-Nb$_2$O$_5$ reduced to a form of NbO$_2$ via an intermediate step:

$$T\text{-Nb}_2\text{O}_5 \underset{30.0\,\text{GPa}}{\overset{\text{shocked to}}{\longrightarrow}} \text{cryst. Nb}_{12}\text{O}_{29} \underset{40.0\,\text{GPa}}{\overset{\text{shocked to}}{\longrightarrow}} \text{cryst. Nb}_{0.94}\text{O}_2 .$$

It is well known that compression can drive solid-state oxidation or reduction and that transitions that are sluggish with static pressure can be facile with shock compression [13–15]. Atomic mobility occurs because shock waves cause microscopic shear and strain in the sample; also, the temperature rise associated with shock compression can enhance the transformation [15]. These considerations led us to investigate the effect of static compression on T-Nb$_2$O$_5$ to see whether the transition observed by Kikuchi et al. could be impeded and result in an amorphous state.

The T-Nb$_2$O$_5$ samples were prepared by heating niobia aerogels [16]. The x-ray diffraction patterns of the samples agree with those reported for T-Nb$_2$O$_5$ [17]. We pressurized the samples using a Merrill-Bassett style diamond anvil cell. We monitored the pressure within the cell using the standard ruby fluorescence method or by observing the change in the (111) diffraction line of gold; the pressure was calculated using an equation of state [18]. Details of the optical measurements are given in Ref. [19]. We used no pressure-transmitting fluid, but the linewidth of rubies dispersed across the sample showed that pressure gradients were minimal [20]. While the x-ray measurements were made without a pressure-transmitting fluid, we did observe the color change reported below regardless of whether or not a pressure-transmitting medium (4:1 methanol/ethanol) was used.

There are two principal *in situ* high-pressure experimental observations. First, the gradual disappearance of the diffraction pattern of T-Nb$_2$O$_5$ with compression (see Fig. 1). Clearly, at a pressure of 19.2 GPa the sample is x-ray amorphous. Upon release of the pressure the sample remains amorphous—the x-ray spectrum looks identical to the 19.2-GPa spectrum reported in Fig. 1. Second, the color of the sample changes gradually from white to grey to black during compression. The color change is homogeneous over the sample volume and parallels the disappearance of the diffraction peaks. The black color remains upon release of the pressure. This color change shows that the niobium oxide sample has been reduced since (1) all seven crystalline phases of Nb$_2$O$_5$ are insulators with a white color and (2) all nonstoichiometric NbO$_x$ ($x < 2.5$) compounds have either a definite dark blue or black color [22,23].

To ascertain that reduction occurred through the loss of oxygen, we did two annealing experiments. First, we annealed the reduced and amorphized sample in air at a temperature of 500°C for 1.5 h. During the annealing the sample color changed from black to white; the Raman spectrum of the annealed sample showed the recovery of crystalline T-Nb$_2$O$_5$. Second, we annealed the sample in argon at 500°C for 5 h. (The chamber was evacuated to $\sim 10^{-3}$ torr, then purged with argon 3 times.) The sample remained black in the absence of an oxidizing agent,
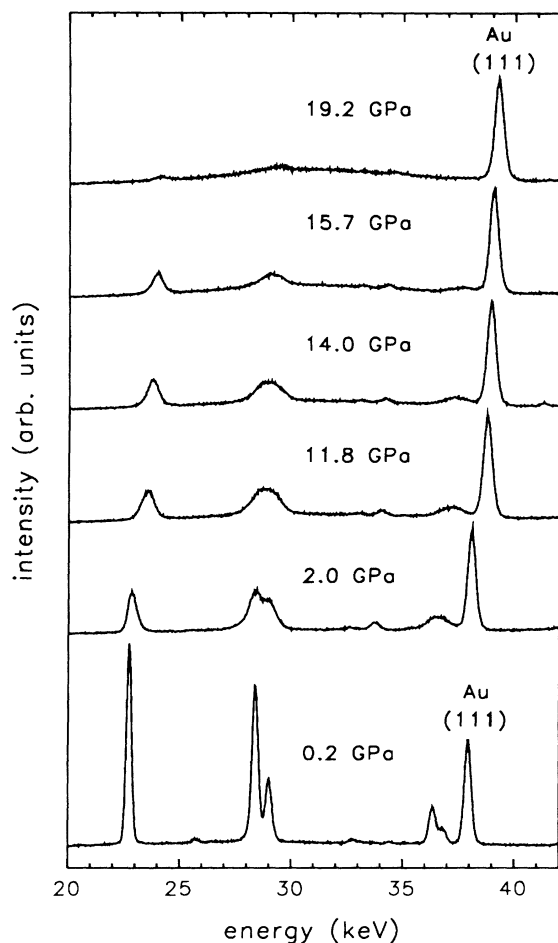
FIG. 1. Energy dispersive x-ray diffraction patterns of a T-Nb2O5 sample at various pressures. The spectra have been normalized to the intensity of the Au(111) peak. The x-ray diffraction patterns were measured at CHESS (Cornell High Energy Synchrotron Source) using a Ge solid-state detector [21]. *Ed* for all measurements was determined, with a piece of gold foil, to be 89.34 keV Å.
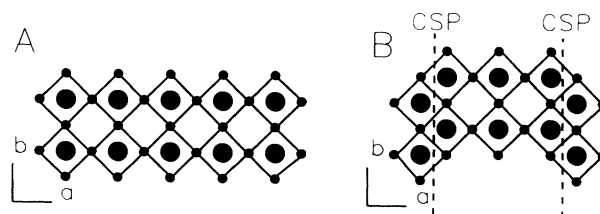

FIG. 2. (A) The ReO3 structure is composed of cations surrounded by an octahedral arrangement of oxygen atoms that share corners. (B) Crystallographic shear can remove a row of oxygens and change a column of corner-sharing octahedra into edge-sharing units. This results in the formation of a crystallographic shear plane (CSP).

thus showing that reduction did occur during compression. We cannot quantify the extent of reduction due to the small amount of sample [O(10 μg)] produced in the diamond anvil cell. However, we can place a lower limit on the extent of reduction: Wadi and Morikawa found that the T-Nb2O5 crystal structure is retained until the oxygen-to-niobium ratio falls below 2.488 [24].

Our results show clearly that T-Nb2O5 is reduced and becomes amorphous when statically compressed. The difference in atomic mobility between static pressure and shock-induced transformations suggests that the amorphous state results because the shock-induced reaction T-Nb2O5→ crystalline Nb12O29 is impeded, i.e., an amorphous niobium oxide with a stoichiometry between those of Nb2O5 and Nb12O29 is formed. We suggest a general atomic mechanism for the pressure-induced amorphization or reduction of T-Nb2O5 based on electron

microscopy studies of the ambient pressure oxidations of NbO$_x$ ($x < 2.5$) compounds to the H phase of Nb2O5 [23,25–27]. The crystal structures of H-Nb2O5 and nonstoichmetric NbO$_x$ compounds are crystallographic shear structures based on the ReO3 structure. The ReO3 structure is composed of cations surrounded by an octahedral arrangement of oxygen atoms which share corners. The crystal structure of T-Nb2O5 is considered to be a "disordered" form of H-Nb2O5; it consists of distorted octahedra and pentagonal bipyramids. The niobium structures based on the ReO3 structure are generated by the formation of crystallographic shear (CS) planes; i.e., a row of oxygen atoms is removed by changing adjacent columns of corner-sharing octahedra to edge-sharing units (see Fig. 2). The CS planes divide the structure into small blocks of $m \times n$ octahedra. The H-Nb2O5 structure, for example, contains 5×3 and 4×3 blocks, whereas only 4×3 blocks exist in Nb12O29 [28,29]. It is by the formation of CS planes that the oxidation of NbO$_x$ compounds occurs because crystallographic shear can change the oxidation state of the central cation by changing the cation/oxygen ratio.

The oxidations of NbO$_x$ compounds to H-Nb2O5 take place by a homogeneous solid-state reaction, instead of by a reconstructive nucleation and growth mechanism. Rather than occurring at some oxygen/crystal interface the oxidation occurs through open channels in the crystal structure; oxygen diffuses into the solid followed by unit readjustments of the atomic positions into a superlattice [23,25]. This superlattice rearranges into the H-Nb2O5 crystal structure by a lateral displacement of CS planes into a regularly spaced arrangement [25,30].

Since the oxidations of NbO$_x$ compounds have low activation energies and occur with only unit displacements of the atomic positions, it is likely that a similar mechanism can be used to describe the pressure-induced amorphization or reduction of pentavalent niobium oxides [27]. Specifically, when compressed T-Nb2O5 loses oxygen, this results in many "defect" sites in the structure. Since the mobility provided by shock waves is absent, the defects cannot move into the regularly spaced configuration of the CS planes of a crystalline nonstoi-

chiometric NbO_x compound. The resulting pressure-induced amorphous state is then largely a "defective" T-Nb_2O_5 structure [31].

The conclusions that the amorphous state is defective T-Nb_2O_5 and that the reduction mechanism involves crystallographic shear are supported by two pieces of experimental evidence. First, wavelength dispersive spectrometry (WDS) shows that the niobium atomic density in the ambient pressure T-Nb_2O_5 is very similar to that of the pressure-amorphized sample. A sample, in a WDS measurement, is bombarded with x rays that cause the sample to emit x-ray fluorescent radiation characteristic of a particular atom. The intensity of the emitted radiation, as measured by a wavelength spectrometer, is proportional to the atomic concentration [32]. The percent difference between the scattering from the niobium in T-Nb_2O_5 and in the pressure-induced amorphous phase was at most 0.7% [33]. If the amorphous phase were a disordered $Nb_{12}O_{29}$ structure, the percent difference in the scattering would have been $\sim14\%$ [28,32,34]. Second, we looked at compounds where CS planes can and cannot occur to test whether crystallographic shear is a mechanism for the pressure-induced reduction. Specifically, we studied the pressure-induced color changes of H-Nb_2O_5 and $KNbO_3$. Initially both samples are white; when pressurized to 20.0 GPa H-Nb_2O_5 turns black, while $KNbO_3$ stays white. In the H-Nb_2O_5 structure CS planes can easily form because the interstitial sites among the octahedra are empty. Contrast this to the $KNbO_3$ structure where CS planes cannot easily occur because the potassium atoms fill the interstitial sites, thus impeding the movements of the niobium octahedra [35]. Chen and Feng, in fact, found that it is almost impossible to find CS planes in $KNbO_3$ crystals [36]. These experiments confirmed our view that CS is the mechanism of reduction when the niobium cations are reduced by compression.

In this Letter we have shown that a pressure-induced amorphization can result from an impeded reduction. Furthermore, the reduction reaction occurring simultaneously with the amorphization suggests an atomic mechanism for the amorphization, viz., the formation of defect sites in the T-Nb_2O_5 lattice. We have begun a high-resolution electron microscopy study of the pressure-induced changes of T-Nb_2O_5 to further test the proposed mechanism.

Note added.—Recently Fecht proposed a model for solid-state amorphization based on defect-induced melting [37]. He shows that when the defect concentration is above a critical level a crystalline solid will collapse into a disordered state. The pressure-induced amorphization and the proposed mechanism are consistent with Fecht's model.

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