

Kinetics of a first-order crystalline-amorphous transformation in zirconium tungstateXiaozhi Yan,^{1,2,*} Xiangting Ren,² Guangai Sun,¹ Dong Li,³ Xin Li,^{1,3} Duanwei He,^{3,†} and Wenge Yang^{2,4}¹*Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, People's Republic of China*²*Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, People's Republic of China*³*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, People's Republic of China*⁴*High Pressure Synergetic Consortium (HPSynC), Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, USA*

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A combination of *in situ* volumetric measurements, Raman spectroscopy, x-ray diffraction, differential thermal analysis, and transmission electron microscopy was used to investigate the crystalline-amorphous transformation of zirconium tungstate at high pressure and room temperature. Zirconium tungstate transformed at about 1.2 GPa to an amorphous phase which was recoverable to ambient conditions. The volume contraction and temperature increase in the sample during pressure-induced amorphization indicate that it was a first-order phase transition. The kinetics data are consistent with a model where an amorphous phase occurs by the formation of nuclei without noticeable growth. However, our results conflict with the three-dimensional interface-controlled growth of a new phase in conventional solid-state polymorphic changes.

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I. INTRODUCTION

Pressure-induced amorphization (PIA) plays an important role in many physical processes and it is a promising approach for the commercial production of amorphous materials [1–5]. There has been considerable interest in the PIA effect since its first observation in $\text{Gd}_2(\text{M}_2\text{O}_4)$ in 1972 [6], and (especially) in ice nearly 30 years ago [7–9]. Now, pressure-induced amorphization has been discovered in many materials such as silicon [10], α -quartz [11–13], AlPO_4 [14,15], zeolites [2,16], etc. A large number of experimental and theoretical investigations have been devoted to unfolding a variety of this fascinating phase transformation's aspects under high pressure [17–22]. Several mechanisms have been proposed to explain the process of PIA in solids [3,23,24], including melting effects [8,11], kinetically frustrated phase transitions or decomposition [25,26], as well as the failure of some lattice stability criterion [27,28]. Based on the numerous high-pressure and ambient-pressure experimental data, the supposition that the shear lattice instability is the reason for PIA has become the most popular one [29]. Most of the theoretical descriptions of PIA are based on the assumption that it is a first-order transformation [26,27]. Some studies of temperature-induced amorphization at ambient pressure indicated that the crystalline-amorphous phase transition is a first-order phase transition [30–33]. However, the first-order phase transition assumption has not been well examined in most of the PIA experiments. Moreover, of the many studies devoted to PIA, few have been concerned with kinetics, which is crucial for describing the nucleation and growth process and testing phase transition mechanisms [3].

The cubic (α) ambient pressure phase of zirconium tungstate (ZrW_2O_8) possesses a flexible structure of corner-sharing ZrO_6 and WO_4 polyhedra [Fig. 1(a)] [34,35]. Upon compression, cubic ZrW_2O_8 transforms to a quenchable orthorhombic (γ) phase, that is structurally similar to the α

phase, but the closer proximity of its neighboring WO_4 tetrahedra leads to higher W-O coordination [Fig. 1(b)] [36,37]. Orthorhombic phase ZrW_2O_8 undergoes a phase transition to an amorphous phase at relatively modest pressures beginning around 1.5 GPa [34]. The mechanism for amorphization in ZrW_2O_8 is particularly interesting since crystalline ZrW_2O_8 shows some unusual properties which are believed to be theoretically linked with PIA [34,38]. The great flexibility of the ZrW_2O_8 framework is considered to be the key to its fantastic properties, including isotropic negative thermal expansion (NTE), pressure-induced elastic softening, and PIA [34,39,40]. The PIA in ZrW_2O_8 seems to be attributed to polyhedral rotation and translations accompanied by cation coordination variation [41–44]. However, others studies have advocated that the amorphous phase is actually a kinetically hindered mixture of ZrO_2 and WO_3 , which has since been challenged [43,45].

In this paper, we performed comprehensive experiments to investigate the pressure-induced crystalline-amorphous phase transition in ZrW_2O_8 . We observed that this phase transition was exothermic and the volume of ZrW_2O_8 collapsed with time at a fixed pressure during amorphization, implying that the PIA in ZrW_2O_8 is a first-order transformation. The transformation kinetics data indicate the PIA is achieved mainly by nucleation.

II. EXPERIMENT

Cubic phase ZrW_2O_8 powder with a purity of 99.7% (Alfa Aesar Co., Inc.) was used as the starting material. The initial and quenched samples were characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD) analysis with $\text{Cu } K\alpha$ radiation (DX-2500, Dandong, China). High-pressure Raman spectra were measured by a Raman spectrometer with a 532.1 nm excitation laser. A symmetric diamond anvil cell was employed to generate high pressure. A stainless steel gasket was preindented to about a 40 μm thickness, followed by laser drilling the central part to form a 100 μm diameter hole to serve as the sample chamber. ZrW_2O_8 powder and a small ruby ball were loaded in the chamber.

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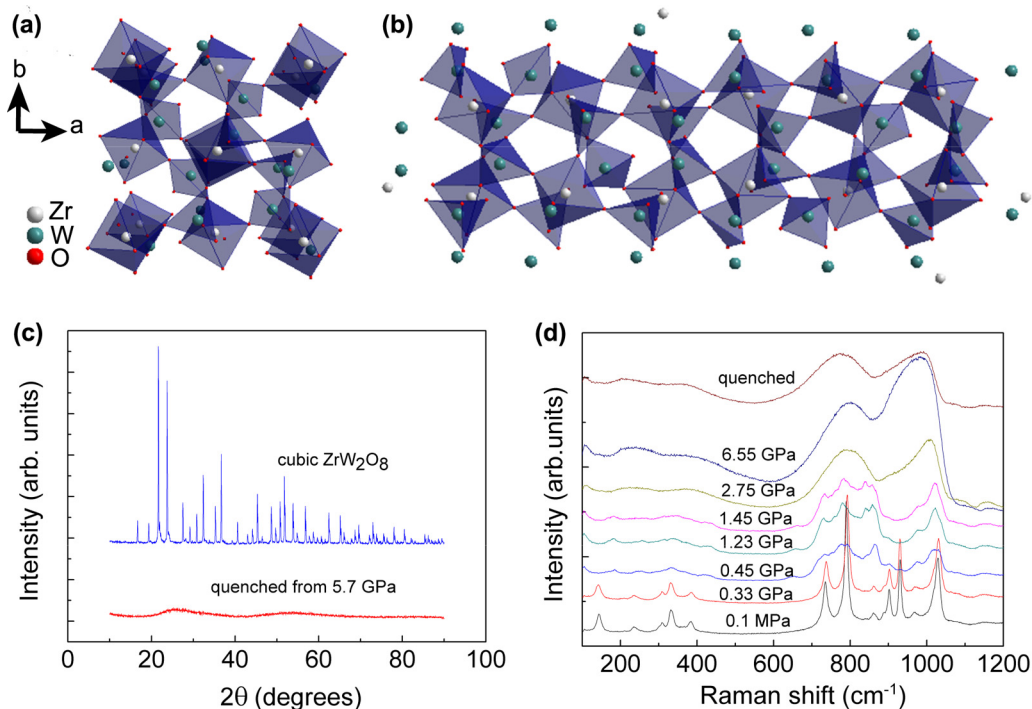


FIG. 1. Crystal structure of the (a) cubic α and (b) orthorhombic γ phases of ZrW_2O_8 viewed along the 001 direction. The blue units represent polyhedra around zirconium or tungsten. (c) X-ray diffraction patterns for the cubic and amorphous phases of ZrW_2O_8 . Data was collected using Cu $K\alpha$ radiation. (d) Raman spectrum of ZrW_2O_8 at various pressures. The Raman modes exhibit splitting in the orthorhombic phase and broaden in the amorphous phase.

Silicon oil was used as the pressure-transmitting medium and the pressures were determined by the ruby fluorescence method [46].

The *in situ* volumetric measurements and differential thermal analysis (DTA) measurements of ZrW_2O_8 were conducted at room temperature using the DS 6×14 MN cubic press. In these experiments, pressure first increased to about 0.7 GPa, followed by a decrease to about 0.4 GPa, from which we increased the pressure again and conducted our measurements. Thereby, the cubic-orthorhombic phase transition was not detected in the volumetric and DTA measurements. The strain gauge technique, which has been applied successfully to the study of compressibility and transformation kinetics of many materials [47,48], was used to monitor the sample's volume change. All details concerning the experiments and preparation of gauges are presented elsewhere [47]. The relative accuracy of the volume measurements (measurement sensitivity) was about 0.02%. The loading of the high-pressure device was performed at a rate of about 0.2 GPa/min. The pressure was controlled by a fixed magnitude with an accuracy of about 0.002 GPa. In experimental run 1, pressure increased continuously to about 5.7 GPa. In experimental runs 2 and 3, the loadings were stopped after attaining the pressure of 1.14 and 1.23 GPa, respectively, and then the pressure was held constant with an accuracy of ± 0.002 GPa. During the process, the time dependence of the sample volume was measured.

Two chromel-alumel thermocouples of 0.05 mm in diameter, protected by alumina tubing, were employed in the measurements of the DTA signals. One of them had a junction in the center of the sample. The other had a junction in the pressure-transmitting medium (pyrophyllite). In this assembly

the pyrophyllite served as a reference sample in the DTA measurements.

Laboratory XRD [Fig. 1(c)] confirmed the starting material was cubic ZrW_2O_8 . The Raman spectrum of the starting material was also in agreement with that reported for cubic ZrW_2O_8 in Refs. [34,49] [Fig. 1(d)]. As the pressure increased above 0.33 GPa, the onset of a cubic-to-orthorhombic phase transition was revealed by new modes arising and some Raman peaks splitting, which was attributed to the lowering of tungsten site symmetry from C_3 in cubic $P2_13$ to C_1 in orthorhombic $P2_12_12_1$. This transition pressure is a little higher than that (0.21 GPa) previously reported by Jorgensen *et al.* [36], while it is lower than the value (0.5 GPa) reported by Pantea *et al.* [39]. Above 2.75 GPa, most of the peaks from the orthorhombic phase disappeared, except two very broad peaks at about 800 and 1000 cm^{-1} , indicating that pressure-induced amorphization occurred.

III. RESULTS AND DISCUSSION

The data of the volumetric measurements are presented in Fig. 2. In experimental run 1 we observed a discontinuous change at about 1.2 GPa, corresponding to the beginning of amorphization in ZrW_2O_8 . The discontinuity of the derivative compression data in run 1 shows the PIA ends at 2.5 GPa, which agrees well with our Raman experiments and published data [49]. The volume reduction in PIA is 11%. Laboratory XRD [Fig. 1(c)] confirmed that the sample quenched from 5.7 GPa was amorphous. When the pressure was maintained at 1.14 and 1.23 GPa (run 2 and run 3), we observed a time-dependent volume decrease (density increase). Thereby, we

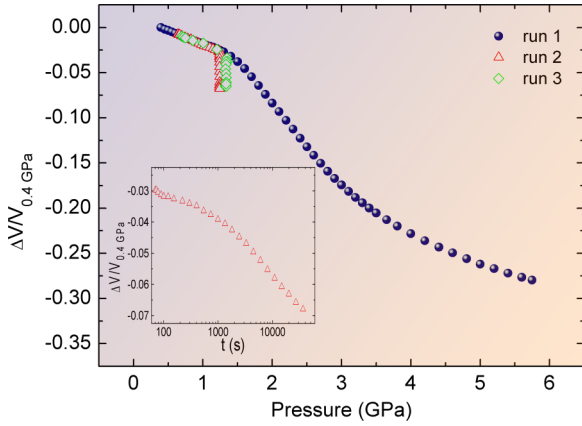


FIG. 2. Change in the volume of the ZrW_2O_8 samples under compression at room temperature. Run 1: The pressure increase rate is 0.2 GPa/min. Run 2: Maintain in a constant pressure of 1.14 GPa. Run 3: Maintain in a constant pressure of 1.23 GPa. The inset shows the time dependences of the volume change in run 2 on the logarithmic scale.

have measured the volume jump during the PIA in ZrW_2O_8 and demonstrate it is a first-order phase transition.

We further confirmed this conclusion using a DTA measurement. DTA in the simplest form denotes the measurement of the temperature difference ΔT between the sample and reference material when placed under the same temperature and pressure conditions. First-order phase transitions, which are accompanied by a volume change and release of latent heat, can be detected as an unusual change in the ΔT . The temperature in our reference material varied little in the whole pressure range of experiment, while in a certain pressure range the sample temperature visibly increased with pressure [Fig. 3(a)], resulting in the increase of the DTA signal [Fig. 3(b)]. A peak in the derivative DTA signal [Fig. 3(c)] also characterized this exothermic process. It should

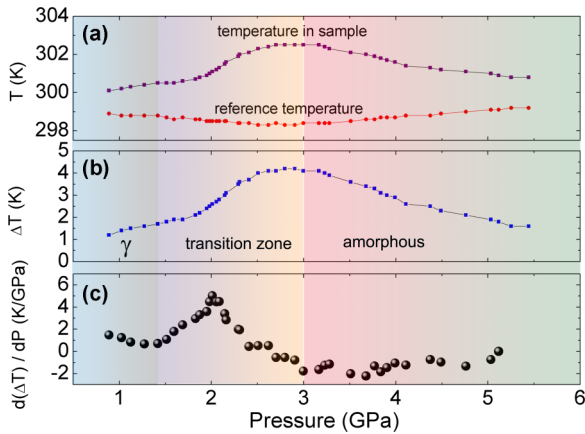


FIG. 3. Signals of the DTA measurements of ZrW_2O_8 under high pressure. (a) Measured temperature in the sample and reference material. The temperature discrepancies detected in these two materials in the pure phase ZrW_2O_8 pressure range may arise from a systemic error. (b) DTA curves generated from the raw data shown in (a). (c) The derivative of the DTA signals.

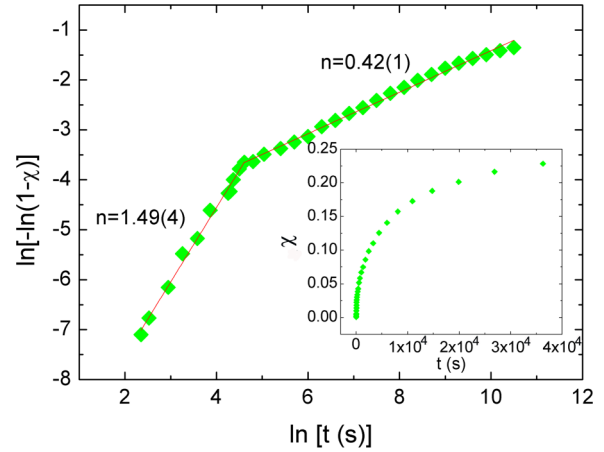


FIG. 4. The Avrami coordinates $\ln[-\ln(1 - \chi)]$ as a function of $\ln(t)$ at a constant pressure of 1.14 GPa. The inset shows the time dependencies of a phase fraction of amorphous ZrW_2O_8 .

be noted that the temperature-induced crystalline-amorphous phase transition under ambient pressure is also evidenced to be exothermic [30–33], indicating a similarity between these two types of amorphization. Furthermore, the pressure range of this peak is from 1.4 to about 3 GPa, corresponding to the pressure range of the orthorhombic-amorphous transformation in ZrW_2O_8 .

We investigated the kinetics of the crystalline-to-amorphous phase transition in ZrW_2O_8 at room temperature by monitoring the time-dependent change in the amorphous phase fraction (χ) (see the inset in Fig. 4). The transformed fraction of the sample is given by $\chi(t) = \Delta V(t)/\Delta V$, where $\Delta V(t)$ is the volume reduction at a certain point in time and ΔV represents the total volume reduction during amorphization. The nucleation and growth process is normally modeled by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation [50]

$$\chi(t) = 1 - \exp(-kt^n),$$

where k is the reaction constant related to the activation energy, and n is the Avrami exponent, reflecting the characteristics of nucleation and growth during the phase transition. The most useful way of analyzing the experimental data is usually to plot the curve of $\ln[-\ln(1 - \chi)]$ against $\ln(t)$. Usually, the local Avrami exponent, i.e., the slope of the curve, is used to trace the transformation's underlying mechanisms. Figure 4 shows the plot of $\ln[-\ln(1 - \chi)]$ vs $\ln(t)$ for the data collected at 1.14 GPa (run 2). This curve undergoes a slope decrease from 1.49 to 0.42 at $\ln[t(s)] = 4.5$ (corresponding to a $\sim 2.5\%$ phase fraction of the amorphous ZrW_2O_8), which divides the curve into two segments. Such small values of the Avrami exponent have also been reported in the studies of temperature-induced amorphization [32,33]. The variation of the Avrami exponent has been reported in many studies and may be attributed to the variation of the new phase nucleation rate [51].

Based on the observations that amorphous lamellae existed in some PIA materials [1,13] and some materials even show dramatic memory retention of the initial crystal orientations [12,14,15,17], a displacive phase transition mechanism has

been proposed, where PIA is triggered by the onset of elastic instability, while crystalline topology is preserved [3,27]. Keen *et al.* argued that the PIA in ZrW_2O_8 arises from polyhedral rotation and translations, indicating that it is a displacive transformation [42]. The Avrami exponent should be larger than 3 for a three-dimensional interface controlled growth [51], which distinctly conflicts with our observation. However, it has also been suggested that the growth of an amorphous domain in a pressure-induced displacive crystalline-amorphous transformation is negligible [27,29]. Consequently, the dimensionality of the growth can be regarded as zero and the observed Avrami exponent in our experiment could correspond to an increasing nucleation rate in the first stage of a displacive phase transition and decreasing nucleation rate in the second stage.

The PIA of ZrW_2O_8 has also been considered to be a hindered decomposition into ZrO_2 and WO_3 [45]. In this way, the PIA of ZrW_2O_8 is diffusion controlled. In a diffusion-controlled phase transition, it was suggested that the Avrami exponent varies between 1 and 2.5 in the initial stage [51]. Accordingly, the Avrami exponent agrees with this description. However, such room-temperature diffusion-controlled PIA seems to be unrealistic because the diffusion of atoms may be inhibited at low temperature and high pressure [3,26].

The kinetics of the PIA was further elucidated via TEM characterization (Fig. 5). Three samples were decompressed from maximum pressure of 1.5, 2, and 5.7 GPa, respectively, to quench the high-pressure transformation microstructures. In the sample recovered from 1.5 GPa, no amorphous domains with a size larger than 2 nm were observed [Fig. 5(a)]. As pressure increased from 1.5 to 2.5 GPa, the phase fraction of the amorphous increased from 10% to 57%. Meanwhile, the sizes of the amorphous domains did not obviously increase and are still smaller than 2 nm [Fig. 5(b)]. These characteristics are in accordance with the aforementioned displacive phase transition model, in which the critical-size nucleus is nearly reduced to a single unit cell and the growth of amorphous domains is negligible [27,29]. TEM images and electron diffraction patterns showed complete amorphization for the sample recovered from 5.7 GPa, confirming that the loss of sharp diffraction and Raman spectra in previous studies was due to amorphization instead of the crystalline size reduction. We also observed that amorphization of ZrW_2O_8 can be induced by grinding in an agate mortar. After 40 min of grinding, ZrW_2O_8 totally transformed to amorphous [Fig. 5(d)], indicating that shear stress plays an important role in the PIA. This is also in consistence with the displacive phase transition model of PIA.

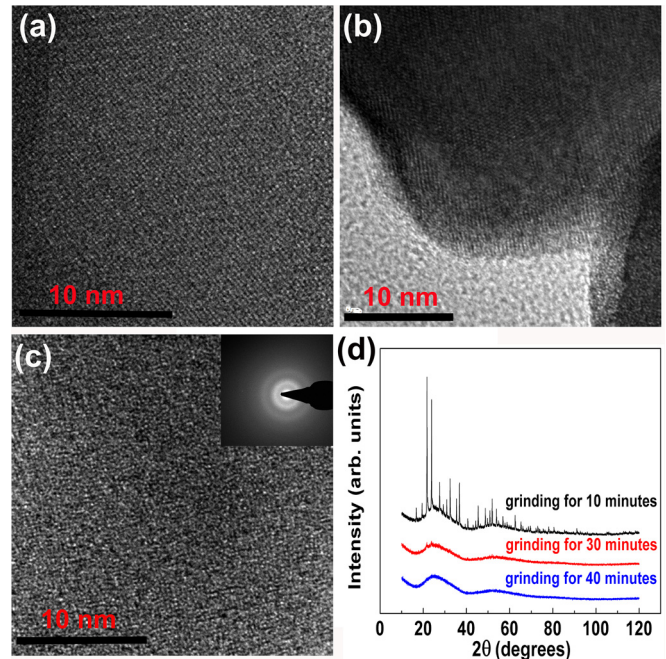


FIG. 5. (a)–(c) TEM characterization of the crystalline-to-amorphous transition process. (a) Randomly distributed amorphous domains in the sample recovered from 1.5 GPa. (b) The domain size of the amorphous recovered from 2.5 GPa is comparable to that shown in (a). (c) High-resolution TEM image of the sample recovered from 5.5 GPa. Inset: Selected area electron diffraction patterns. (d) XRD patterns of samples ground for different times.

IV. CONCLUSIONS

In conclusion, we demonstrated that the crystalline-amorphous transformation in ZrW_2O_8 is a first-order phase transition by the volume drop and temperature increase in our samples during the phase transition. Furthermore, we investigated the phase transition kinetics of PIA in ZrW_2O_8 . The experimental results presented here support an unusual displacive transformation model in which the PIA proceeds only through nucleation while the growth process is negligible.

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