

Understanding exceptional thermodynamic and kinetic stability of amorphous sulfur obtained by rapid compression

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Amorphous sulfur (*a*-S) with excellent stability is obtained by rapid compression method. The prepared *a*-S has a single glassy phase and exhibits a wide supercooled liquid region of 112 K and much high thermal and kinetic stability at room temperature compared to that of conventional *a*-S fabricated by quenched method. The substantial improved thermal and kinetic stability is attributed to low energy state induced by rapid compressing process. The stable *a*-S is a model system for facilitating the studies of the nature of glasses and supercooled liquids. © 2009 American Institute of Physics. [DOI: 10.1063/1.3064125]

Sulfur, which has been used for several thousands of years, has ever played a crucial role in the history of human beings as an important constitute of powder first invented in ancient China. Nowadays, sulfur is an important cross-linking agent for the production of rubber goods of all kinds, especially for the manufacture of vehicular tires¹ and for exploring polymeric materials. Sulfur is one of the most complex elements as far as the variety of molecular forms and crystalline states are concerned.²⁻⁴ Amorphous sulfur (*a*-S), as one of S allotropes, is used for vulcanization as it is more soluble in both natural and synthetic rubbers than any of its crystalline polymorphs.⁵ Traditionally, *a*-S is prepared by quickly quenching liquid sulfur above 159.4 °C.^{6,7} However, *a*-S has high tendency for crystallization in supercooled liquid state.⁵ Because as-quenched *a*-S has a glass transition temperature T_g below room temperature (RT) and cannot be kept even at RT because of the high instability, which is unfavorable for its practical application and some basic issues studied. Therefore, the stable *a*-S is of significance for industrial application and fundamental research.

A liquid-glass transition can be induced either by decreasing the temperature through T_g or by increasing the pressure through the glass-transition pressure P_g in liquids.⁸ Rapid cooling for preparing amorphous materials has been very mature.⁹ Although preparing amorphous materials by compression is very reasonable in physics, it still faces a series of technical problems.¹⁰ In this letter, exceptional stable bulk *a*-S with unique natures was obtained by using a recently developed rapid compression method.¹⁰ The rapid compressing at a settled temperature is an entirely different thermodynamic path to prepare glassy materials compared to the traditional method of quenching at a fixed pressure. The prepared *a*-S has a much wider supercooled liquid region and much greater kinetic stability.

Figure 1 illustrates the schematic plan of the preparation process. The sulfur 99.9999% in purity was filled in an Al container. A set of tungsten carbide piston cylinder with a resistance coil heater was used to produce high pressure and temperature. The samples were prepressed in 0.17 GPa and melted at 175 °C, then solidified the melt through a rapid

compression from 0.17 to 2 GPa in 20 ms, and finally cooled down naturally to RT and decompressed slowly to ambient pressure.¹⁰ The rapid compression solidified the liquid sulfur into solid sulfur with a compressing rate of 1.0×10^{11} Pa/s at 175 °C. For comparison, the conventional method was also applied to prepare *a*-S by quenching the sulfur melt at 175 °C in liquid nitrogen at ambient pressure. The structure of S was examined by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu $K\alpha$ radiation. Differential scanning calorimetry (DSC) was performed under a purified argon atmosphere in a Mettler Toledo DSC822e. Acoustic velocities were measured using a pulse echo overlap method with carrying frequency of 10 MHz.¹¹

The picture of the *a*-S obtained by rapid compression (20 mm in diameter and 6 mm in thickness) is shown in the inset of Fig. 2. In contrast to pale yellow color of crystalline sulfur, the *a*-S has uniform brown color indicating the homogeneous structure. The XRD pattern of the *a*-S at RT shown in Fig. 2 exhibits only the two broad maxima associated with an amorphous phase. Figure 3 shows good pliability, translucence, and excellent extensibility of the compressed *a*-S which are distinguished from crystalline sulfur, which is brittle solid and has opacity at RT. The *a*-S obtained by rapid compression, like a typical rubber, can be easily stretched by hands and shows good restorability. When the *a*-S transforms

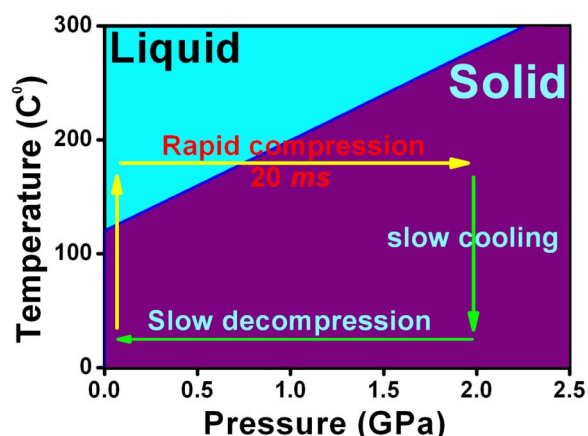


FIG. 1. (Color online) The schematic plan of preparation of *a*-S by rapid compression based on the liquid-solid phase diagram of sulfur.

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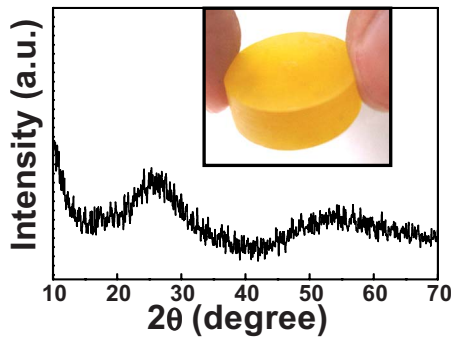


FIG. 2. (Color online) The XRD pattern at RT for the *a*-S obtained by rapid compression method, and the inset shows its picture.

into crystalline state, the properties of elasticity and translucence disappear.

The thermodynamic properties of the compressed and quenched *a*-S were measured by DSC and shown in Fig. 4(a). The DSC curves for both *a*-S obtained under pressure and conventional quenching show a distinct glass transition onset at T_g and obvious crystallization events, which further confirm their amorphous structure. The remarkable result is that the two *a*-S samples are markedly different. The *a*-S obtained by rapid compression shows a glass transition temperature of $-11\text{ }^\circ\text{C}$, larger than that of the quenched *a*-S ($T_g = -18\text{ }^\circ\text{C}$). Only one crystallization peak shown in DSC curve for the compressed *a*-S indicates that *a*-S has a single amorphous phase, while two broad crystallization peaks are shown in the DSC curve for the quenched *a*-S, implying two step crystallization corresponding to two amorphous phases in the *a*-S contained by normal quenching. Furthermore, the compressed *a*-S exhibits a very wide supercooled liquid region of $112\text{ }^\circ\text{C}$ derived from the DSC curve, while for the quenched *a*-S, there is only a small supercooled liquid region of $27\text{ }^\circ\text{C}$. These results indicate that the compressed sample and its supercooled liquid state are thermodynamically and kinetically more stable compared to that of the quenched *a*-S.

The excellent high thermal stability of compressed *a*-S allows taking appropriate time to carry through acoustic experiments. Figure 4(b) shows the temperature dependent longitudinal wave velocity at a warming rate of $1.0\text{ }^\circ\text{C}/\text{min}$. The knee point corresponding to thermodynamic T_g detected by DSC can be found in the measured data. Except for the

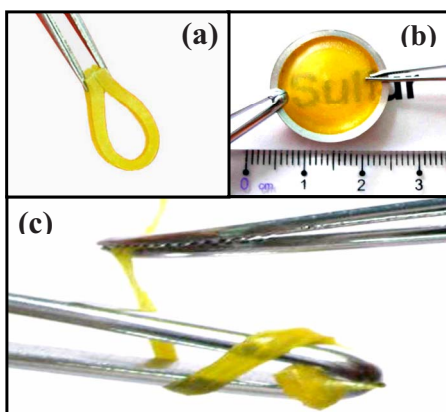


FIG. 3. (Color online) (a) shows the good pliability, (b) indicates the translucence, and (c) exhibits the excellent extensibility.

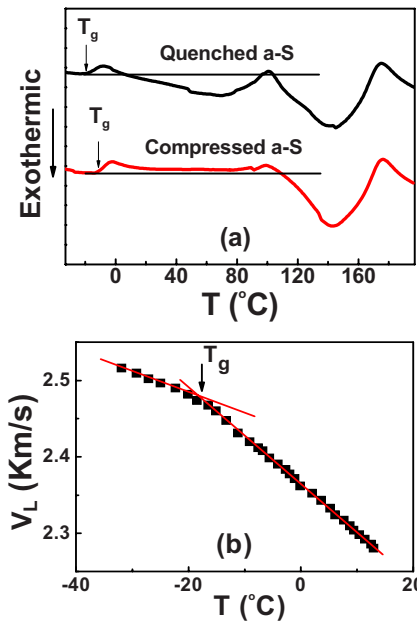


FIG. 4. (Color online) (a) The DSC curves at a heating rate of $0.667\text{ }^\circ\text{C}/\text{s}$ for the quenched and compressed *a*-S. (b) The dependence of longitudinal acoustic wave velocity on temperature for the compressed *a*-S.

glass transition, no other transition points can be detected in the acoustic measurement, which further confirms single amorphous S phase. The velocity from -30 to $13\text{ }^\circ\text{C}$ decreases about 9.2% , and the acute decrease in velocity indicates the softening process.¹¹

Table I lists the density and elastic moduli (Young's modulus E , shear modulus G , bulk modulus B , and Poisson's ratio ν) at $0\text{ }^\circ\text{C}$ of the compressed *a*-S. The low G , relative high B , and high Poisson's ratio (the ν at RT is extrapolated to 0.40) imply the good deformability and plasticity at RT.¹¹ The density of the compressed *a*-S is $1.94\text{ g}/\text{cm}^3$, which is slightly higher than the density of $1.92\text{ g}/\text{cm}^3$ for the quenched *a*-S, which indicates that rapid compression can induce more compact structure than conventional quenched method. The Kauzmann temperature is very close to T_g , which is in favor of low energy state and high thermal stability.¹²⁻¹⁴

The glassy materials with low T_g are normally unstable. For example, the monatomic amorphous metals such as Bi and Pb have been made by deposition from the vapor, but these prove no kinetic stability and crystallize when the temperature is raised even at 15 K .¹⁵ At RT, the conventional *a*-S prepared by quenching is highly unstable and crystallizes in minutes. Due to the poor stability, it is unfavorable for carry out experiments such as acoustic measurement for the quenched *a*-S. The time scale of the amorphous-to-crystalline phase transition in the two kinds of *a*-S is characterized by the temperature-time-transition (TTT) diagram, which gives the time to reach full crystallization. The isothermal crystallizations of quenched *a*-S at ambient pressure were carried out at different temperatures and the results are summarized in the TTT diagram in Fig. 5. From the diagram one can see the sketch of the typical nose shape for the quenched *a*-S in the range of 10 s . The results indicate that the quenched *a*-S is very unstable when it is heated above T_g . At RT, the quenched *a*-S will be fully crystallized in 100 s . However, the crystallization times for compressed *a*-S at three representative temperatures are much longer than that

TABLE I. The parameters at 0 °C for the α -S obtained by rapid compression.

	E (GPa)	G (GPa)	B (GPa)	ν	T_K (°C)	T_g (°C)	ρ (g/cm ³)
α -S	5.75	2.08	7.94	0.379	-63	-11	1.94

of quenched sample, as shown in Fig. 5. At RT, it takes 80 min to reach the fully crystalline state for the compressed α -S, while at -4 °C in the fridge (higher than its T_g), the compressed α -S can be kept over 1 month without any detectable crystallization. The results indicate the excellent stability of the compressed α -S in contrast to quenched α -S.

The outstanding thermal stability of compressed α -S consequently attributes to the special rapid compressing process, where 2 GPa pressure is almost instantaneously applied to the sulfur melt at a compressing rate of 1.0×10^{11} Pa/s.¹⁰ The rapid compressing process generates enough fast solidifying rates without considering temperature rise, as indicated in Fig. 1. The high pressure can be homogeneously distributed through the whole sulfur melt, and a very quick glass transition happens on the liquid sulfur.¹⁰ Therefore, the resulting α -S gains a homogeneous structure of single amorphous phase. However, the quenched method always leads to structural inhomogeneity of polyphase in the prepared samples. Although the quenched process can reach a very high cooling rate, the cooling rate is very uneven between the inside and outside of the glass-forming liquid because of the slowness of heat transfer and the poor thermal conductivity of sulfur.¹⁶ At the same time, considering the sharp variation in the structure of liquid sulfur with the temperatures,^{1,2} the quenched history naturally leads to different amorphous phases and serious structural inhomogeneity.

Amorphous systems can be described in terms of a potential energy landscape, with thermodynamics and kinetics controlled by the minima and barriers on the landscape, respectively.^{17,18} Glassy materials actually are stuck in local minima on the potential energy landscape, and crystalline state locates in the lowest site of energy landscape corresponding to the most stable state. Conventional glasses are

usually prepared by quenching the melt but accessing low energy states by this route is impractically slow. For obtaining stable amorphous materials, approaching the lowest site in the energy landscape is a direct way.^{14,18} The quenched glasses normally have low density compared to crystalline state and self-moving tendency toward the lower site in the energy landscape.¹⁹ High pressure can also effectively elevate the activation energy for crystallization.²⁰⁻²³ Therefore, the α -S prepared by rapid compression with a denser structure could have a lower position in the energy landscape, which makes the compressed α -S gain highly stable amorphous structure.

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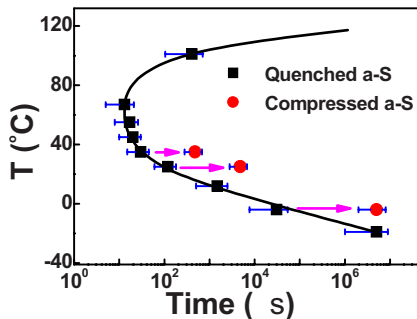


FIG. 5. (Color online) The TTT diagram summarizes the isothermal crystallizations of quenched α -S at normal pressure which were carried out at different temperatures. The data of compressed α -S at three representative temperatures are also shown.

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