高 压 物 理 学 报

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高压下正交相 $CsPbI_3$ 钙钛矿纳米棒的带隙调制

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摘要: 全无机卤化物钙钛矿由于其稳定性强, 且具有良好的光学性质, 是一种很有前途的光电材料。然而, 有效地设计其带隙以满足实际应用需求仍是亟待解决的关键问题。通过控制合成的反应时间和温度, 对铯铅碘(CsPbI$_3$)纳米材料进行形貌调控, 合成出形貌均一、结晶性良好的棒状 CsPbI$_3$ 纳米材料。进一步利用金刚石对顶砧, 结合原位高压紫外-可见吸收光谱, 对 CsPbI$_3$ 纳米棒在高压下的带隙变化进行研究, 发现高压下 CsPbI$_3$ 纳米棒的带隙减小, 带隙的可调控性为纳米材料在光伏电池领域的应用奠定基础。研究结果不仅有助于在原子尺度上建立 CsPbI$_3$ 纳米棒的结构特性关系, 而且为全无机钙钛矿纳米材料的实际应用提供重要线索。

关键词: 卤素钙钛矿; 金刚石对顶砧; 高压; 带隙调制

中图分类号: O521.2 **文献标识码:** A

金属卤化物钙钛矿(Metal Halide Perovskites, MHP)具有优良的电荷输运性能、广泛的化学可调谐性[1−2]等优点, 是一种很有前途的光电材料, 在高效率的光伏电池、发光二极管、激光器、光电探测器[3]等领域得到广泛应用。其中, 全无机卤化物钙钛矿 $CsPbX_3$(X=Cl, Br, I)表现出优异的稳定性[4−5]、超高的光致发光量子产率[6]、宽色域发光特性等优点, 预示着全无机卤化物钙钛矿的发展前景。控制合成具有高质量和良好形貌的纳米材料, 是将基础研究和应用研究推向新的一维光子和电子纳米结构的前提, 因而成为研究人员重点关注的问题。

压力作为一种重要的热力学参数[7], 为研究全无机钙钛矿纳米材料的结构和电子行为提供了有力手段[8−10]。利用金刚石对顶砧(Diamond Anvil Cell, DAC)等装置, 可以实现极端高压环境, 从而缩小原子间距, 形成紧密堆积[11−13]。近年来, 对 MHP 材料的高压研究掀起了一波新的热潮, 然而所研究的大多数材料仅限于一些独立的分子群, 有机金属卤化物钙钛矿[14]的不稳定性及其对氧/水的敏感性在很大程度上限制了其实际光伏应用, 因此铯铅碘($CsPbI_3$)钙钛矿纳米棒的合成及高压诱导带隙调控[15−16]对于全无机钙钛矿纳米材料的研究和应用具有很大的推广意义。

本研究采用一种无催化剂液相合成 $CsPbI_3$ 纳米棒的方法, 通过调控反应时间和反应温度, 对正交相的 $CsPbI_3$ 纳米材料进行形貌调控, 以期合成出形貌均一且结晶性良好的 $CsPbI_3$ 纳米棒; 采用 X 射线衍射(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和原位高压紫外-可见吸收光谱, 对 $CsPbI_3$ 纳米棒结构进行表征, 结合高压技术探究 $CsPbI_3$ 纳米棒在高压条件下的带隙变化。期望这样的单晶纳米材料能够成为进一步研究结构-功能关系的理想平台, 促进未来纳米光电子应用的发展。

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1　实　验

将 0.125 g Cs_2CO_3(纯度 99.9%)、0.5 mL OA(油酸,工业级 90%)和 12.5 mL ODE(十八烯,工业级 90%)装入三颈瓶中,在希莱克系统的氮气保护下加热,同时用磁力搅拌器搅拌,将溶液缓慢升温至 120 ℃,呈无色澄清状,此时 Cs_2CO_3 已充分溶解于溶剂中,然后将溶液降温至 100 ℃ 备用。

将 12.5 mL ODE、1.25 mL OA、1.25 mL OLA(油胺,工业级 90%)和 0.25 g PbI_2(纯度 99.9%)装入三颈瓶中,在氮气保护下缓慢加热至 120 ℃,加热搅拌 1 h 使 PbI_2 完全溶解至澄清,然后将温度提高到 170 ℃,快速注入 2 mL 的油酸铯溶液。持续保持温度在 170 ℃ 并搅拌,2 h 后取出合成好的 $CsPbI_3$ 溶液,此时溶液呈亮黄色。将合成好的溶液放入装有 C_6H_{14}(正己烷,纯度 97.0%)的离心管中,先在 8000 r/min 的转速下离心 5 min,然后在 8500 r/min 的转速下离心 3 min,最后倒掉上层液体封装。

采用 TEM 和 JEM-2200FS 型高分辨透射电镜(High Resolution Transmission Electron Microscopy, HRTEM)(200 kV)对样品进行表征。在砧面直径为 400 μm的对称 DAC 装置上进行原位高压实验。选取 T301 不锈钢作为垫片,用金刚石压砧在垫片中心预压一个凹痕,在凹痕中心钻入直径为 120 μm的孔,形成样品室。将样品装入样品腔,红宝石球放在上砧面,采用红宝石标压法测定实际压力。原位高压紫外-可见吸收光谱由光纤光谱仪(海洋光学,QE65000)测得,选用氘灯-卤灯作为光源。

2　实验结果及讨论

2.1　$CsPbI_3$ 纳米棒的形貌表征

通过 TEM、HRTEM 和 SEM 对合成的 $CsPbI_3$ 纳米棒样品结构进行表征,如图 1 和图 2 所示。合成的 $CsPbI_3$ 纳米棒长度约 3 μm(如图 1(a)所示);$CsPbI_3$ 纳米棒的晶面间距为 0.77 nm,样品呈金黄色粉末(见图 1(b))。图 1(c)是暗场扫描透射电镜(STEM)图像(左下角)和相应的 Cs(蓝色)、Pb(红色)和 I(绿色)元素映射图像。从图 2 可以看到,合成的 $CsPbI_3$ 纳米棒的形貌比较清晰,棒的形态比较明显且规则,棒的直径为 478.8 nm,结晶度良好。图 3 为合成的 $CsPbI_3$ 纳米棒的 XRD 图像,可以看出所得的 $CsPbI_3$ 纳米棒为正交晶系结构,并且具有较好的结晶性。

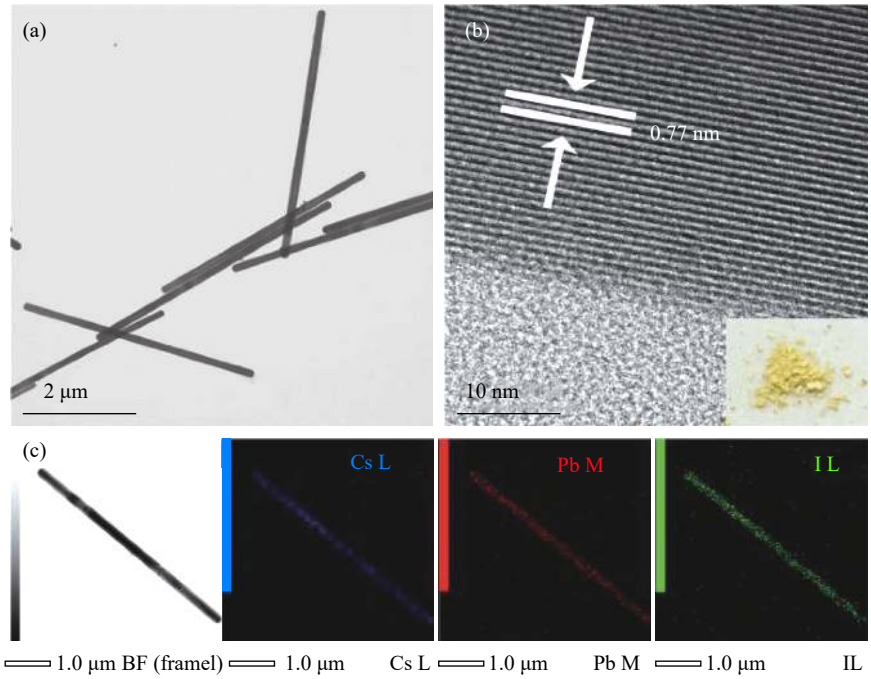


图 1　$CsPbI_3$ 纳米棒的 TEM 图像 (a)、HRTEM 图像 (b) 和映射图像 (c)

Fig. 1　TEM image (a), HRTEM image (b) and mapping images (c) of $CsPbI_3$ nanorods

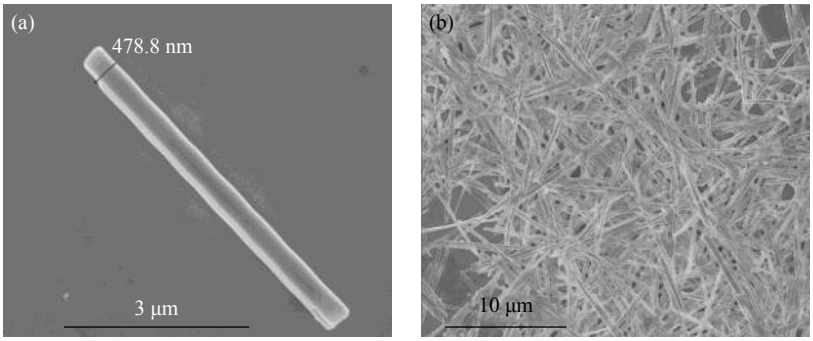


图 2　$CsPbI_3$ 纳米棒的 SEM 图像

Fig. 2　SEM images of $CsPbI_3$ nanorods

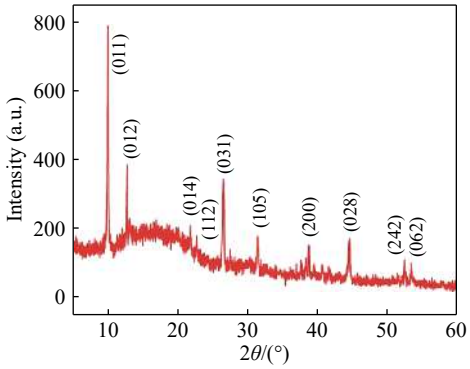


图 3　$CsPbI_3$ 纳米棒的 XRD 图像

Fig. 3　XRD image of $CsPbI_3$ nanorods

2.2　高压下 $CsPbI_3$ 纳米棒的带隙变化

对 $CsPbI_3$ 纳米棒进行原位高压紫外-可见吸收光谱测试，结果见图 4。在加压过程中，吸收峰的峰位出现连续红移，强度逐渐减弱，直到 7.03 GPa 时，吸收峰消失；持续加压至 10.17 GPa 时，出现非晶化，卸压可逆。如图 5 所示，卸压后 $CsPbI_3$ 纳米棒的 HRTEM 图和 STEM 图显示，$CsPbI_3$ 纳米棒基本保持棒的形态，晶格也比较明显。

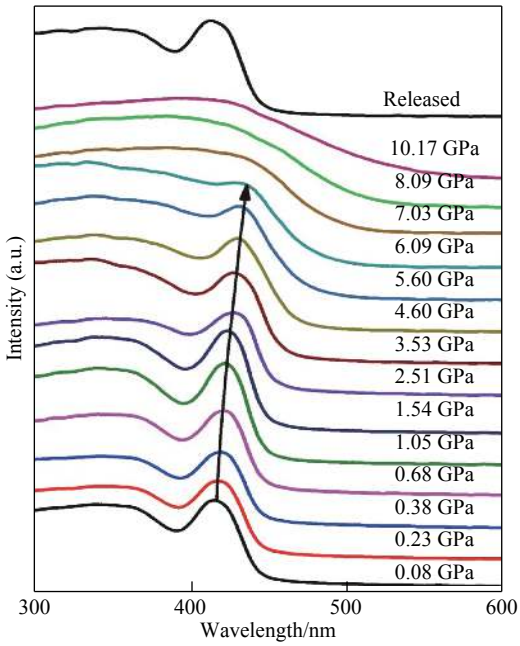


图 4　压力下 $CsPbI_3$ 纳米棒吸收光谱的变化

Fig. 4　Changes of absorption spectra of $CsPbI_3$ nanorods under pressure

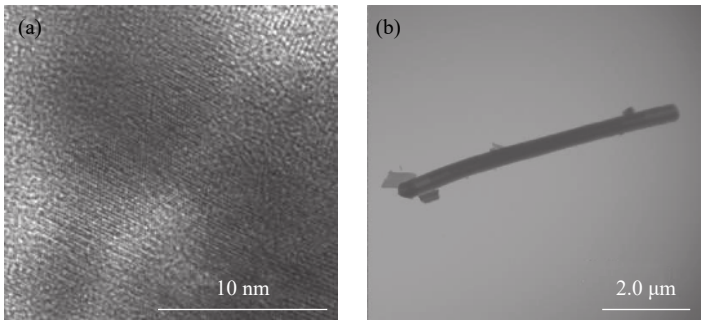


图 5　卸压后的 $CsPbI_3$ 纳米棒的 HRTEM 图像 (a) 和 STEM 图像 (b)

Fig. 5　HRTEM image (a) and STEM image (b) of $CsPbI_3$ nanorods after decompression

吸收峰的变化与带隙的改变有直接联系，因此通过不同压力下的紫外-可见吸收光谱可以得到 $CsPbI_3$ 纳米棒的带隙演化。图 6 显示了 $CsPbI_3$ 纳米棒的带隙随压力的变化。不同压力下的带隙是通过

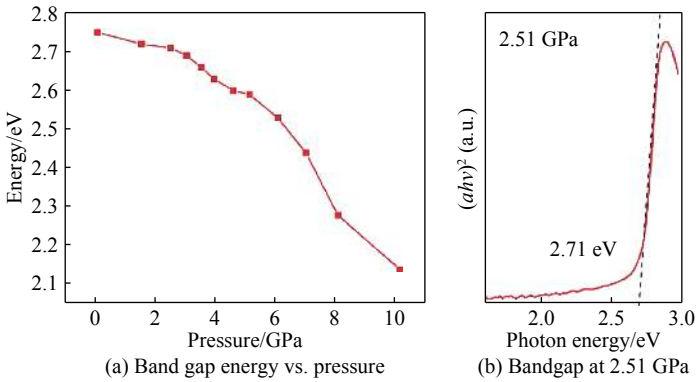
将 Tauc 图的线性区域外推到能量轴截距确定的。以压力为 2.51 GPa 时为例，利用 Tauc plot 公式，对 $CsPbI_3$ 纳米棒的带隙值进行拟合计算

$$E = 1240/\lambda \tag{1}$$

式中：E 为光子能量，单位 eV；λ为波长，单位 nm。采用 Kubelka-Munk 变换，对 $CsPbI_3$ 纳米棒的带隙值 E_g进行拟合计算

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{2}$$

式中：A 为边缘-宽度参数，$E=h\nu$为入射光子能量，α为常数。图 6(b) 为 $CsPbI_3$ 纳米棒在 2.51 GPa 压力下的 Tauc 图，其横轴为 E，纵轴为$(\alpha h\nu)^2$，可以看出，当压力为 2.51 GPa 时，$CsPbI_3$ 纳米棒的带隙值为 2.71 eV。



(a) Band gap energy vs. pressure　(b) Bandgap at 2.51 GPa

图 6　$CsPbI_3$ 纳米棒带隙与压力的关系

Fig. 6　Relationship between bandgap and pressure of $CsPbI_3$ nanorods

通过分析 $CsPbI_3$ 纳米棒的带隙值随压力变化，可以得出：$CsPbI_3$ 纳米棒在常压下的带隙为 2.75 eV；随着压力的增加，带隙不断减小，晶面间距变小，键长变短；当压力增加到 10 GPa 时，带隙减小到 2.14 eV。

3　结　论

采用一种无催化剂液相合成 $CsPbI_3$ 纳米棒的方法，通过调控合成的反应时间和温度，合成出形貌均一且结晶性良好的棒状 $CsPbI_3$ 纳米材料，借助红宝石标压技术和吸收光谱，对 $CsPbI_3$ 纳米棒进行了高压下带隙调控研究。通过高压实验证实，$CsPbI_3$ 纳米棒的未来研究将集中于其光电应用。本研究合成的 $CsPbI_3$ 纳米棒可作为一个理想平台，用于研究纳米级光电器件的基本性质以及开发基于全无机钙钛矿结构的纳米光电子器件等，具有良好的应用前景。

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Band Gap Modulation of Orthorhombic Cesium Lead Iodide Perovskite Nanorods under High Pressure

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Abstract: The all-inorganic halide perovskite is a promising photoelectric material because of its strong stability and good optical properties. However, it is still a key problem to effectively design the band gap to meet the practical application requirements. By controlling the reaction time and temperature, the morphology of cesium-lead-iodine ($CsPbI_3$) nano-material could be controlled, and the rod-like $CsPbI_3$ nano-material with uniform morphology and good crystallinity was synthesized. The band gap changes of $CsPbI_3$ nanorods under high pressure were further studied by using diamond pair anvil and *in situ* high pressure ultraviolet-visible absorption spectroscopy. It is found that the band gap of $CsPbI_3$ nanorods decreases under high pressure, and the tunable band gap lays the foundation for the application of nano-materials in the field of photovoltaic cells. The results can not only help to establish the structural properties of $CsPbI_3$ nanorods on the atomic scale. It also provides an important clue for the practical application of all-inorganic perovskite nano-materials.

Keywords: halide perovskites; diamond anvil cell; high pressure; band gap modulation

DOI: 10.11858/gywlxb.20180597

机械合金化结合高压烧结制备 PbSe-PbS 固溶体合金的热电性能

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摘要: 硒化铅(PbSe)作为一种无碲热电材料受到广泛关注。采用机械合金化结合高压烧结方法制备了 PbSe-PbS 固溶体合金($PbSe_{1-x}S_x$),并研究了 Se/S 含量对其结构和热电性能的影响。结果表明:采用机械合金化法能够快速合成出 $PbSe_{1-x}S_x$ 固溶体合金粉末,高压烧结实现了其快速致密化;通过调整 Se/S 比例可以实现 $PbSe_{1-x}S_x$ 电输运性能和导电类型的调控;固溶体合金能够实现短波声子散射,显著降低 PbSe 材料的热导率;当 $x = 0.5$、温度为 600 K 时,$PbSe_{1-x}S_x$ 的最高品质因子达到 0.54,比 PbSe 的品质因子(0.33@450K)高 64%。

关键词: PbSe; 热电材料; 机械合金化; 高温高压; 品质因子

中图分类号: O521.2 **文献标识码:** A

基于塞贝克效应和珀尔帖效应的热电材料是一种能够实现热能和电能直接转换的功能材料[1],可用于制造温差发电机及热电制冷设备。目前,以室温条件下性能最好的 Bi_2Te_3 基热电材料制成的制冷设备已经开始商业化应用[2],而基于中高温区热电材料的温差发电技术仍局限于深层空间探测器等少数不计成本的领域[3]。温差发电技术在利用工业余热、汽车尾气和地热等低品位热源发电方面具有潜在、巨大的商用价值,因而近年来中国、日本以及欧美等国家对中高温区热电材料的研究越来越重视。

目前热电材料研究的关键是提高工作效率。热电材料的工作效率主要由品质因子 ZT 决定,其中 $Z = \sigma S^2/\kappa$(σ、S、κ 分别为材料的电导率、Seebeck 系数和热导率),T 为绝对温度[4-5]。σS^2 被称为功率因子(Power Factor, PF),可以通过控制材料的载流子浓度、调整能带结构进行优化[6];热导率主要由晶格热导率和电子热导率两部分组成,其中电子热导率正比于电导率[7-8],晶格热导率可以通过制备纳米晶[9-10]、纳米复合材料[11]、固溶体合金[12],引入空位或位错缺陷[13]等手段降低。因此,目前提升热电性能主要依靠提高功率因子或降低晶格热导率两种途径。

碲化铅(PbTe)是目前唯一商业化应用的中温区热电材料[5, 14-15],具有性能高、各向同性、化学性质稳定、载流子浓度容易控制等诸多优点。然而,由于 Te 在地壳中的储量较少[16],价格较为昂贵,开发无 Te 的高性能材料已成为热电材料领域的研究重点。Se 与 Te 同属第六主族元素,而地壳中 Se 的含量更丰富[16]。PbSe 和 PbTe 具有相同的晶体结构[17],同时也具有很多相似的性能。因此,近年来 PbSe 基热电材料受到热电材料研究者的广泛关注[18-20]。

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本研究采用机械合金化法制备 PbSe 及 $PbSe_{1-x}S_x$ 固溶体合金粉末，并利用高压烧结方法实现其快速致密化，测试并分析在室温到 600 K 温度条件下 $PbSe_{1-x}S_x$ 固溶体合金的热电性能。

1　实　验

将纯度为 99.9% 的 Pb 粉、99.95% 的 Se 粉和 99.99% 的 S 粉按 $PbSe_{1-x}S_x$（x=0, 0.25, 0.50, 0.75）化学配比称量后放入不锈钢球磨罐中，抽真空并充入氩气保护。将球磨罐置于行星式球磨机中，转速设定为 350 r/min，高能球磨 2 h 合成 PbSe-PbS 固溶体合金粉末。取出合成粉末，用液压机粉压成ø10.5 mm × 4 mm 的圆柱体，组装于叶蜡石块中。在国产六面顶液压机 SPD6 × 1 200 上高压烧结（压力为 3.0 GPa，温度为 1 000 K）30 min。合成压力标定由 Bi、Ba、Tl 的压致相变点校正曲线获得，温度由 K 型热电偶测得。

采用日本真空理学 D/MAX-RA 衍射仪 (Cu 靶)，对样品进行 X 射线衍射（X-Ray Diffraction, XRD）分析。样品的电导率和赛贝克系数测试采用塞贝克系数/电阻分析系统 LSR-3(Linseis) 在氦气气氛下进行，测试温度范围为 300～600 K。热导率通过 $\kappa=D\rho_s c_p$ 计算得到，其中 D 为热扩散系数，c_p 为材料的定压比热容，ρ_s 为样品的密度。D 通过激光导热仪 LFA457（NETZSCH）测得，c_p 根据杜隆-珀蒂定律计算得到，ρ_s 根据阿基米德原理利用密度天平进行测量。

2　结果与讨论

图 1 为机械合金化合成 $PbSe_{1-x}S_x$ 样品的 XRD 谱。可见，PbSe 样品的特征衍射峰数据与标准衍射卡片（PbSe: No.06-0354）数据基本一致。从图 1(b) 可以看出，随着样品中 S 含量的增大，最强峰（200）逐渐向高角度偏移，并趋近于 PbS 标准卡片（PbS: No.05-0592）的峰位。根据布拉格公式 $2d\sin\theta=\lambda$（d 为晶面间距；θ 为衍射角；λ 为 X 射线波长，对于 Cu 靶，λ = 0.154 06 nm），晶面间距与衍射角成反比。本研究中由于 S 的原子半径比 Se 的原子半径小，因此随着 S 含量的增加，晶面间距减小，衍射角向高角度方向偏移。这些结果表明：采用机械合金化法能够成功合成出 $PbSe_{1-x}S_x$ 固溶体。

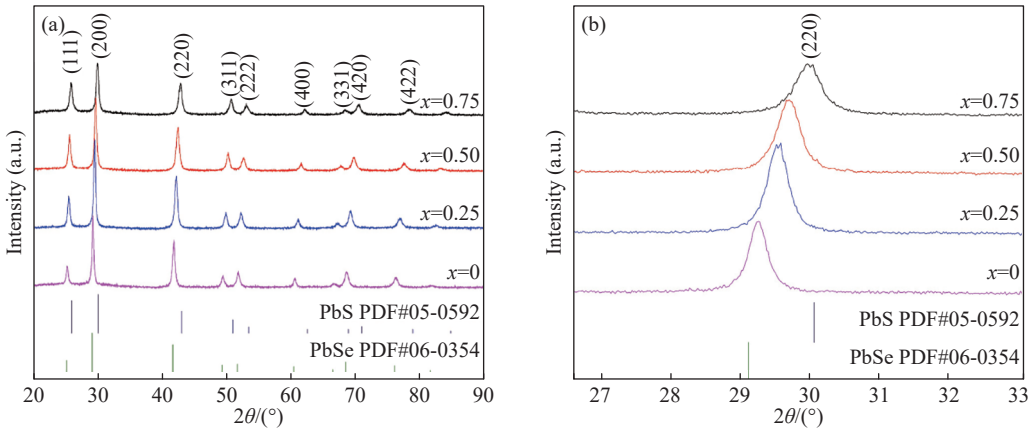


图 1　采用机械合金化法合成的 PbSe-PbS 固溶体（$PbSe_{1-x}S_x$）XRD 谱

Fig. 1　XRD patterns of PbSe-PbS solid solutions ($PbSe_{1-x}S_x$) synthesized by mechanical alloying method

通过对 XRD 谱进行精修以及密度天平，分别获得样品的理论密度和实际密度，进而获得样品的相对密度（实际密度与理论密度之比），结果显示：当 x = 0, 0.25, 0.50, 0.75 时，$PbSe_{1-x}S_x$ 的相对密度分别为 96.7%、95.9%、97.4% 和 97.7%。机械合金化方法合成的 $PbSe_{1-x}S_x$ 固溶体合金粉末经过高压烧结后，块体材料的密度均达到理论密度的 95% 以上，说明高压烧结方法能够实现 $PbSe_{1-x}S_x$ 的快速致密化。图 2(a) 显示了 $PbSe_{1-x}S_x$ 的电阻率（ρ）随温度的变化，可见，电阻率随着 S 含量的增加而增大。当 x = 0, 0.25 时，电阻率随着温度的升高逐渐增大，表现出金属导电特性；而当 x>0.25 时，电阻率随着温度的升

高而逐渐减小, 表现出半导体特性。这种由金属导电特性向半导体导电特性的转变, 说明富 S 样品的载流子浓度远小于富 Se 样品的载流子浓度, 这与样品的禁带宽度、点缺陷浓度等因素有关。首先, PbS 的禁带宽度(0.4 eV)远大于 PbSe 的禁带宽度(0.27 eV)[21], $PbSe_{1-x}S_x$ 固溶体合金的带隙宽度应随着 S 含量的增大而增大, 载流子浓度相应地减小。其次, 由于机械合金化和高压烧结工艺均属于非平衡态制备方法, 不同组分样品受制备工艺的影响而引入空位或反位缺陷, 缺陷的引入会影响材料的载流子浓度。

$PbSe_{1-x}S_x$ 固溶体的 Seebeck 系数(S)如图 2(b)所示。可以看出, 当 $x = 0$ 时, Seebeck 系数为正值, 表明 PbSe 为 p 型半导体; 而 $x = 0.5$ 时, Seebeck 系数为负值, 表明 $PbSe_{0.5}S_{0.5}$ 为 n 型半导体, 且 Seebeck 系数随温度的变化较小。而当 x 为 0.25 和 0.75 时, $PbSe_{1-x}S_x$ 的 Seebeck 系数随着温度的增大由正值变为负值, 即出现 p-n 型转变。p 型 $PbSe_{1-x}S_x$ 固溶体的 Seebeck 系数最大值约为 600 μV/K(300 K), n 型 $PbSe_{1-x}S_x$固溶体的 Seebeck 系数绝对值最大约为 450 μV/K(600 K)。$PbSe_{1-x}S_x$ 导电类型的变化与其电子结构和缺陷浓度有关, PbSe 和 PbS 均属于窄带隙半导体, 因此 $PbSe_{1-x}S_x$ 固溶体在高温条件下会发生“双极效应”, 大量电子从价带跃迁至导带, 导致 Seebeck 系数变化。而机械合金化和高压条件下 $PbSe_{0.5}S_{0.5}$ 的阴离子空位形成能可能较小, 所以在测试温度范围内均表现为电子导电。

由 $PbSe_{1-x}S_x$ 固溶体电阻率和 Seebeck 系数计算出功率因子, 如图 2(c)所示。可以看出: 当 x = 0, 0.25 时, 功率因子随着温度的升高逐渐减小; 而当 x = 0.50, 0.75 时, 功率因子随着温度的升高而增大。在室温下, PbSe 的功率因子最大, 约为 1 100 μW/(m·K^2), 而高温(600 K)下, $PbSe_{0.25}S_{0.75}$ 的功率因子最大, 约为 600 μW/(m·K^2), 这主要是由于 Seebeck系数的绝对值在 600 K 时达到最大值。由此可以得出, PbSe 和 PbS 形成固溶体合金能够有效地调节 PbSe 和 PbS 的电输运性能。

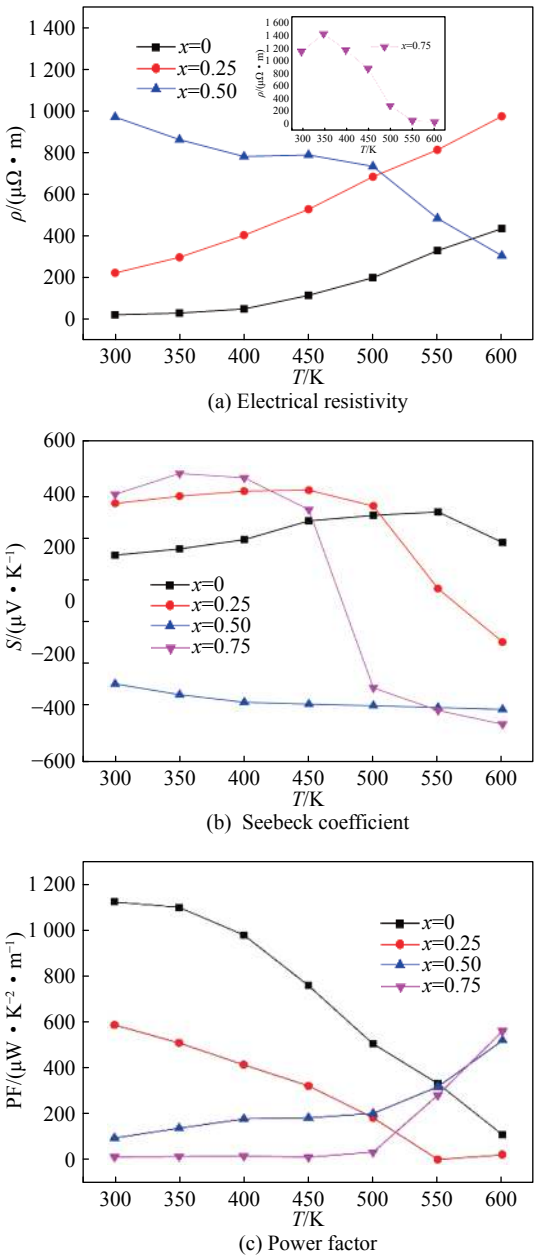
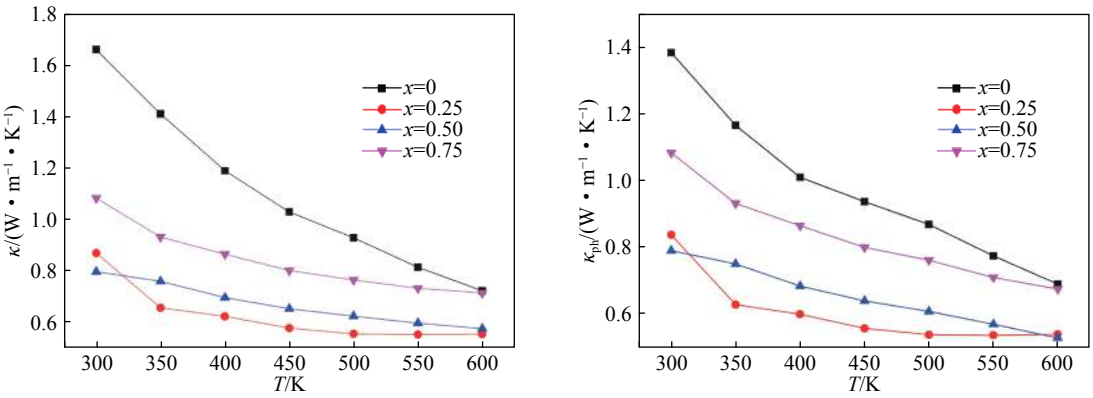


图 2　PbSe-PbS 固溶体($PbSe_{1-x}S_x$)的电学性能

Fig. 2　Electrical properties of PbSe-PbS solid solutions ($PbSe_{1-x}S_x$)

$PbSe_{1-x}S_x$ 固溶体的热导率(κ)随温度的变化情况如图 3(a)所示。热导率随着温度的升高逐渐减小, 在 x = 0.25、测试温度为 550 K 时, 热导率最小, 约为 0.55 W/(m·K), 表明 PbSe 和 PbS 形成固溶体有利于热导率的降低。图 3(b)为 $PbSe_{1-x}S_x$ 固溶体的声子热导率(κ_{ph})随温度变化图谱, 这里声子热导率 $\kappa_{ph} = \kappa - L\sigma T$, $L = 2.45\times10^{-8}$(W·Ω)/K^2 为洛伦兹常数, 声子热导率随着温度的升高逐渐减小, 这是由于高温时声子散射由 Umklapp 过程占主导。随着 S 含量的增加, 声子热导率先减小后增大, 这是由于在 Se 位固溶 S 会产生主原子和杂质原子之间的质量差异(质量场涨落)和尺寸差异(应力场涨落), 从而产生原子量级点缺陷, 增强短波声子散射。



(a) Total thermal conductivity　　(b) Phonon thermal conductivity

图 3　PbSe-PbS 固溶体的热输运性能

Fig. 3　Thermal transport properties of PbSe-PbS solid solutions

机械合金化合成 $PbSe_{1-x}S_x$ 固溶体的品质因子如图 4 所示。可以看出，除了 $x = 0.50$ 和 0.75，其他 $PbSe_{1-x}S_x$ 固溶体的品质因子均随着温度的升高先增大后减小，在 450 K 附近具有最大值。而当 $x = 0.50$ 和 0.75 时，品质因子随着温度的升高而逐渐增大，当 $x = 0.50$、温度为 600 K 时，品质因子最大，约为 0.54，与未掺杂 PbTe 的结果（0.48[21]，0.46[22]）相近。

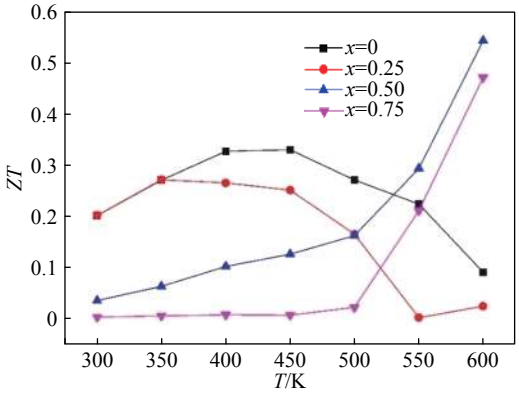


图 4　PbSe-PbS 固溶体（$PbSe_{1-x}S_x$）的品质因子

Fig. 4　Figure-of-merits of PbSe-PbS solid solutions ($PbSe_{1-x}S_x$)

3　结　论

采用机械合金化法成功制备出 $PbSe_{1-x}S_x$ 固溶体合金，通过高压烧结方法制备出致密块体，并对其热电性能进行了研究。结果表明，在 PbSe 的 Se 位固溶 S 能够有效地调控 PbSe 的电输运性能和导电类型，功率因子的最高值向高温区移动，晶格热导率得到有效的降低。$PbSe_{0.5}S_{0.5}$ 的品质因子最高达到 0.54（@600K），比 PbSe 提高 64%。

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Thermoelectric Properties of PbSe-PbS Solid Solutions Prepared by Mechanical Alloying Method and High Pressure Sintering

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Abstract: Lead selenide (PbSe) has received extensive attention in recent years as a non-tellurium thermoelectric material. In this paper, PbSe-PbS solid solution alloys ($PbSe_{1-x}S_x$) were prepared by mechanical alloying combined with high pressure sintering method. The influence of Se/S content on its structure and thermoelectric properties was studied. The results demonstrate that the mechanical alloying method can rapidly synthesize $PbSe_{1-x}S_x$ solid solution alloy powder, and achieve rapid densification by high pressure sintering. The electrical transport properties and conductivity type of $PbSe_{1-x}S_x$ powder can be controlled by adjusting the Se/S ratio; solid solution alloy can realize short-wave phonon scattering, which significantly reduces the thermal conductivity of PbSe material. When x = 0.5 and the temperature is 600 K, the highest quality factor of $PbSe_{1-x}S_x$ is 0.54, which is 64% higher than that of PbSe (0.33@450 K).

Keywords: PbSe; thermalelectric material; mechanical alloying method; high temperature and high pressure; figure of merit

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Symmetrization and Chemical Precompression Effect of Hydrogen-Bonds in H_2-H_2O System

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Abstract: Hydrogen hydrate (H_2-H_2O) excited significant interest as an environmentally clean and efficient hydrogen storage material. Here we conducted a high-pressure experimental research on hydrogen hydrate combined with *in-situ* Raman spectroscopy and synchrotron X-ray diffraction measurements. Our results indicated that the cubic C_2 phase with stoichiometry 1∶1 of H_2 and H_2O transformed to a new tetragonal phase C_3 after packing more hydrogen molecules above 24.5 GPa. The structure of C_3 was determined to be $P4_1$ with a 1∶2 ratio of H_2O to H_2, and could survive down to 8.6 GPa upon decompression. Two districted behaviors of guest hydrogen clusters were observed with increasing pressure. One showed blue-red frequency shift transition similarly as pure hydrogen, the other continuously blue-shifted to higher frequencies in the whole pressure range. Fermi resonance between the deformational mode and softened stretching mode was firstly detected, indicating that the hydrogen-bond was symmetrized at around 55 GPa. The complicated behaviors of hydrogen molecules and interactions with water molecules in hydrogen hydrate provided a different insight into the guest-host system under pressure.

Keywords: high pressure; hydrogen-bond symmetrization; hydrogen hydrate

CLC number: O521.2 **Document code:** A

Hydrogen is the most widespread element in the universe with lots of unique properties and potential applications. The metallic hydrogen was not only predicted to be a high T_c superconductor at extreme pressures, but also to be a high energy density material, which would have great applications in military projects and energy sources[1−4]. The pressure-induced insulator to metal transition of hydrogen are of fundamental interest to condensed matter physics and chemistry as well as planetary astronomy[5−6]. In view of the difficulties in technology of pressing pure hydrogen, the metallization pressure of hydrogen is proposed to decrease in the hydrogen-rich materials because of the chemical precompression effect[7]. Many hydrogen-rich compounds are also high energetic, or potential hydrogen storage materials, attracting considerable attentions in recent years[8].

Hydrogen hydrate was known as the typical clathrate hydrates in solid state at high pressures, exciting great interest for its unusual behaviors under pressure and expected hydrogen storage properties. A series of researches on solid hydrogen hydrate were performed at various pressures and temperatures by experiments and theoretical simulations[9−25]. Two typical clathrate structures, filled ice II and Ic (phase C_1 and C_2) at relatively low pressures were firstly defined in 1993[9]. The guest hydrogen molecules occupied the voids in the host water framework with

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a very high stoichiometry of 1∶1 in phase C_2, which was attractive as a hydrogen-storage material. The subsequent works suggested the cubic phase would survive up to 60 GPa as long as the structural stability enhanced with hydrogen-bond symmetrization above 30 GPa[10] . However, Machida *et. al*[16, 19] found that hydrogen molecules extracted from the C_2 phase at around 20 GPa, giving rise to a transition to poor-hydrogen phase. The new phase was predicted as the trigonal or tetragonal symmetries in X-ray diffraction (XRD) measurements and molecular dynamics simulation[15, 23–24]. Moreover, the *ab initio* variable-composition evolutionary simulations showed that the C_2 phase would lose stability and transformed to a tetragonal phase with 2∶1 hydrogen and water molecules[25] .

In hydrogen hydrate, the stability of clathrate structure was mainly depended on the framework of host water molecules, which was assembled by hydrogen-bonds. Therefore, the pressure of hydrogen-bond symmetrization would be significantly lower than that in pure ice because of the packing efficiency of the guest hydrogen molecules[10]. The Fermi resonance should also be observed as a convincing evidence of hydrogen-bond symmetrization, while it has not been detected up to now[15] . Furthermore, the behaviors of hydrogen molecules and hydrogen-bonds were expected to show a different insight of precompression effect in this typical of material with hydrogen contained, because it had been proved that the interaction between hydrogen and water molecules played a significant role in phase transitions[18]. We expected that a systematic experimental study combined with diamond anvil cell (DAC) and *in-situ* spectroscopy measurements would give a clear understanding on the phase transitions, hydrogen behaviors and hydrogen-bond symmetrization in the hydrogen hydrate system.

Here, the hydrogen hydrate was studied by the *in-situ* Raman spectroscopy and synchrotron XRD measurements up to 71.4 and 63.0 GPa, respectively. Two distinct pressure-induced behaviors of hydrogen clusters were observed above 24.5 GPa. The Fermi resonance appeared at 29.0 GPa and persisted up to 49.0 GPa. The extrapolation line indicated that the hydrogen-bonds in the water framework symmetrized at around 55 GPa in hydrogen hydrate.

1　Experiment Details

Symmetric DACs equipped with flat anvils of 300 μm was used to generate pressures in *in situ* Raman scattering and angle-dispersive XRD measurements. Rhenium gasket (with an initial thickness of 200 μm) was preindented to about 30 μm and then the sample cavity was drilled in the centre with a diameter of 120 μm. The pressure in the DAC was calibrated by the ruby fluorescence method. A tiny aluminum ball with a diameter of 10 – 15 μm and liquid deionized water were loaded in the chamber. The hydrogen was generated after an excess laser heating run on the aluminum ball at 0.4 GPa. The final products in the chamber were hydrogen and aluminum oxide[26]. The CW solid state laser at 1064 nm was introduced into the optical system using polarizing beam-splitter cubes and focused into a flat top focal spot from two sides of the DAC using the Mitutoyo near-IR×20 and ×10 long-working distance objective lenses. The focal laser spots were about 10 – 15 μm in diameter, making it possible to heat the aluminum balls. The backscattering geometry was adopted for confocal measurements with incident laser wavelengths of 457, 488, and 561 nm in the Raman measurements (the 488 nm laser line was used in the current measurement). The XRD experiments were collected at the synchrotron beam line, sector 13 of the Advanced Phonon Source (APS) of the Argonne National Laboratory with the wavelengths of 0.3344 Å (GSECARS).

2　Results and Discussion

The pure hydrogen hydrate sample was generated after sufficient laser heating runs at 0.4 GPa before further compression. As shown in Fig.1, the representative vibrons for hydrogen rotons and stretching mode appeared at

358, 590, 816, 1035 and 4146 cm^{-1}. With further compression to 2.2 GPa, the liquid sample crystallized to phase I with appearance of several sharp Raman peaks. The phase I was described as clathrates phase C_1 in the first study[9]. In the clathrates structure, the hydrogen molecules occupied the voids of the hydrogen-bonded water framework, it was therefore recognized as a filled ice phase with space group $R\bar{3}$ defined by XRD measurement on a single crystal. The other clathrates phase (C_2) was also observed at 3.4 GPa in this experiment as shown in Fig.1(a), whose structure was confirmed as *Fd*3*m* by XRD in previous study[9]. The stoichiometry of hydrogen and water molecules was almost 1 ∶ 1 in phase C_2, which therefore attracted many attentions as a potential hydrogen-storage material.

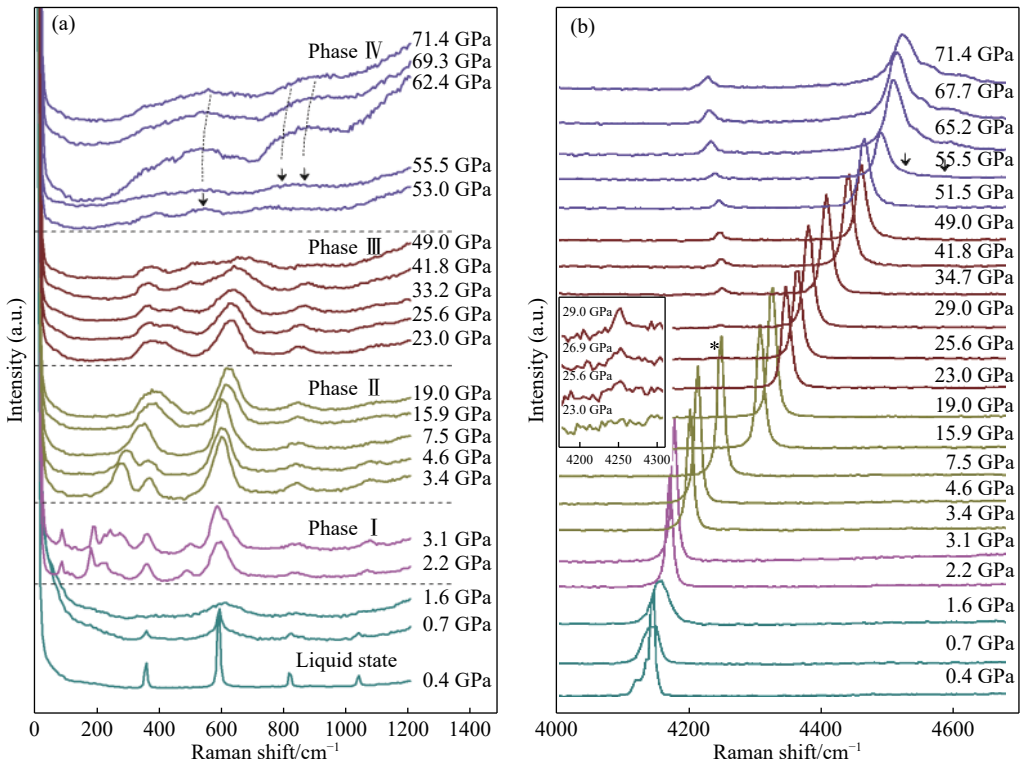

Fig. 1　The evolution of Raman spectra of hydrogen hydrate with increasing pressure from 0.4 to 71.4 GPa. (a) The lattice peaks in the region of 0–1200 cm^{-1}, where the spectra in each phase were marked by different colors and divided by dashed lines; the arrows marked three new broad peaks in high pressure phase IV; (b) The stretching peaks of H_2 at various pressures, symbol * referred a new peak at 25.6 GPa in phase III, and the two shoulders at 55.5 GPa were marked by black arrow.

With increasing pressure, the rotation mode of H_2 at 375 cm^{-1} splitted into two peaks while other peaks in the region of 0–1200 cm^{-1} became much broader above 23.0 GPa. A new stretching peak of hydrogen with frequency of 4929 cm^{-1} appeared at 25.6 GPa. Therefore, it is inferred that a solid-solid transition from C_2 to a new phase occurred at 23.0 GPa, which was named as C_3 by convention in the hydrogen hydrate system. The pressure dependences of the stretching peaks were plotted in Fig.2. It is notable that the stretching peak at 4929 cm^{-1} blue-shifted to 4254 cm^{-1} below 38.4 GPa at first, and then red-shifted to 4231 cm^{-1} persistently up to 71.4 GPa. The frequency transition from blue-shift to red-shift was similar to the characteristic behavior of pure hydrogen under pressure[27] . Therefore, it was simply attributed to the extraction of guest hydrogen molecules at the ultimate pressure in previous experimental studies[16, 19]. However, similar transformation was also observed in the S-H system during the synthesis of $(H_2S)_2H_2$ from H_2S, and $(H_2S)_2H_2$ became a currently known highest T_c superconductor in its *Im*-3*m* phase[28–29]. Meanwhile, the *ab initio* variable-composition evolutionary simulation predicted that the C_2 phase would become metastable and transformed to a novel tetragonal phase C_3 ($P4_1$) with

2∶1 ratio of hydrogen and water molecules[25]. In the predicted phase C_3, eight hydrogen molecules were located at the center of chair-like H-O rings therefore it had the highest hydrogen concentration among all hydrogen hydrates. A further XRD measurement was performed up to 63 GPa here to explore the structure of C_3. As shown in Fig.3, the phase C_2 was determined by its characteristic diffraction lines of (110), (220), (311), (400), (331) and (422) at 7.6 GPa[9]. Above 24.5 GPa, a splitting of (220) line was observed, which was marked by red arrows in Fig.3, indicating the structure transformed from cubic $Fd3m$ to tetragonal space[24]. A rough Pawley refinement of the theorical predicted $P4_1$ structure was performed with our experimental spectrum of 24.5 GPa. The refined lattice parameters were $a = b = 5.046$ Å and $c = 5.523$ Å, in consistent with the simulated results[25].

In the filled ice structures, the water molecules were connected by O-H···O hydrogen-bonds and further formed clathrate framework after crystallization. As the H proton occupied the midpoint between two oxygen ions, the O-H···O hydrogen-bonds became symmetric. In solid water, the phase X with symmetric hydrogen-bond formed at 60 GPa and kept stable to at least 210 GPa[31]. It was reported that the correlation between the $\nu_{\text{O-H}}$ and $d_{\text{O-H}\cdots\text{O}}$ in hydrogen hydrate was similar as solid water, making the clathrate a model system for ice at pressures reduced by a factor 2 because of the packing efficiency in the filled ice structures[9−10]. Therefore, it is considered that this symmetric bonding construction is more important to the stability of high-pressure phases in hydrogen hydrate. As shown in Fig.4, the O-H stretching peaks moved into the diamond 2rd Raman vibration region and disappeared at 29.0 GPa. Meanwhile, a weak peak appeared at 1549 cm^{-1} with intensity increasing gradually. It was assigned to the typical vibrational coupling between the deformational mode and soften stretching mode, which was the characteristic behavior during hydrogen-bond symmetrization and also had been detected at about 45 GPa in solid ice[31]. The coupling effect enhanced with pressure increasing up to 40 GPa and then disappeared above 45.8 GPa, indicating that the soften stretching mode further shifted into

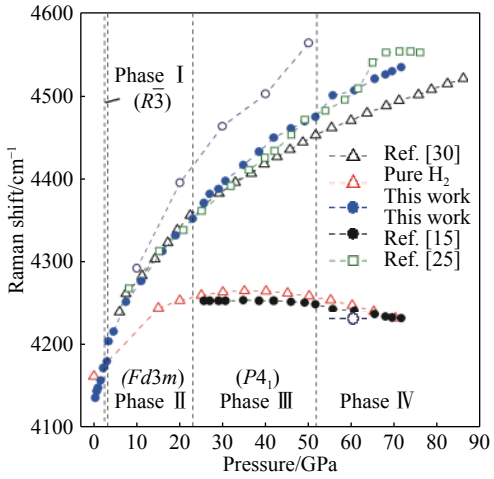

Fig. 2　The frequency shifts of H-H stretching mode in hydrogen hydrate at various pressures in this work and referred researches. Symbols: the solid black and blue circles indicated frequency shifts collected in this work; the red triangle was frequency shift of pure H_2 while the rest black triangle, green square and blue circle were hydrogen in hydrogen hydrate which were cited from previous experimental and theorical studies[15, 25, 30]. The pressure boundaries of each phase were marked by vertical dashed lines.

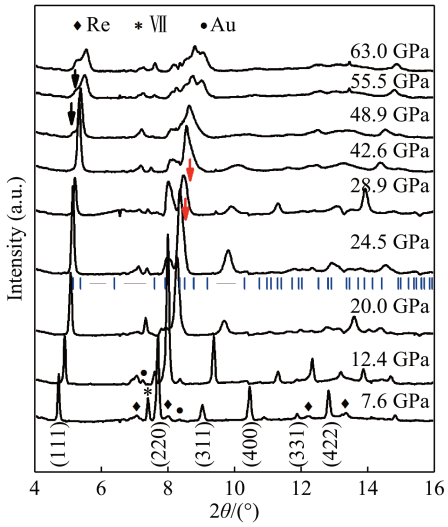

Fig. 3　The synchrotron XRD measurement of hydrogen hydrate up to 63.0 GPa. The phase C_2 was confirmed by characteristic diffraction lines (111), (220), (311), (400), (331) and (422) at 7.6 GPa. The splitting of line (220) was marked by red arrows at 24.5 GPa, while the splitting of line (111) at 48.9 GPa was marked by black arrows. A rough Pawley refinement of the theorical predicted $P4_1$ structure was performed with our experimental spectrum of 24.5 GPa, the short blue lines showed the calculated diffraction lines of refined structure with Materials Studio program.

lower frequency region. Above 53.0 GPa, it is notable that three broad peaks at 539, 783 and 856 cm^{-1} became more intense with increasing pressure, which were attributed to coupling between the soften stretching mode and the translational and rotational modes. We further simulated the frequency shifts of the soften stretching mode by extrapolation of the existed data with the function $v_{OH}=(v_0^2-aP)^{1/2}$ given in Ref.[32], where v_0 and a are parameters, suggesting a soft-mode behavior. As shown in Fig.4(b), the transition region of 52–57 GPa was in well consistent with our Raman spectra as shown in Fig.1(a), suggesting that the hydrogen-bond symmetrized at around 55 GPa.

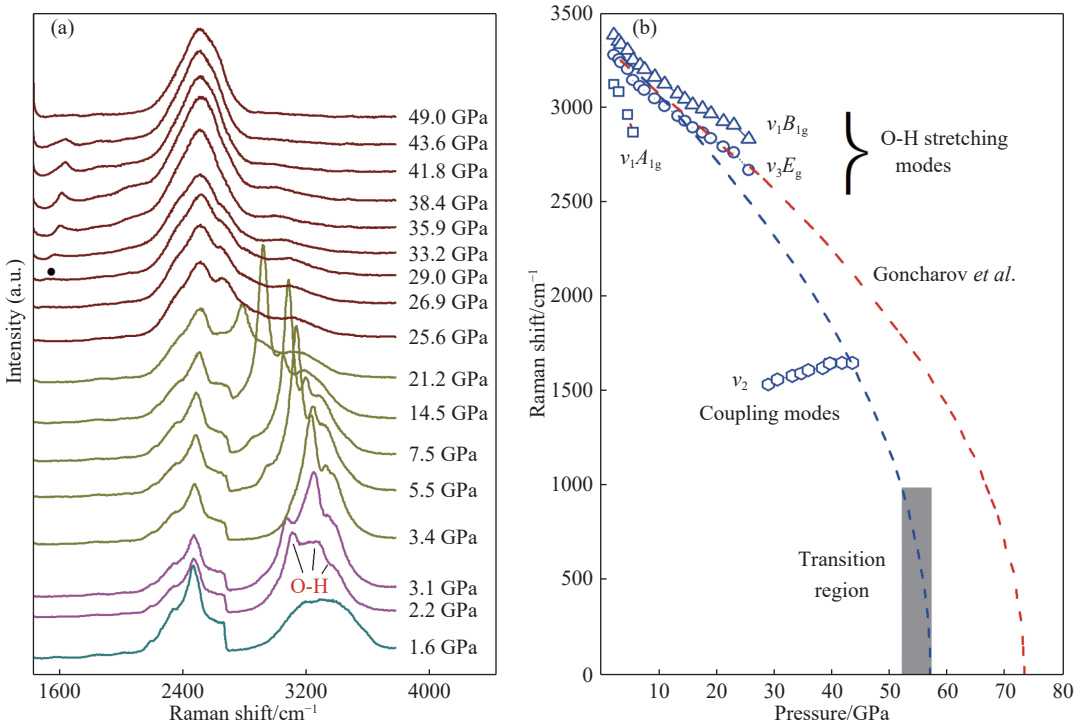

Fig. 4　(a) The soften evolution of O-H stretching peaks with increasing pressure from 2.2 to 29.0 GPa; the intensity of deformational peak increased above 29.0 GPa owing to the Fermi resonance with the soften O-H stretching mode, which further shifted to low frequency region above 49.0 GPa. (b) The pressure dependence of the O-H stretching mode; the blue line guided the extrapolation of the soften O-H stretching mode, the red dashed line showed the O-H stretching mode in solid water for comparison[31].

With increasing pressure, two weak shoulders marked by arrows in Fig.1(b) appeared at 4539 and 4599 cm^{-1} at 55.5 GPa, indicating that the hydrogen-bond symmetrization completed at around 55 GPa and caused further phase transition from phase C_3 (space group $P4_1$) to a new high-pressure phase IV (named C_4 as customary). Meanwhile, three broad peaks marked by arrows appeared throughout the region of 400–1000 cm^{-1}, which were assigned to the complicated coupling between the soften stretching modes and the translational and rotational modes[31]. Moreover, only one splitting of line (111) which was related to hydrogen atoms of water molecule was collected in the XRD patterns at 48.9 GPa, indicating that the phase IV was slightly distorted Phase C_3 as in the case of phase VII of ice[31].

The interactive effect between guest hydrogen and host water molecules played a vital role in stabilizing the filled ice structure. Basically, it lowered the pressure of hydrogen-bond symmetrization as described above. Furthermore, it can provide extra positive pressure acting as the chemical precompression effect on the guest hydrogen molecules. As shown in Fig.2, the stretching peak of guest hydrogen blue-shifted from 4136 cm^{-1} at 0.4 GPa to 4535 cm^{-1} at 71.4 GPa, which had not drawn sufficient attentions in previous studies. In the most recent study, similar abnormal blue-shift behavior of hydrogen vibron was interpreted as a negative chemical

pressure on H_2 molecules in $Ar(H_2)_2$[30]. Obviously, the enhancement of blue-shift was attributed to a larger chemical pressure coming from packing efficiency. Although the interpretation of a negative chemical effect was in consistent with the metallization mechanism of molecule dissociation, however, here we preferred to assign this behavior to the isolated guest hydrogen clusters in the specific filled ice structures, which was differ from the bulk pure hydrogen sample.

During decompression, the phase transitions were reversible with great hysteresis as shown in Fig. 5. The phase C_4 persisted down to 39.7 GPa with disappearance of shoulders marked by red arrows, while the tetragonal hydrogen rich phase C_3 even survived to 8.6 GPa with the disappearance of representative stretching peak marked by black arrows. Moreover, it is notable that the stretching peak at higher frequency showed consistent shifting tendency in the whole experimental circle, indicating that the pressure induced behaviors of guest hydrogen molecules were relatively independent to the phase transitions in hydrogen hydrate system.

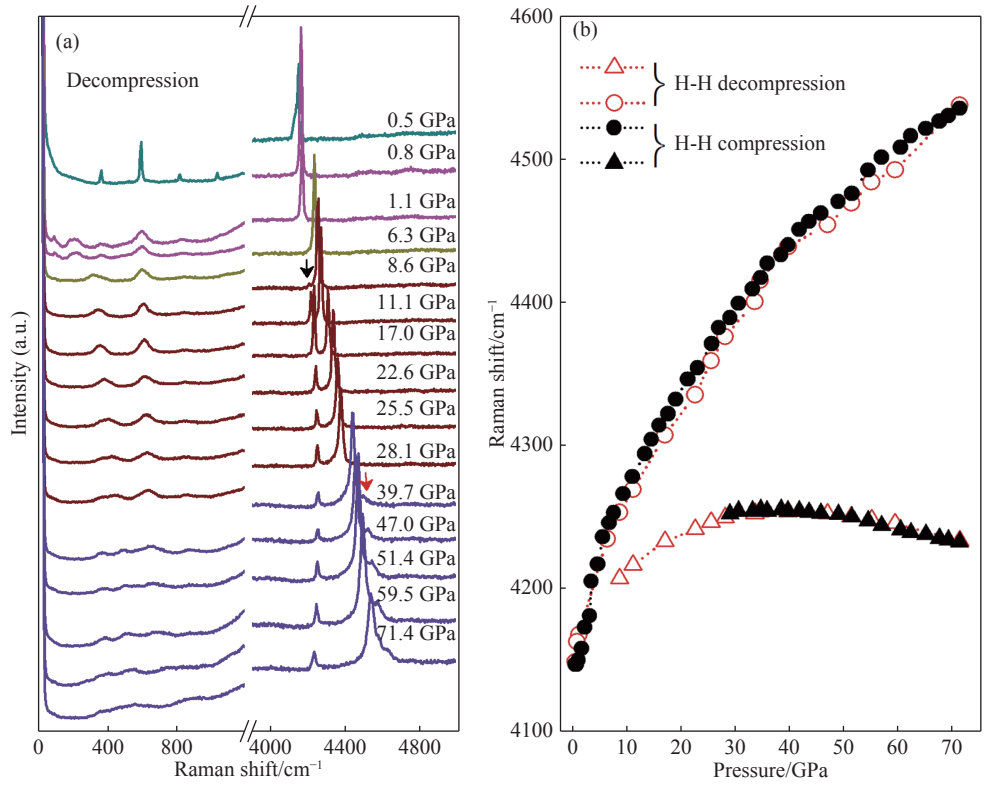

Fig. 5　(a) The Raman spectra of hydrogen hydrate under decompression. (b) The comparison of pressure dependences of the H-H stretching mode during the compression and decompression process. The red and black arrows marked the disappeared peaks at 39.7 and 8.6 GPa, respectively.

3　Conclusion

Raman spectroscopy and synchrotron XRD measurements of hydrogen hydrate were performed at high pressures. A new tetragonal hydrogen rich phase C_3 was identified above 24.5 GPa by experiments in consistent with previous theorical simulation. The Fermi resonance of the deformational mode and the soften stretching mode was firstly observed in Raman spectroscopy between 29.0–45.8 GPa, providing strong evidence of hydrogen-bond symmetrization at around 55 GPa. Two distinct pressure-induced behaviors of guest hydrogen molecules were observed in the sample, presenting complicated interactions among guest hydrogen molecules, host water molecules and external pressures. These behaviors would give a further understanding of the guest-host system.

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氢水化合物中氢键对称化和预压作用下氢行为

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摘要: 氢水化合物作为潜在的环境友好型储氢含能材料引起了众多关注。结合金刚石对顶砧装置和原位拉曼光谱测量、同步辐射 X 射线衍射光谱测量两种表征手段，试图深入理解高压驱动下氢的特征行为，寻找可能的高压富氢相。结果显示，目前已知最高含氢比例 1∶1 的相 C_2 在压力 24.5 GPa 时发生相变，更多的氢分子特征峰随相变出现。通过对理论预测结构的拟合，该相最终被确定为 $P4_1$，氢水比例达到 2∶1，且在卸压时能够稳定保存至 8.6 GPa。考虑到冰中氢键对称化对压致相变和结构稳定性的重要作用，着重观测了氢键的行为，首次探测到水分子之间氢键对称化过程中完整的费米共振现象。通过对 O-H 对称伸缩振动模式软化行为的拟合，最终确定氢键对称化发生在 55 GPa，同时拉曼光谱测量显示有更进一步相变伴随发生。氢水化合物中不同氢团簇对化学预压作用表现出截然不同的应激反应，这在此体系中也是首次被注意到，对含氢体系和纯氢中氢的金属化研究具有一定参考作用。

关键词: 高压；氢键对称化；氢水化合物
中图分类号: O521.2　　**文献标识码:** A

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金刚烷的高压拉曼光谱研究

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摘要: 对金刚烷（$C_{10}H_{16}$）进行了常温原位高压拉曼光谱研究, 最高压力为 25 GPa。通过分析高压拉曼光谱, 结合拉曼频移随压力的变化情况, 得出在实验压力范围内 $C_{10}H_{16}$ 发生了多次相变。0.6 GPa 时, $C_{10}H_{16}$ 由常温常压下的无序相（α相）转变为有序相（β相）; 继续加压至 1.7 GPa 时, 第 2 次结构相变开始, 直至 3.2 GPa, 第 2 次相变完全结束; 第 3 次相变开始于 6.3 GPa, 结束于 7.7 GPa; 22.9 GPa 时发生了第 4 次结构相变。另外, 首次在拉曼光谱上探测到第 3 次相变过程中晶格振动峰的变化, 说明第 3 次相变并非前人报道的等结构相变。

关键词: 金刚烷; 高压; 拉曼散射; 相变

中图分类号: O521.2 **文献标识码:** A

球状分子晶体结构一直是近年来的研究热点, 如 C_{60}[1]、C_{70}[2] 等。金刚烷（$C_{10}H_{16}$）是典型的具有高对称性的球状晶体结构分子。常温常压条件下, $C_{10}H_{16}$ 的晶体结构是具有 $Fm3m$ 对称群的立方相（α相）, 每个 $C_{10}H_{16}$ 分子包括 4 个 CH 基团和 6 个 CH_2 基团, 并且该分子是取向无序的[3–5]。低温 X 射线探测结果表明, 无序的α相在 208 K 下会转变为有序的四方相[6]。温度在控制材料的稳定性中起着重要的作用, 而压力作为独立的热力学参量, 也能够显著改变材料的晶体结构和性质[7–12]。Ito 等[13] 发现, 在压力的作用下, 材料会发生由无序相向有序相的转变。这一有趣的无序与有序之间的互相转变引起了广大科研工作者的极大兴趣, 其中 $C_{10}H_{16}$ 在高压下的结构和性质引起了人们的关注。

相比于理论研究[14–15], 对金刚烷的实验研究比较丰富。早在 1973 年 Ito 等[13] 就对常温下的金刚烷进行了高压 X 射线衍射研究, 发现 0.48 GPa 时金刚烷由原来的无序相转变为有序相, 而这一有序相正是前人在低温时发现的$P\bar{4}2_1c$相。由于其实验压力最高仅为 0.8 GPa, 因此金刚烷在更高压力下的行为仍未知。1979 年, Burns 等[16] 通过测量金刚烷在常温下的拉曼光谱, 也观测到无序相到有序相的转变。2000 年, Rao 等[17] 将金刚烷的拉曼散射实验压力提高到 26 GPa, 发现在压力的作用下金刚烷发生了一系列相变, 相变压力点分别为 0.5、2.8 和 8.5 GPa, 并推测金刚烷在 24 GPa 可能还会发生一次相变。同年, Vijayakumar 等[18] 将金刚烷的同步辐射 X 射线衍射实验压力提高到 25 GPa, 他们认为有序的四方相一直稳定存在到 12.5 GPa, 但是当压力大于 16 GPa 时, 四方相和单斜相都符合其 X 射线衍射谱的指标化结果, 而当压力大于 22 GPa 时, 只有单斜相符合。

综上所述, 尽管在高压下已经对金刚烷开展了一些研究, 但是其高压相变序列仍存在争议。为此, 本研究对金刚烷进行常温拉曼光谱测试, 最高压力为 25 GPa。通过分析拉曼光谱, 验证前人发现的 3 次相变, 并观测是否有其他相变。

1 实验方法

$C_{10}H_{16}$ 样品购于 Alfa 公司, 为高纯粉末。样品的封装在氮气保护的手套箱中完成。高压产生装置

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采用 Mao-Bell 式金刚石对顶砧 (Diamond Anvil Cell, DAC), 金刚石直径为400 μm, 封垫材料采用T301 钢, 预压厚度约50 μm, 样品腔直径约150 μm。由于 $C_{10}H_{16}$ 样品非常软, 可以提供良好的静水压环境, 因此样品腔中没有放置其他传压介质。将红宝石与样品一起封装在样品腔中, 整个实验过程中的压力标定根据红宝石 R1 的荧光确定。

高压拉曼实验在吉林大学超硬材料国家重点实验室的共聚焦拉曼散射系统上完成。该系统的激发光源是由相干公司(Coherent Company)生产的固体二极管倍频 Nd: Vanadate 单纵模激光器, 波长为532 nm, 最大输出功率可达 2.0 W。散射光谱的测量采用 Acton Spectra Pro500i 光谱仪和液氮制冷的CCD 探测仪完成, 光谱仪的焦距为 500 mm。实验前, 用标准硅片的峰位对系统进行校准。实验过程中, 每个拉曼散射谱的采谱时间为 120 s。

2　结果与讨论

常温常压下 $C_{10}H_{16}$ 分子具有 T_d 对称群, 其不可约表示为: $\Gamma=5\boldsymbol{A}_1+\boldsymbol{A}_2+6\boldsymbol{E}+7\boldsymbol{F}_1+11\boldsymbol{F}_2$[16], 其中 $\boldsymbol{A}_1$、$\boldsymbol{E}$、$\boldsymbol{F}_2$ 具有拉曼活性。图 1 为常温常压下测得的 $C_{10}H_{16}$ 拉曼谱。$C_{10}H_{16}$ 的常温常压拉曼谱可分为 4 个部分。(1) 波数在 2800～3000 cm^{-1} 范围内, 对应于 CH、CH_2 基团的 C–H 伸缩振动模式, 其中处在 2916 cm^{-1} (ν_{17}) 的最强峰为 CH 基团的 C–H 伸缩振动峰, 2941 cm^{-1} (ν_{18})、2893 cm^{-1} (ν_{16}) 及 2847 cm^{-1} (ν_{15}) 对应 CH_2 基团的 C–H 伸缩振动峰。(2) 波数在 1350～1500 cm^{-1} 范围内时, 处在 1434 cm^{-1} (ν_{14}) 的峰对应于 CH_2 的剪切振动, 处在 1367 cm^{-1} (ν_{13}) 的峰对应于 CH 的弯曲振动。(3) 波数在 700～1300 cm^{-1} 范围内, 处在 1225 cm^{-1} (ν_{12}) 的最强峰对应 CH 的弯曲振动, 而 972 cm^{-1} (ν_8)、951 cm^{-1} (ν_7)、760 cm^{-1} (ν_6) 处的峰对应于金刚烷骨架上 C-C 伸缩振动, 1097 cm^{-1}(ν_9) 处的峰对应于 C–H 的摇摆振动; 此外, 在 1197 cm^{-1} (ν_{11}) 和 1193 cm^{-1} (ν_{10}) 处探测到两个微弱的峰, 这是之前报道中从未被探测到的。在 Rao 等[17] 的研究中, 虽然没有在常压下观测到这两个峰, 但是在无序相向有序相转变之后, 1200 cm^{-1} 处出现的新峰实际上就是本研究观测到的ν_{11}和ν_{10}, 之所以他们认为只有一个峰, 可能是由探测器的分辨率不同导致的。(4) 波数在 100～700 cm^{-1} 范围内, 处在 441 cm^{-1} (ν_4) 的最强峰对应 C–C–C 键的变形振动, 其他晶格振动都在 400 cm^{-1} 以下, 其中对于 640 cm^{-1} (ν_5) 处的峰, 前人都未曾在常温常压下观测到, 只有 Bistričić等[19] 在低温下观测到该峰。表 1 列出了常温常压下 $C_{10}H_{16}$ 的拉曼振动峰及其与前人指认的对比。

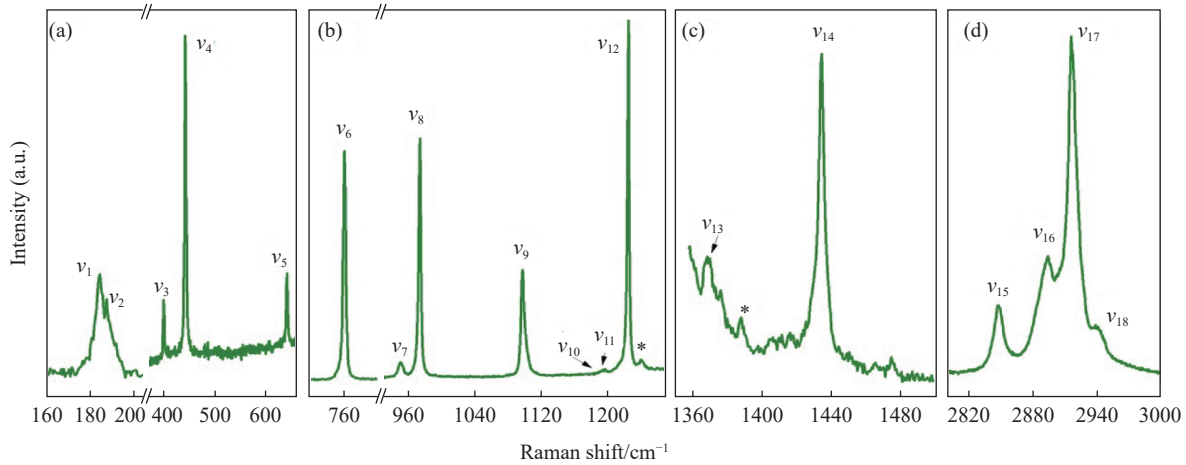

图 1　常温常压下金刚烷的拉曼谱

Fig. 1　Raman spectrum collected at ambient conditions

在本高压原位拉曼实验中, 最高压力达 25 GPa, 图 2～图 5 给出了不同波段的拉曼振动峰随压力变化情况以及振动频移随压力的变化。从图 2(a)～图 5(a) 中可以很明显地看出, 当压力升至 0.6 GPa 时, 晶格振动和内模振动都发生了明显的变化。首先, 在ν_3的低频区出现了一个新峰, 我们称之为ν_3', 而常压时的ν_4(441 cm^{-1})劈裂成两个峰ν_{4a}和ν_{4b}, 同时ν_5也劈裂成两个峰ν_{5a}和ν_{5b}。在 910 cm^{-1} 处出现了一个新

表 1　常温常压下金刚烷拉曼振动峰的指认以及与文献的对比

Table 1　Assignments and vibrational frequencies (cm^{-1}) of observed Raman modes of $C_{10}H_{16}$ at ambient condition

Frequency/cm^{-1}					Mode
This work	Ref.[20]	Ref.[17]	Ref.[16]	Assignment	
2941	2944	2943	2940	ν_{18}	C–H stretching mode
2916	2917	2913	2915	ν_{17}	C–H stretching mode
2893	2895	2983	2894	ν_{16}	C–H stretching mode
2847		2845	2847	ν_{15}	C–H stretching mode
	1474				
	1450				
1434	1437	1440	1435	ν_{14}	CH_2 scissor mode
1367	1371			ν_{13}	CH bending mode
	1315				
1225	1223	1225	1221	ν_{12}	CH bending mode
1197				ν_{11}	
1193				ν_{10}	
1097		1102	1097	ν_9	C–H rock mode
974	972	976	971	ν_8	C–C stretching mode
950	951			ν_7	C–C stretching mode
761	760	759	759	ν_6	C–C stretching mode
640				ν_5	Lattice mode
441	443	440	442	ν_4	C–C–C deformation mode
399				ν_3	Lattice mode
187				ν_2	Lattice mode
184				ν_1	Lattice mode

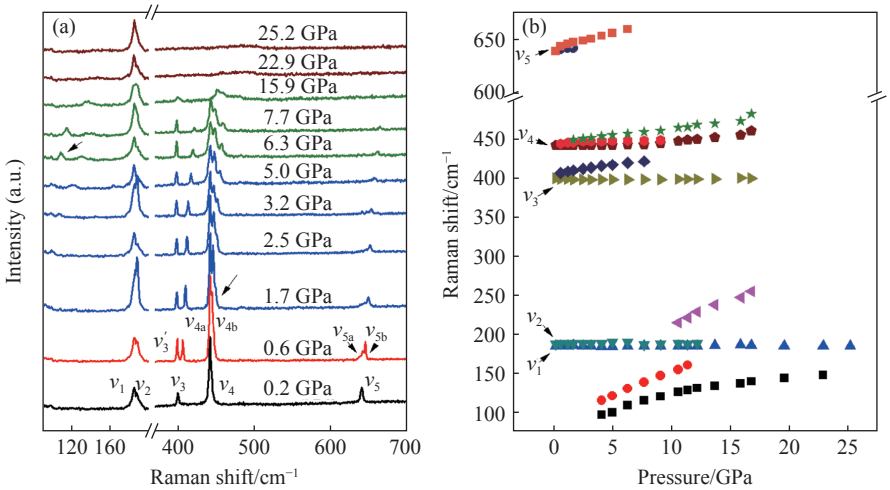

图 2　298 K、低于 25 GPa 压力下 $C_{10}H_{16}$ 的晶格振动峰及其拉曼频移随压力的变化

Fig. 2　Lattice vibration modes of solid $C_{10}H_{16}$ measured to 25 GPa at 298 K (a) and the pressure dependence of the corresponding Raman shift (b)

的弱峰, 并且一直保持到本实验的最高压力。除此之外, 常压时的ν_8(974 cm^{-1})劈裂成两个峰ν_{8a}和ν_{8b}。在 1107 cm^{-1} 处也出现了微弱的峰, 并随着压力的增大而越来越明显; 在 1111 cm^{-1} 处出现了一个相对较

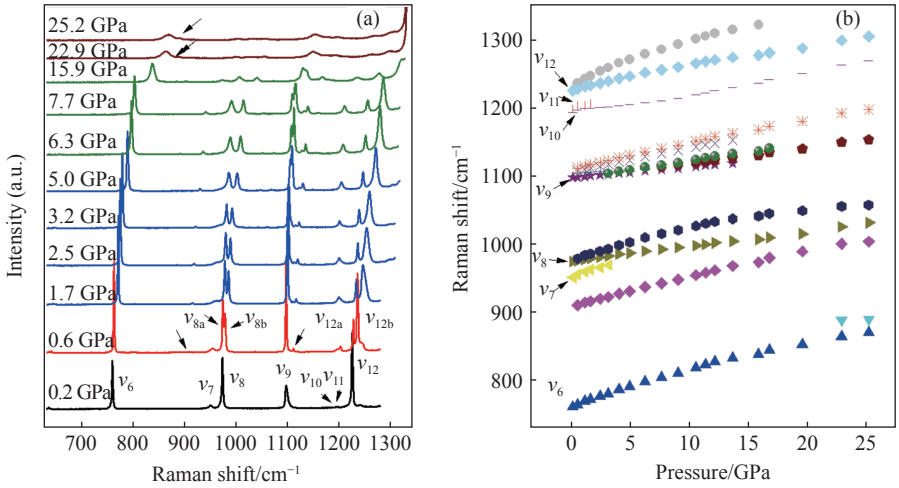

图 3　$C_{10}H_{16}$ 的内模振动峰 (700～1300 cm^{-1})(a) 及其拉曼频移随压力的变化 (b)

Fig. 3　Representative Raman spectra of $C_{10}H_{16}$ of internal vibrational modes (a) and the Raman shift versus pressure (b) in the frequency range of 700–1300 cm^{-1}

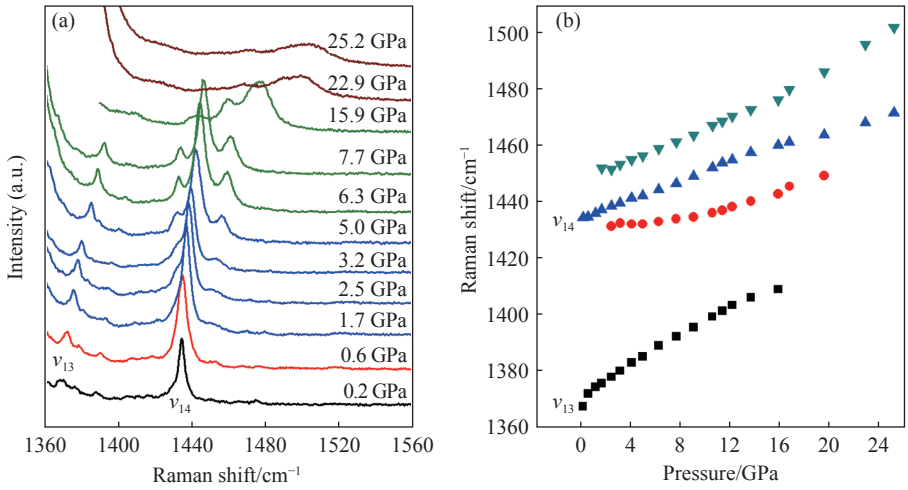

图 4　$C_{10}H_{16}$ 的内模振动峰 (1300～1500 cm^{-1})(a) 及其拉曼频移 (b) 随压力的变化

Fig. 4　Representative Raman spectra of $C_{10}H_{16}$ of internal vibrational modes (a) and the Raman shift versus pressure (b) in the frequency range of 1300–1500 cm^{-1}

明显的峰; 而在常压下非常微弱的两个峰 1193 cm^{-1} 和 1197 cm^{-1} 也变得非常明显。同时, ν_{12}劈裂成两个峰, 而ν_{17}劈裂成 3 个峰。这些变化都说明 0.6 GPa 时 $C_{10}H_{16}$ 发生由常温常压下的无序相向有序相($P\bar{4}2_1c$)的转变, 这个新的有序相称之为β相。对这个有序的四方相进行群论分析可知, 理论上应该有 90 个独立的拉曼振动峰, 而本研究观测到的拉曼振动峰个数远远小于理论数, 该现象也出现在很多其他具有范德华力的分子结构中, 如 HCN[21]。从本研究获得的拉曼谱上看, 有些变化与前人报道很吻合, 同时在第一次相变中观测到文献中第 2 次相变才出现的现象。这种差异可能是由于所采用设备的分辨率不同所导致的。

继续加压至 1.7 GPa, ν_4继续劈裂成 3 个峰, 并且随着压力的增大, 劈裂越来越明显。同时, 在ν_{14}的高频区, 出现了一个宽包(1451 cm^{-1}), 随着压力的增大, 其强度也随之增强, 直到本实验的最高压力, 其强度已经超过主峰强度。而在 Rao 等[17] 的报道中, 直到 2.7 GPa 才探测到这一新峰。晶格振动和内模振动区同时出现新峰说明在该压力点 $C_{10}H_{16}$ 发生了结构相变, 称该新相为γ相。继续加压至2.5 GPa, 在 1431 cm^{-1} 处出现了一个宽包, 随着压力的增大, 其强度越来越强。当压力达到 3.2 GPa 时, 在 1103 cm^{-1} 处出现了一个新峰, 至此第 2 次相变结束。分析拉曼谱可以看出, $\beta\rightarrow\gamma$相的转变是一个缓慢的转变过

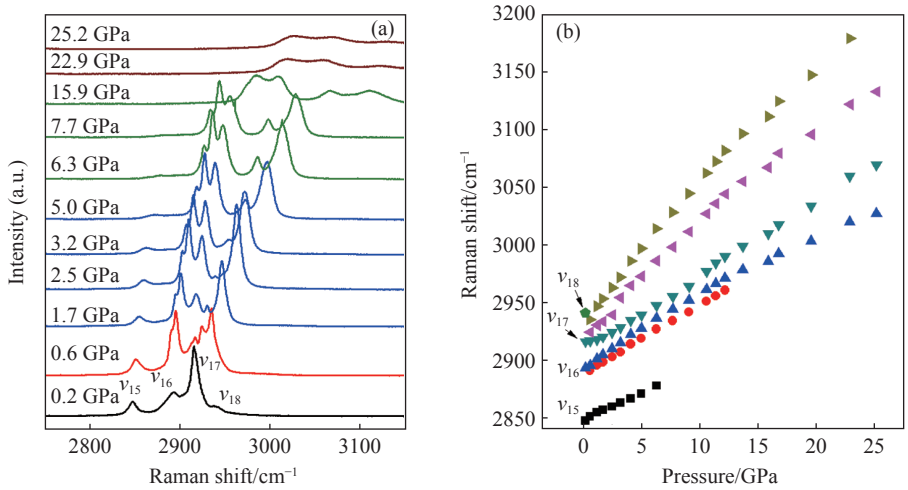

图 5　$C_{10}H_{16}$ 的 C–H 伸缩振动峰 (2800～3100 cm^{-1})(a) 及其拉曼频移 (b) 随压力的变化

Fig. 5　Representative Raman spectra of $C_{10}H_{16}$ of C–H stretching modes (a) and the Raman shift versus pressure (b) in the frequency range of 2800–3100 cm^{-1}

程, 并非瞬间完成。Rao 等[17] 认为$\beta \rightarrow \gamma$相的转变压力点为 2.8 GPa, 然而在 3.1 GPa 时他们也观测到常压时处于 1100 cm^{-1} 的峰开始变得不对称, 即所谓的劈裂, 当压力大于 3.1 GPa 时拉曼峰才完全表现为γ相的拉曼峰。因此, $\beta \rightarrow \gamma$的结构转变过程是在某个压力区间内完成的。

缓慢升高压力至 6.3 GPa 时, 在 109 cm^{-1} 位置出现了新的晶格振动峰, 如图 2(a) 中箭头所示, 这是前人从未报道过的新峰。这一现象说明 $C_{10}H_{16}$ 发生了新的结构相变, 我们称之为δ相, 这并不是 Rao 等[17] 认为的等结构相变。值得注意的是, 在此压力点, 内模振动区域并没有新峰出现, 说明在该结构相变过程中分子之间先发生变化。直到压力达到 7.7 GPa 时, ν_9继续劈裂成 3 个峰, 说明分子内部也发生了变化, 至此第 3 次相变结束。22.9 GPa 时, 在 888 cm^{-1} 处出现了一个新峰, 如图 3(a) 中箭头所示, 并且随着压力的增大, 其强度也增强, 说明 $C_{10}H_{16}$ 很可能发生了第 4 次相变, 称该新相为ε相。需要说明的是, 在 Vijayakumar 等[18] 对 $C_{10}H_{16}$ 的高压同步辐射 X 射线研究中并没有发现第 2 次和第 3 次相变, 可能是因为 X 射线探测不到 H 原子的变化, 而第 2 次和第 3 次相变极可能是由 H 原子的变化引起的。相变后的高压结构还需更多的研究来验证, 如中子衍射实验、高压理论计算等。另外, 从图 2(b)～图 5(b) 中可以看出, 所有拉曼振动频移均随着压力的增大发生蓝移, 说明各原子间的间距随着压力的增大呈逐渐减小的趋势, 并且在本实验压力范围内, 没有形成氢键。

3　结　论

对金刚烷的高压拉曼光谱进行了研究, 发现金刚烷在压力的作用下经历了$\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta \rightarrow \varepsilon$的一系列相变, 相变压力点分别为 0.6、1.7、6.3 和 22.9 GPa, 与前人报道的结果相吻合。首次在拉曼光谱上探测到第 3 次相变过程中晶格振动峰的变化。具体的高压结构还有待于同步辐射 X 射线衍射以及高压理论计算来确定。

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Raman Scattering Investigations of Adamantane under High Pressure

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Abstract: Results of Raman scattering measurements under pressure up to 25 GPa on adamantane ($C_{10}H_{16}$) carried out at room temperature are reported. The analysis of Raman data indicated four phase transitions. The ambient pressure disordered *Fm*3*m* structure (α-$C_{10}H_{16}$) transformed to a high pressure ordered phase at 0.6 GPa. Continue to pressurize to 1.7 GPa, the second structure phase transition began, and completely accomplished until 3.2 GPa. The third transition began at 6.3 GPa, ended at 7.7 GPa. $C_{10}H_{16}$ transformed to a new phase at 22.9 GPa. Because of the new lattice peak occurred during the third transition, it was defined to a first-order transition.

Keywords: adamantane; high pressure; Raman scattering; phase transition

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榍石的冲击高压行为与辐照损伤效应对比研究

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摘要: 高压和辐照这两种极端条件会造成晶体材料的晶体结构发生改变或损伤。以榍石($CaTiSiO_5$)为研究对象, 利用冲击高压和样品回收技术, 探索冲击高压作用后结构的变化规律, 并与辐照造成的损伤榍石作对比研究, 认识冲击高压与辐照造成榍石结构损伤的异同。研究表明: 冲击高压作用下, 晶态的榍石出现结构损伤和非晶化, 出现类似于榍石的辐照损伤现象, 但具体过程和受损的晶体结构有明显不同。具体表现为: X 射线衍射、红外和拉曼光谱的特征峰强度减弱, 谱线变宽, 细节丢失; 冲击高压导致晶态榍石拉曼光谱的 Ti–O 伸缩振动主峰出现红移, 与辐照损伤蜕晶化过程出现的蓝移相反。此外, 晶胞参数 a、b、c 和晶胞体积 V 减小, 与辐照损伤过程相反。

关键词: 榍石; 冲击; 高压; 辐照损伤; 非晶化

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榍石(Titanite)因其优良的化学稳定性和核素包容能力, 被用作放射性核素固化的备选材料[1], 引起了核物理、材料科学和环境学工作者的广泛关注。此外, 某些天然榍石晶体具有较高的 U、Th 含量[2], 其在 U-Th/Pb 同位素定年中也得到了广泛应用[3-4]。理想榍石的化学式为 $CaTiSiO_5$, 纯净榍石属于单斜晶系, 空间群 $P2_1/a$(晶胞中的分子数 Z=4), 晶胞参数 a=0.706 9 nm、b=0.872 2 nm、c=0.656 6 nm、β=113.86°。榍石的晶体结构如图 1所示, 其最大的特征是: $[CaO_7]$多面体、$[SiO_4]$四面体和$[TiO_6]$八面体以共棱的形式正反相间排列成链, 沿[011]方向延伸; $[TiO_6]$八面体近似平行 a 方向以共顶(O_1 连接)的形式连接成链[5-6]。

榍石属于钙钛硅酸盐矿物, 常压下加热到 496 K 左右时, 结构发生相变, 由 $P2_1/a$ 转变为 $A2/a$。这种转变主要是由于 TiO_6 八面体中的 Ti 原子从偏心位置向中心位置移动所引起的[5, 7]。1996 年 Kunz 等[8]在室温条件下首次采用金刚石对顶砧(Diamond Anvil Cell, DAC)技术对榍石的高压结构进行了研究, 发现在压强为 6.95 GPa 时榍石发生 $P2_1/a \rightarrow A2/a$ 结构相变, 且认为此高压相变与 496 K 下 $P2_1/a \rightarrow A2/a$ 相变的机理不同。Angel 等[9]也证实了该相变的存在, 但是所报道的相变点在 3.351～3.587 GPa 之间。2000 年 Kunz 等[10]再次利用原位 X 射线衍射(XRD)技术研究了榍石在不同温度和压力同时作用下结构的变化规律, 并将压强相变点核实在 3.5 GPa。2001 年 Rath 等[11]在更高压强 10.5 GPa 处发现榍石结构发生新的 $A2/a \rightarrow$

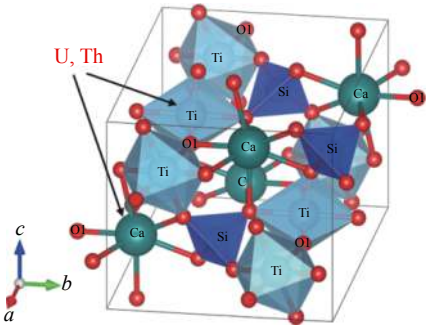

图 1 榍石晶体结构示意

Fig. 1 Schematic crystal structure of titanite

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$P\bar{1}$相变。2006 年祝向平等[12]对天然榍石进行原位高压能量色散 XRD 实验研究，结果表明榍石在 3.9 GPa 和 10.9 GPa 分别发生 $P2_1/a \rightarrow A2/a$ 和 $A2/a \rightarrow P\bar{1}$结构相变，证实了前人的研究，并首次确定在 10.9～25.1 GPa 压力区间很可能稳定存在$P\bar{1}$相。在核素固化材料应用中，认识和评估其物理特性是一个重要环节。目前，榍石的高压相变研究大多局限于静高压下的结构相变分析，尚未有冲击高压作用后的相关数据。在本工作中，首次利用冲击产生高压的方法作用核素固化材料——榍石，采用 XRD、拉曼光谱、红外（IR）光谱等手段进行表征，探索榍石在动高压下的结构变化。

榍石作为放射性锕系核素固化体的备选材料，其固化体中的放射性核素发生 α 衰变，在此过程中释放的高能量 α 粒子和反冲核会与晶格上的原子碰撞，耗散大部分能量，形成一个局域的、极快的（皮秒量级）高温高压环境[13-14]。计算机模拟表明 α 衰变过程形成了聚合作用、剪切形变和高密集区域，这些效应可能与局部高压有关[15]。认识和理解 α 衰变在核素固化体中产生的局部应力和压力对进一步认识辐照损伤过程、理解蜕晶态的结构、评估固化体的长期稳定性具有重要的科学意义。然而，直接测试和分析晶体中 α 衰变导致的局部效应十分困难，为此有学者利用实验室冲击高压实验来模拟和认识 α 衰变中可能的局部高压行为[16]，因为冲击波作用与 α 衰变过程存在极其类似的压力和温度[17-18]。当然，放射性核素衰变导致固化体的辐照损伤过程远比一般的冲击过程更为复杂，并且 α 衰变中的局部高压过程比一般实验室中的冲击高压作用时间（微秒量级[19]）短。这类对比模拟研究可能为核素固化材料中辐照损伤效应带来新的认识，同时研究榍石在冲击高压下的响应也可能有助于理解榍石固化体的辐照损伤过程。有研究报道，核素固化材料锆石（$ZrSiO_4$）在冲击高压、辐照等物理过程中可能出现不同的非晶化结构[16, 20]。为此，希望通过对比冲击高压作用后的榍石和辐照损伤榍石，研究它们在晶体结构和光谱学特征上的异同。

1　实验方法

本实验采用人工合成的晶态榍石和含 U、Th 的天然榍石。晶态榍石由前体 $CaCO_3$、TiO_2 和 SiO_2 按化学计量比在 1 330 ℃ 烧结 1 h 而成。XRD 分析表明，其具有较高的结晶度；然而，通过对比榍石和石英的红外吸收光谱，估计其中约有 6% 的 α-石英杂相。天然榍石（编号 2974，来自剑桥大学 Sedgwick 博物馆）中含有放射性核素 U、Th，晶体结构已被这些核素辐照损伤[21]（估计辐照剂量为 10^{18} α-decay/g[22-23]）。晶态合成榍石用于冲击高压实验，天然辐照损伤榍石用于对比研究。

利用西南交通大学高温高压物理研究所的二级轻气炮，进行榍石的冲击高压实验。为了对动高压作用后的样品进行回收，以完成后续各类表征分析，制造了一套回收装置，其设计参照了前人的冲击回收装置[24-25]，结构如图 2 所示。为了兼顾冲击高压实验和后续样品分析的要求，铜质样品盒内矿物样品的尺寸设计为ø6 mm×1 mm，内装 0.085 g 榍石粉末样品，用探杆在 1 GPa 压强左右压实。样品回收装置包括样品盒、回收桶和卸能块。矿物样品在样品盒内承受飞片的正面冲击，避免直接面对飞片冲击而飞散，冲击后多余的破坏性能量通过卸能块吸收。冲击实验结束后，通过电火花线切割机切割冲击变形的装置主体，取出样品盒，收集经过冲击高压作用的榍石样品。

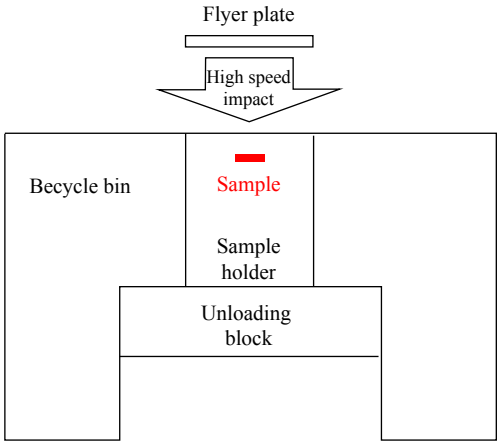

图 2　样品回收装置示意图

Fig. 2　Schematic diagram of sample recovery unit

由于被冲击的样品量很少（0.085 g），且冲击波在固体内的传播速度极高，可认为冲击过程中飞片的冲击压强近似等于样品的冲击压强[18]。此时，可利用飞片材料（铜）的冲击绝热线，根据公式 $p=\rho_0(C_0+\lambda u)u$（其中 p 为冲击波加载压力，ρ_0 为材料初始密度，C_0 和 λ 为材料的冲击波压缩参数，u 为

飞片速度)[19]计算出两次冲击实验的冲击压强为 61.4 和 83.8 GPa。冲击温度采用《Shock Waves: Equations of State》中的公式(5.44)[17]估算, 两次实验的冲击温度分别为 1 507 和 1 890 K。冲击温度的不确定性来源于无氧铜材质的样品盒在冲击过程中发生形变而造成的粉末密实度变化, 因此高速飞片撞击靶体时估算出的样品温度只可作为参考。

利用 XRD、拉曼光谱和红外光谱对样品结构变化进行表征。XRD 实验采用 Bruker D8 FOCUS 粉末衍射仪, 起止角 10°～90°, 扫描步长 0.02°, 扫描时间 608.25 s, 管电压 40 kV, 管电流 40 mA, Cu 靶。拉曼光谱表征采用 Nicolet ALMEGA XR 光谱仪, 波数区间 90～1 300 cm^{-1}, 仪器分辨率 0.9 cm^{-1}, 激光波长 532 nm, 激光功率 4.5 mW。对每个样品进行 5 次测试后, 实验数据取平均值, 每次测试时间 300 s。红外吸收光谱表征采用压片法, 将 1 mg 样品(粒径几微米)与 200 mg 溴化钾(光谱级)混合均匀, 压片后, 在 120 ℃ 烘箱内保温 12～23 h 除水。傅里叶红外光谱仪采用 ThermoFisher Nicolet iS50, 波数区间 400～4 000 cm^{-1}, 分辨率 2 cm^{-1}。

2　结果分析

2.1　XRD 分析

合成晶态榍石以及经 61.4 和 83.8 GPa 冲击压缩后的合成晶态榍石的 XRD 谱如图 3 所示, 选取榍石最具代表性的 2θ 区间 27°～35°, 其中 31.5°处有一个微弱小峰, 图 3 中未画出, 其他间断处无榍石峰。从图 3 中可以看出, 原始样品在 33.1°附近出现 $(22\bar{1})$ 和 $(21\bar{2})$ 晶面衍射峰, 可以认为该人工合成榍石为 $P2_1/a$ 相[8]; $(21\bar{1})$、(002)、(130) 和 (022) 晶面衍射峰随着冲击压力的升高, 强度逐渐降低, 半峰宽增大, 且细节丢失严重; 特别是代表 $P2_1/a$ 相的晶面衍射峰在 83.8 GPa 冲击压强下几乎消失不见, 说明晶态榍石在冲击高压作用下晶体结构出现了缺陷、应力以及可能的非晶化。XRD 峰半峰宽的变化可反映样品损伤或结晶度的改变情况。以主峰 $(21\bar{1})$ 为例, 高斯函数拟合得出原始晶态榍石样品的半峰宽为 0.155, 61.4 GPa 时为 0.183(变化 18%), 83.8 GPa 时为 0.234(变化 51%)。

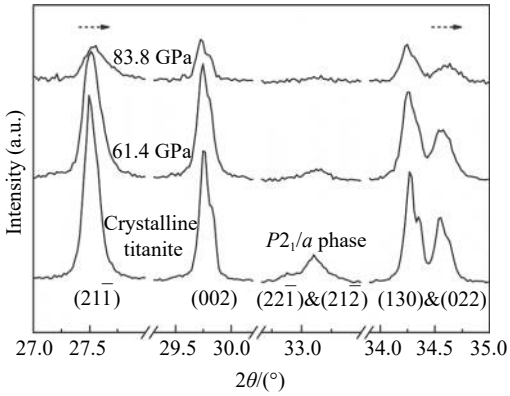

图 3　合成的晶态榍石及经 61.4 GPa 和 83.8 GPa 压强冲击后榍石的 XRD 谱

Fig. 3　XRD patterns of synthetic crystalline, 61.4 GPa and 83.8 GPa pressure shocked titanite

在 XRD 图谱中, $(21\bar{1})$ 和 (022) 晶面衍射峰随着冲击压力的升高向高角度方向偏移, (002) 和 (130) 晶面衍射峰向低角度方向微弱偏移, 表明冲击高压作用使晶格产生应力和缺陷。采用 GSAS 软件对 3 组 XRD 数据进行结构精修(2θ 区间为 27°～35°), 结果见表 1, 其中 wRp 和 Rp 为拟合误差, C^2 为拟合优度。结果显示: 晶胞参数(a、b、c、β)和晶胞体积(V)均随着冲击压力的升高而减小。说明榍石在冲击高压作用下, 一方面晶胞出现收缩, 致密度增加, 但似乎仍维持着其晶体结构; 另一方面, 由于压力作用导致晶体结构出现缺陷, 即出现损伤。这些共同效应可能影响榍石中原子间的作用力、结构基团的连接和取向。

表 1　XRD 谱结构精修数据

Table 1　Rietveld refinement data by XRD patterns

Pressure/GPa	a/Å	b/Å	c/Å	β/(°)	V/Å^3	wRp	Rp	C^2
0	7.10	8.77	6.60	113.82	376.37	0.11	0.08	3.79
61.4	7.06	8.74	6.58	113.81	371.75	0.07	0.06	3.08
83.8	7.05	8.72	6.56	113.79	368.86	0.04	0.04	1.18

辐照损伤的榍石有体积膨胀、密度减小[2, 26]等物理特性的改变。冲击高压导致榍石的晶胞参数和晶胞体积减小说明其密度增大，表现出与辐照损伤过程相反的特性，意味着冲击高压和辐照损伤导致榍石晶体结构受损和非晶化的过程和机理不同。此外，如图 4 所示，冲击高压作用使榍石主峰（$21\bar{1}$）晶面衍射峰向高角度偏移，然而对于天然辐照损伤榍石该晶面衍射峰位出现在低角度，这也说明冲击和辐照在榍石结构中引起的损伤是不同的。

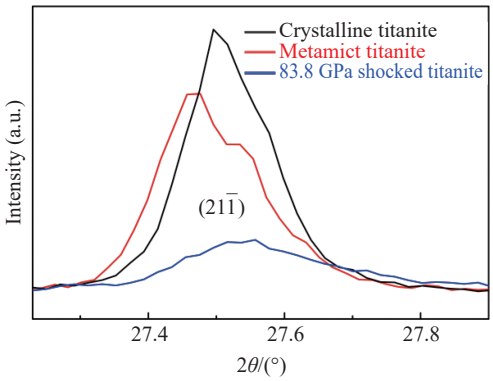

图 4　辐照损伤榍石和 83.8 GPa 冲击榍石 XRD 图谱

Fig. 4　XRD patterns of radiation damaged and 83.8 GPa shocked titanite

2.2　光谱分析

根据群论，榍石 $P2_1/a$ 相的振动模式[27]为：$\Gamma_{\text{optic}}=24\boldsymbol{A}_{\text{g}}+24\boldsymbol{B}_{\text{g}}+23\boldsymbol{A}_{\text{u}}+22\boldsymbol{B}_{\text{u}}$（$\boldsymbol{A}_{\text{g}}$ 和 $\boldsymbol{B}_{\text{g}}$ 为拉曼激合，$\boldsymbol{A}_{\text{u}}$ 和 $\boldsymbol{B}_{\text{u}}$ 为红外激合），即拉曼振动模式有 48 个，红外振动模式有 45 个。受测试条件（频率区间）限制以及部分峰的信号微弱，光谱实验一般无法测量所有理论预测的红外和拉曼峰。根据此前的研究[21-22, 28]，榍石拉曼光谱中波数低于 400 cm^{-1} 的峰归属于 Ca–O、Ti–O、Si–O 的复杂相互作用，400～500 cm^{-1} 可能代表 Si–O 弯曲振动，500～700 cm^{-1} 为 Ti–O 伸缩振动，高波数段 790～1 020 cm^{-1} 为 Si–O 伸缩振动。对于红外（IR）吸收光谱，530 cm^{-1} 以下的峰归属于 Ca–O、Ti–O、Si–O 的复杂相互作用，530～600 cm^{-1} 代表 Si–O 弯曲振动，600～770 cm^{-1} 为 Ti–O 伸缩振动，770～1 300 cm^{-1} 为 Si–O 伸缩振动。

人工合成的无损伤晶态榍石经过冲击高压后，其拉曼光谱（见图 5）出现的最明显变化是特征峰强度降低、半峰宽增大、峰位偏移、诸多峰细节丢失。例如：在 400～700 cm^{-1} 区间峰强度随冲击压力的升高急剧下降，谱线变宽；在 Si–O 伸缩振动的高波数段，855 和 872 cm^{-1} 两个峰在 61.4 GPa 压强时合并为 859 cm^{-1} 一个峰；在 400 cm^{-1} 以下代表 Ca–O、Ti–O、Si–O 复杂相互作用的低波数段细节信息丢失更明显，谱线严重变宽。

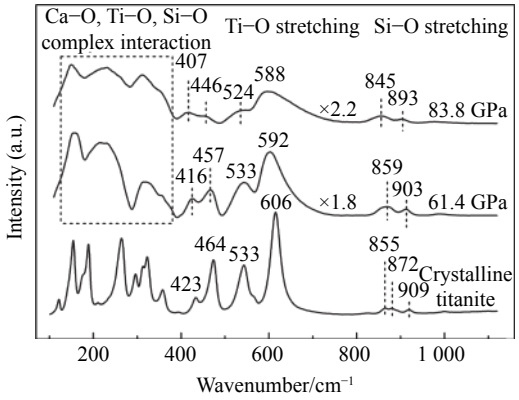

图 5　合成的晶态榍石及经 61.4 和 83.8 GPa 压强冲击后的榍石拉曼光谱

Fig. 5　Raman spectra of synthetic crystalline, 61.4 GPa and 83.8 GPa shocked titanite

合成晶态榍石经高压冲击后的红外吸收光谱变化情况如图 6 所示。每个样品均是 1 mg 合成晶态榍石与 200 mg 溴化钾均匀混合后压片测量，振动峰的相对强度和峰宽可以反映样品的结晶度。如图 6 所示，榍石特征峰强度随压力的升高而降低，包括低波数区间的 Ca–O、Ti–O、Si–O 相互作用特征峰、Si–O 弯曲振动峰、Ti–O 伸缩振动峰和 Si–O 伸缩振动峰。与此同时，Si–O 弯曲振动和 Si–O 伸缩振动特征峰的半峰宽（FWHM）随着冲击压力的升高而增大（见图 6 右上角），Si–O 振动峰（如 804、943 和 990 cm^{-1}）在冲击高压作用下消失。红外光谱证明合成榍石在高压冲击后的结晶程度降低，短程有序性降低，非晶化程度增强，与前文的 XRD 和拉曼光谱所得结果一致。

在红外光谱研究中，还注意到榍石中含有微量杂相 SiO_2（α-石英）（见图 6）。早在 1978 年，Schneider[29]就对 α-石英进行了冲击高压实验，红外透射光谱显示：压强为 30 GPa 时，位于 1 100 cm^{-1} 附近代表 Si-O 反对称伸缩振动的特征峰强度降低且宽化，但未消失；61.4 GPa 时，α-石英的红外信号完全消失，可能表明 α-石英在此冲击高压下由晶态转变为非晶态。考虑到石英在样品中只是微量存在，而且石英的行为不是本研究重点，在此就不做进一步讨论。

拉曼光谱显示冲击高压和 α 辐照造成的榍石损伤结构不同, 如图 7 所示: (1)不管是峰形还是峰位, 都存在很大的差异; (2)冲击高压样品中 Ti-O 伸缩振动峰位出现红移(606 和 533 cm^{-1} 处的特征峰分别红移至 588 和 524 cm^{-1}), 说明[TiO_6]八面体基团仍然存在, 可能出现了原子间相互作用力的改变、键长和振动取向的变化以及局部应力; 而辐照损伤导致 Ti–O 伸缩振动峰蓝移(606 和 533 cm^{-1} 处的特征峰分别蓝移至 646 和 544 cm^{-1}), 主要是由于[TiO_6]基团向[TiO_5]基团转变造成的[21], 说明辐照相比于冲击高压造成的榍石[TiO_6]八面体的损伤程度更大; (3)冲击高压造成晶态榍石在低波数段(100～400 cm^{-1})出现 3 个微弱的宽峰, 且明显比辐照损伤变化更大, 考虑到该范围内的振动峰主要与[CaO_7]多面体和[SiO_4]四面体的转动和平动有关[22], 说明冲击高压导致的损伤对 Ca–O 或 Si–O 基团的影响更严重。结合图 7 中 Si–O 伸缩振动波段(790～1 020 cm^{-1})冲击高压对 Si–O 基团的影响小于辐照损伤, 可以进一步推断冲击高压导致低波数段峰位和峰形发生巨大变化的主要原因在于 Ca–O 基团的严重损伤, 即冲击高压造成 Ca–O 基团的损伤程度大于辐照损伤。

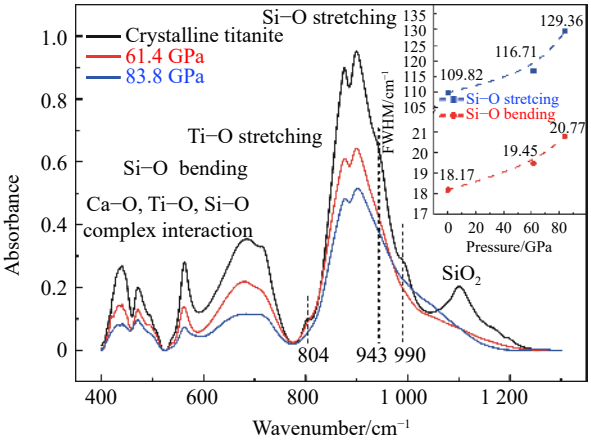

图 6　合成晶态榍石及经 61.4 和 83.8 GPa 冲击后榍石的红外光谱(插图显示 Si-O 弯曲振动峰和 Si-O 伸缩振动峰的半峰宽随压力变化情况)

Fig. 6　Infrared spectra of synthetic crystalline, 61.4 GPa and 83.8 GPa pressure shocked titanite, with insection showing FWHMs of Si-O bending and Si-O stretching vibration as varying with shock pressure

红外吸收光谱(见图 8)亦可证明上述论断。相比于冲击高压损伤, 辐照损伤下的 Si–O 伸缩振动峰半峰宽更大, Ti–O 伸缩振动峰强度的变化更明显, Ca–O 振动峰强度的变化更小, 证明辐照导致[TiO_6]八面体和[SiO_4]四面体的受损程度更大, [CaO_7]多面体的损伤程度更小。定量计算后, 冲击和辐照造成榍石各基团的损伤情况列于表 2。

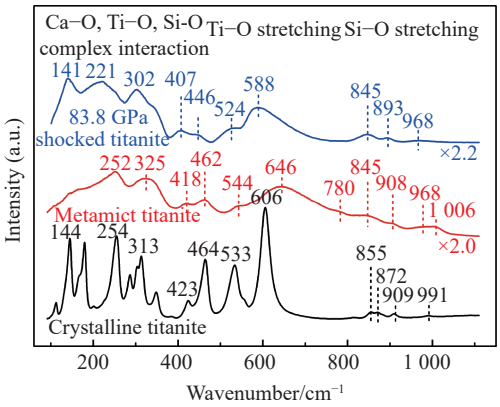

图 7　辐照损伤榍石和 83.8 GPa 冲击榍石拉曼光谱

Fig. 7　Raman spectra of radiation damaged and 83.8 GPa shocked titanite

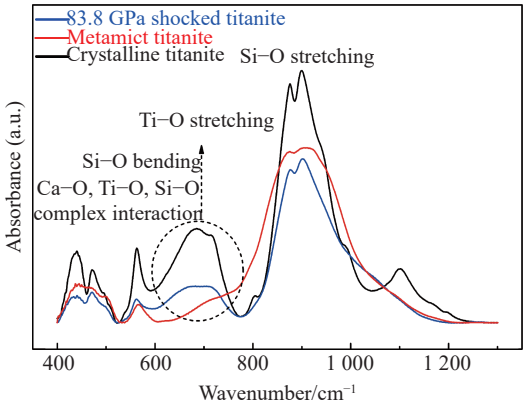

图 8　辐照损伤榍石和 83.8 GPa 冲击榍石的红外光谱

Fig. 8　Infrared spectra of radiation damaged and 83.8 GPa shocked titanite

表 2　高压冲击和核辐照对榍石各基团的影响

Table 2　Influence of shock and α-decay radiation on structural units of crystalline titanite

Structural unit	Impact of shock	α-decay radiation
[CaO_7] polyhedra	Decrease in IR intensity by 63%	Decrease in IR intensity by 49%
[TiO_6] octahedra	Decrease in IR intensity by 61%	Decrease in IR intensity by 77%
[SiO_4] tetrahedra	Increase in IR band width by 19%	Increase in IR band width by 59%

3　讨　论

下面将讨论冲击高压引起榍石损伤的一些物理过程和有关因素(如晶粒细化、加压-卸压阶段的作用、冲击可能导致的熔融)。(1)冲击高压作用往往会造成晶态材料晶粒细化,从而在晶界处出现不可逆转的结构损伤或缺陷,这或许是导致晶面衍射峰强度降低和半高宽增加的部分因素。然而,红外和拉曼光谱分析涉及的尺度在几个晶胞范围,一般冲击细化难以达到该尺度;另外,光谱不仅可探测因晶粒细化而造成的损伤,还能观察晶粒内部缺陷。红外和拉曼光谱数据表明,冲击高压造成晶态榍石的[TiO_6]、[CaO_7]和[SiO_4]结构基团发生不同变化,此现象不能简单地用晶粒细化解释。因此我们认为尽管晶粒细化可能对样品产生一定的影响,但是冲击造成的损伤应主要来源于冲击导致的结构缺陷和应力,以及缺陷聚集而产生的非晶化。(2)在冲击实验中榍石晶体结构损伤究竟出现在加压还是卸压阶段是一个有意思的科学问题。本实验结果显示,压力越高,对榍石造成的损伤程度越大(见图 3、图 5 和图 6),并且压力增加出现在加压过程。另外,分子振动的响应时间(皮秒量级)远小于保压时间(毫秒量级[19]),冲击造成的压力有足够时间传递给晶格,进而造成损伤,因此可以认为加压过程是造成榍石损伤的主要阶段,卸压是压力减小过程,应该不是引起榍石损伤的主要阶段。(3)在 83.8 GPa 冲击实验中,所估算出的温度 1 890 K 超过榍石在常压下的熔点(约 1 600 K[30]),但是否超过了榍石在此压强下的熔点不得而知,因为目前还没有相关实验数据。对比 83.8 GPa 高压冲击后榍石和熔融玻璃 $CaTiSiO_5$ 冷却凝固后“榍石”的红外[21]和拉曼[22]光谱,可以看出它们在 Si-O 伸缩振动区间有明显不同。这似乎也说明,在本高压冲击实验条件下,高压导致的熔化未出现,因此可认为榍石从晶态到非晶态的转变不是由冲击导致的熔化引起的。

高压和辐照是两种极端条件,都会造成晶体材料晶格改变和损伤。当两个因素同时作用于材料时,材料的物理性能会如何变化?目前的研究相当有限,冲击高压响应相关研究大都局限于晶体材料,辐照损伤材料的高压行为研究也仅有少量文献报道。Ríos 等[31]利用金刚石对顶砧(DAC)对辐照损伤的锆石加载压力,观察原位 XRD 谱发现,当压力为 7 GPa 时信号出现异常。Trachenko 等[32]发现严重损伤锆石在 4 GPa 出现非晶态到非晶态转变,计算结果表明,此过程伴随着 Zr 原子配位数的增加。理论上,高压在某种程度上类似于高温,可以给辐照损伤矿石提供能量,高温可以使辐照损伤结构出现恢复[33-34],这是否预示着高压下辐照损伤晶体也会出现再结晶?这是一个有意义的研究课题,然而尚没有相关实验证据。为此,我们正在针对辐照损伤榍石进行冲击高压实验,相关结果将另文讨论。

4　结　论

以核素固化材料榍石为研究对象,利用冲击高压和样品回收技术,探索材料在冲击高压作用后结构的变化规律,并与辐照损伤榍石作对比研究,认识冲击高压和辐照造成榍石结构损伤的异同。研究表明:在冲击高压作用下,合成晶态榍石的晶格产生局部应力和缺陷,出现非晶化,类似于辐照损伤的表象,但具体过程和受损的晶体结构有明显不同。具体表现为:冲击高压导致榍石晶胞参数和晶胞体积减小,与辐照损伤过程相反;拉曼光谱中 Ti–O 伸缩振动主峰出现红移,与辐照损伤蜕晶化过程出现的蓝移相反。

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A Comparative Study on Influence of High-Pressure Shocking and Radiation Damage on Titanite

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Abstract: High pressure shock and α-decay radiation are two extreme conditions capable of leading to damages on crystal lattices of solid materials. The present work investigated the influence of shocking on the structural variations of titanite ($CaTiSiO_5$) using a gas gun shock-wave technology. The results were used to compare the similarities and differences in spectral and structural changes between shocked and α-decay radiation damaged titanite, as α-decay radiation process was considered as involved in a fast high pressure process. The results showed that high pressure shock and α-decay radiation can both produce defective crystal lattice and even amorphous phases in titanite, resulting in a decrease in band intensity, a line boarding and a loss of spectral details in X-ray diffraction patterns, infrared and Raman spectra. However, there are distinct differences in the detailed processes and damage mechanisms between the two processes. High-pressure shock causes the main peak of the Ti-O stretching vibration in titanite shifts to a lower frequency, which is opposite to its behaviour in radiation damaged samples. Furthermore, shocking leads to a reduction of unit cell parameters *a*, *b*, *c* and cell volume *V*, quite contrary to a unit-cell swelling caused by radiation damage.

Keywords: titanite; shock; high pressure; radiation damage; amorphous

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镁铝合金的冲击熔化行为实验研究

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摘要: 采用反向碰撞实验技术,结合具有高时空分辨率的全光纤激光干涉测速技术,对镁铝合金开展了极端动态压缩条件下的动力学行为实验研究,获得了镁铝合金在 30～73 GPa 压力范围内的 Hugoniot 和声速实验数据。深入的数据分析表明,所获得的 Hugoniot 数据与早期的 Hugoniot 数据一致,但是纵波声速却呈现出明显的向体波声速转变的趋势,对应冲击加载下镁铝合金的固-液熔化相变,相变压力区间为 40～57 GPa。

关键词: 冲击压缩;熔化;声速;镁铝合金;相变

中图分类号: O521.2 **文献标识码:** A

镁铝合金(MB2)作为一类特殊的合金材料,具有低密度、高强度、易机械加工、耐腐蚀等特点,广泛应用于车辆工程、航空航天等领域,其动态加载下的力学和物理特性对相关结构设计等具有重要意义。国内外对 MB2 合金的早期研究主要集中于力学特性方面,通过开展低压动态响应特性实验研究,获得了材料的弹塑性响应[1]、动态损伤[2]及层裂行为[3]的初步认识,近年来 Millett 等[4]通过一维冲击加载研究了 MB2 合金在早期变形和位错条件下随加载应力、加载脉宽而变化的弹塑性和剪切强度行为。另外,对动态加载下 MB2 合金的物态方程及相变研究已开展了一系列工作,主要集中于冲击 Hugoniot 数据测量[5],然而与动态加载下物理、力学特性紧密相关的相变研究尚处于起步阶段。声速作为应力扰动在材料中传播的定量表征参量,是获知材料动态响应特性(如相变、屈服强度、剪切模量)的主要途径之一[6–7],然而相关的研究工作却鲜见报道。

本研究拟采用反向碰撞实验技术[8–9],结合具有高时空分辨率的全光纤激光干涉测速技术 DPS (Doppler Pin System)[10],对 MB2 合金开展 30～73 GPa 压力范围内的冲击 Hugoniot 及声速测量实验,并与早期实验数据进行对比验证,分析 MB2 合金的冲击熔化行为。

1 实 验

本研究涉及低压力区的声速测量,为此采用反向碰撞实验设计,即将样品材料制作成飞片,撞击 LiF 透明窗口,其原理如图 1 所示。在拉氏坐标下,飞片以速度 W 直接撞击窗口($t=t_1$),在飞片和窗口中分别产生左行冲击波和右行冲击波,引起飞片/窗口界面粒子速度的突跃。当飞片中的左行冲击波到达后界面时,将反射中心稀疏波,该稀疏波的波速就是材料在冲击压缩下的声速。如果样品材料发生冲击熔化,则中心稀疏波将以单一塑性波的形式在样品内传播,并在飞片/窗口界面处($t=t_2$)发生卸载,引起粒子速度的下降。如果样品材料没有发生冲击熔化,则中心稀疏波包括传播速度较快的弹性波和传播速度相对较慢的塑性波。当传播速度较快的弹性卸载波到达飞片/窗口界面时($t=t_2$),界面粒子速度下降,在速度剖面上形成第 1 个拐点;当塑性卸载波到达飞片/窗口界面时($t=t_3$),界面粒子速度再次突变,在速度剖面上形成第 2 个拐点;当后续稀疏波陆续到达飞片/窗口界面时,会导致界面粒子速度的连续下降;如果在卸载过程中样品材料发生相变,则也会在速度剖面上形成拐点。

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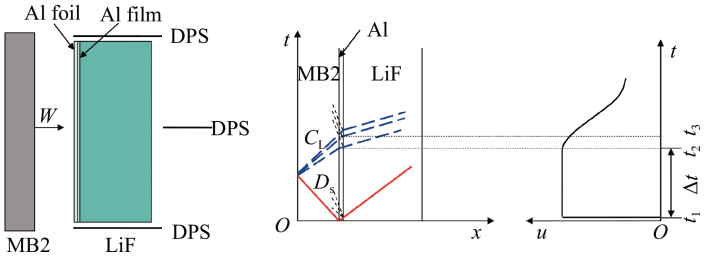

(a) Experimental set-up　　(b) Wave interaction

图 1　反向碰撞实验示意图

Fig. 1　Schematic of backward-impact experimental configuration

根据图 2 所示的界面连续性条件(其中 p 为冲击压力, u 为粒子速度), 结合 Rankine-Hugoniot 关系[11], 可以得到样品内的冲击波速度 D_s 为

$$D_s = \frac{\rho_{0w} D_w u_w}{\rho_{0s}(W - u_w)} \tag{1}$$

式中: D、ρ、W 分别为冲击波速度、密度和飞片速度, 下标 s 和 w 分别对应样品和窗口。如果窗口材料的 D-u 曲线满足线性关系

$$D_w = C_{0w} + \lambda_w u_w \tag{2}$$

式中: C_{0w} 和 λ_w 为窗口材料的 Hugoniot 参数, 则(1)式可表示为

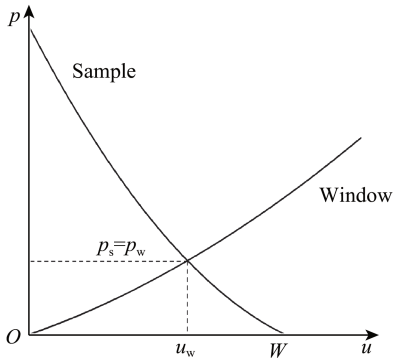

图 2　反向碰撞实验 p-u 图

Fig. 2　p-u relation for backward-impact experiment

$$D_s = \frac{\rho_{0w}(C_{0w} + \lambda_w u_w) u_w}{\rho_{0s}(W - u_w)} \tag{3}$$

因此, 只需要测得飞片(样品)击靶速度 W 和窗口的波后粒子速度 u_w, 就可以获得样品的粒子速度 u_s(u_s=W–u_w)和对应的冲击波速度 D_s。随后, 由波系作用(见图 1(b))的几何关系可知, 样品材料 Hugoniot 状态的拉格朗日纵波声速 C_L 为

$$C_L = \frac{D_s h_s}{D_s t_{12} - h_s} \tag{4}$$

相应的欧拉纵波声速 C_l 为

$$C_l = \frac{D_s h_s}{D_s t_{12} - h_s} \frac{D_s - u_s}{D_s} \tag{5}$$

式中: h_s 为样品厚度, 下标 1 和 2 对应波剖面上不同的时间点。

可以看到, 反向碰撞法以波剖面测量为基础, 波系作用简单, 通过波剖面的粒子速度及时间信息得到高压声速, 实验数据具有较高的精度, 但是由于可供选择的窗口材料种类较少, 目前使用的 LiF 窗口的阻抗较低, 导致实验压力范围有限。

2　实验结果与分析

实验在中国工程物理研究院流体物理研究所⌀30 mm 二级轻气炮上进行。将 MB2 合金飞片安装在弹丸上, 将弹丸发射至稳定的弹道速度 W, 并撞击 LiF 单晶窗口, 通过 DPS 测量飞片击靶速度以及飞片/窗口界面粒子速度, 获得待测材料的冲击波速度和声速。为了提高测试界面对 DPS 入射光的反射效率, 避免靶室残留气体对测试的干扰, 窗口击靶面上镀 1 μm厚的铝膜并贴 8 μm厚铝箔。LiF 窗口折射率修正采用 Rigg 等[12] 的公式

$$u_w = 0.7895 \times u^{0.9918} \tag{6}$$

式中: u_w 代表修正后的窗口界面粒子速度, u 代表实测界面粒子速度, 二者单位均为 km/s。其中 LiF 密度为 2.638 g/cm^3, 冲击波速度 D 和粒子速度 u 的关系为 D=5.150+1.352u(单位 km/s)[5]。

图 3 给出了 6 发实验测得的 MB2/LiF 界面粒子速度剖面(平台高度随加载压力的增大而升高)。通过界面粒子速度剖面, 由(1)式～(6)式可得 MB2 样品在 30～73 GPa 冲击压力范围内的冲击波速度-粒子速度和声速-压力数据, 实验结果列于表 1, 其中密度采用排水法测量, 实测值为 (1.775±0.004) g/cm^3。冲击波速度-粒子速度数据如图 4 所示, 图中还显示了美国洛斯阿拉莫斯国家实验室(LASL)发表的实验数据[5]。从图 4 中可以看出, 本研究获得的实验数据与已有实验数据具有较好的一致性。

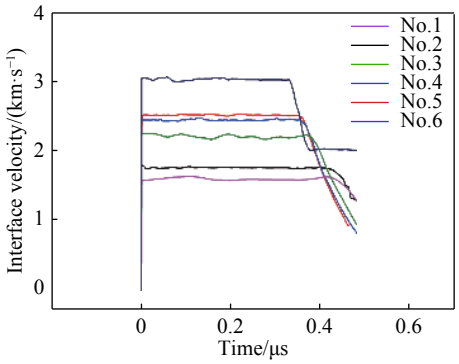

图 3　MB2/LiF 界面粒子速度剖面

Fig. 3　Particle velocity profile of MB2/LiF interface

表 1　MB2 样品冲击实验参数及结果

Table 1　Shock experiment parameters and results of MB2

Exp.No.	h_s/mm	W/(km·s^{-1})	u_w/(km·s^{-1})	u_s/(km·s^{-1})	D_s/(km·s^{-1})	p/GPa	C_l/(km·s^{-1})
1	1.980±0.004	3.949±0.020	1.589±0.016	2.360±0.026	7.303±0.166	30.6±0.4	7.983±0.297
2	1.997±0.004	4.358±0.020	1.763±0.018	2.595±0.027	7.607±0.175	35.0±0.5	9.101±0.394
3	1.978±0.004	5.379±0.027	2.195±0.022	3.184±0.030	8.317±0.191	47.0±0.7	9.167±0.402
4	1.981±0.004	5.928±0.030	2.435±0.024	3.493±0.039	8.746±0.214	54.2±0.9	8.912±0.380
5	1.981±0.004	6.100±0.030	2.514±0.025	3.586±0.039	8.907±0.213	56.7±0.9	8.601±0.348
6	1.987±0.004	7.220±0.036	3.003±0.030	4.217±0.050	9.747±0.245	73.0±1.2	9.723±0.463

从图 3 可以看到: 6 发实验测得的界面粒子速度剖面质量良好, 粒子速度剖面对应的冲击波、卸载波到达样品/窗口界面的特征信号清晰; 加载压力为 30.6 和 35.0 GPa 时卸载剖面的弹-塑性特征明显, 表明 MB2 合金在该冲击压力下尚未完全熔化; 随着加载压力的升高, 卸载剖面的弹-塑性特征逐渐消失, 当加载压力达到 73.0 GPa 时, 弹-塑性卸载特征完全消失, 表明 MB2 已完全进入熔化相区, 与图 5 所示的不同加载压力下声速转变特征一致。

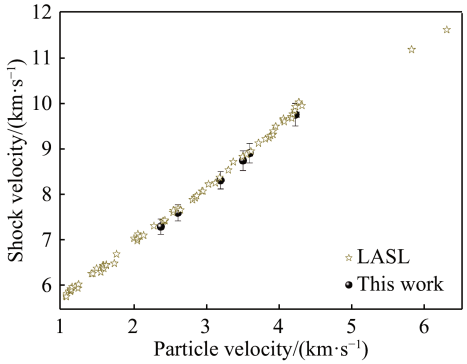

图 4　冲击波速度与粒子速度的关系

Fig. 4　Shock velocity vs. particle velocity

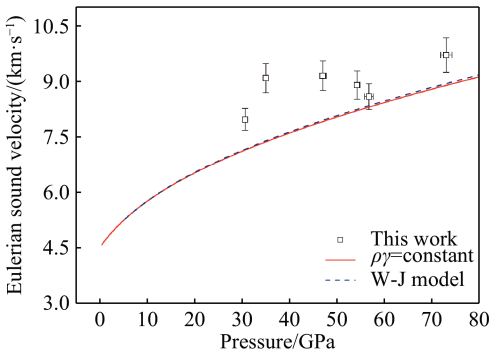

图 5　声速与冲击压力的关系

Fig. 5　Sound velocity vs. shock pressure

如图 5 所示, 当加载压力由 30.6 GPa 增加到 35.0 GPa 时, 纵波声速逐渐增大, 由 7.983 km/s 增大至 9.101 km/s; 但是, 当加载压力增大至 47.0 GPa 时, 纵波声速逐渐向体波声速偏转, 跃变为 9.167 km/s, 预

示着随着加载压力的升高，材料内部的剪切效应减小，冲击熔化发生；直至压力达到 56.7 GPa 时，纵波声速转变为体波声速，由此进一步确认了冲击加载下 MB2 合金发生熔化。Urtiew 等[13] 通过理论预测 MB2 合金在 57 GPa 附近开始熔化，该结果与本研究根据声速判定的冲击熔化区域基本一致，从而进一步证实了 MB2 合金在该压力范围内发生冲击熔化，只是 Urtiew 等预估的理论压力略高。图 5 中的实线是根据以下公式[11] 计算得到的体波声速曲线

$$C_{\mathrm{b}}^2=\frac{1}{2}V^2\left(\frac{\gamma}{V}\right)_{\mathrm{H}}p_{\mathrm{H}}-V^2\frac{\mathrm{d}p_{\mathrm{H}}}{\mathrm{d}V}\left[1-\frac{1}{2}\left(\frac{\gamma}{V}\right)_{\mathrm{H}}(V_0-V_{\mathrm{H}})\right] \tag{7}$$

式中：C_{b} 为体波声速；ρ、γ 分别为密度和 Grüneisen 系数，$\rho\gamma=\rho_0\gamma_0$，$\rho_0$ 为材料初始密度，γ_0=1.43[14]。图 5 中的虚线是基于吴-经方程[15] 计算得到的体波声速曲线。可以看出，理论计算的体波声速曲线较冲击加载实验值偏低约 10%。这主要是由于合金材料自身成键及结合能的影响，难以采用传统的混合法则或物理模型准确计算物态方程的基本参数，如 Grüneisen 系数等，由此导致理论预测结果与实验结果出现差异（通常理论值偏低）。

根据不确定度传递关系[16]，当全部直接测量量（输入量）Y_i 彼此独立不相关时，由其确定的间接测量量 z 的合成不确定度 Δz 由下式确定

$$\Delta z^2=\sum_{i=1}^{N}\left(\frac{\partial f}{\partial y_i}\right)^2\Delta y_i^2 \tag{8}$$

式中：y_i 为输入量 Y_i 的直接测量值，z 为被测量的测量值，f 为 z 和 y_i 的函数关系，N 为输入量的总个数，Δy_i 为直接测量值的不确定度。因而，当密度为 $\rho_{0\mathrm{s}}$、厚度为 h_{s} 的飞片撞击窗口时，样品/窗口界面处粒子速度跳跃，实验测得飞片速度 W、界面粒子速度 u_{w}、时间间隔（剖面平台）t_{12}，相应的测量不确定度为 $\Delta\rho_{0\mathrm{s}}$、Δh_{s}、ΔW、Δu_{w}、Δt_{12}，而窗口 Hugoniot 参数（$\rho_{0\mathrm{w}}$、$C_{0\mathrm{w}}$、λ_{w}）的不确定度（$\Delta\rho_{0\mathrm{w}}$、$\Delta C_{0\mathrm{w}}$、$\Delta\lambda_{\mathrm{w}}$）已知。由于各测量量是独立测量的，（$C_{0\mathrm{w}}$，$\lambda_{\mathrm{w}}$）相互作用项较小，可忽略不计，据此可根据不确定度传递律确定声速测量的不确定度。

如图 6 所示，就该例反碰撞实验（No.2）而言，影响声速测量不确定度的因素很多，包括样品初始密度、厚度、飞片速度、界面粒子速度、追赶时间、窗口材料冲击 Hugoniot 参数等。样品内部冲击压缩状态（如粒子速度、冲击波速度、冲击压力等）均通过飞片速度、界面粒子速度及窗口 Hugoniot 参数计算获得，影响声速测量不确定度的主要因素在于飞片速度、界面粒子速度及稀疏波追赶时间（平台时间），所占比例（即对（8）式中各平方项求和，下同）约为声速测量不确定度的 99%，其余如初始密度、厚度等参量在当前诊断水平下对声速测量不确定度的贡献较小，约占总体的 1%。在现有诊断条件下，飞片速度采用 DPS 直接测量，测量扩展不确定度不大于 0.5%；界面粒子速度剖面的测量不确定度主要受平台区速度及稀疏波追赶时间的影响，影响因素包含干涉信号数据转换精度、窗口折射率修正、起跳及卸载时刻的判断等，综合而言，平台区速度测量的扩展不确定度不大于 1%，追赶时间测量的扩展不确定度约 6 ns。总体而言，传递至声速的测量扩展不确定度不超过 5%。

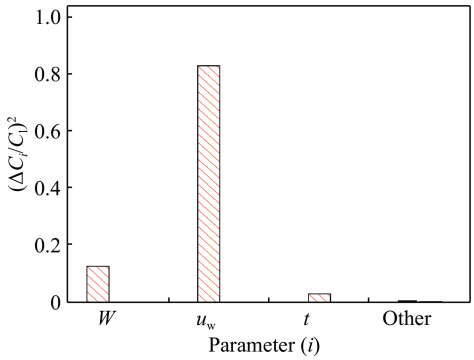

图 6　反碰撞法测量声速实验中不确定度

Fig. 6　Uncertainties for backward-impact experiment based on law of propagation

3　结　论

采用反向碰撞实验技术，结合具有高时空分辨率的 DPS，获得了 MB2 合金在 30～73 GPa 压力范围内的冲击 Hugoniot 及声速数据。随着加载压力的升高，MB2 合金纵波声速呈现出明显的向体波声速转

变的趋势, 预示着材料内部的剪切效应逐渐减小, 冲击熔化发生, 其相变压力区间为 40～57 GPa。该实验结果与不同加载压力下卸载波剖面对应的弹-塑性转变特征完全一致, 由此进一步确认了冲击加载下 MB2 合金熔化相变的发生。

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Melting of MB2 Alloy under Shock Compression

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Abstract: Reverse impact experiments were performed at a shock pressure range from 30 GPa to 73 GPa to investigate the dynamic response of magnesium aluminum alloy. A displacement interferometer system for any reflector was employed to measure the impact velocity and sample/window interface particle velocities. The Hugoniot data obtained in this study had a good agreement with the data published before, however, the sound velocities extracted from our experiments showed a transition from longitudinal to bulk sound velocity. This discontinuity is attributed to melting transition under shock compression, and the transition pressure range is estimated from 40 GPa to 57 GPa.

Keywords: shock compression; melting; sound velocity; magnesium aluminum alloy; phase transition