

Isostructural phase transition and tunable electrical properties of LaI_3 under compression

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(Received 9 November 2024; accepted 27 August 2025; published 10 November 2025)

LaI_3 has emerged as a promising scintillator due to its relatively small band gap. While some studies have explored various dopants to enhance its performance, there remains significant room for optimization, highlighting the importance of further understanding and tuning the intrinsic characteristics of LaI_3 . In this work, the crystal structure and properties of LaI_3 are extensively investigated under high pressure up to 50 GPa. The ambient layered $Cmcm$ - LaI_3 is found to undergo an unexpected isostructural phase transition at ~ 11 GPa, characterized by an anomalous change in the ratio of the a to b lattice parameters. This transition is further supported by Raman spectroscopy, electrical transport measurements, and first-principles calculations. Additionally, ultraviolet-visible absorption experiments indicate that the band gap of LaI_3 gradually narrows and tends toward closure, eventually leading to a metallic state at 37 GPa. This work uncovers an interesting second-order phase transition among lanthanide halides, providing new insights into the fundamental behavior of LaI_3 under high pressure.

DOI: [10.1103/y5bc-l2sj](https://doi.org/10.1103/y5bc-l2sj)

I. INTRODUCTION

Lanthanide halide scintillation crystals possess a novel ability to convert high-energy radiation (including x-ray and γ -ray) or high-energy particles (including α particles and β particles) into ultraviolet or visible fluorescence [1,2]. Among lanthanide halides, LaCl_3 [3] and LaBr_3 [4–7] have been successfully commercialized in various fields, including medical radiology, radiation detection, and high-energy physics [8–10], therefore prompting the pursuit of ideal scintillators. As for the inverse proportion between light output and band gap [11,12], LaI_3 has a relatively small band gap of 3.3 eV in experiments [13], closely matched by HSE06 hybrid functional calculations [14], compared with LaCl_3 (7.0 eV [15]) and LaBr_3 (5.9 eV [16]). Furthermore, in the sequence of chloride, bromide, and iodide compounds, the scintillation response generally tends to be faster [17]. Consequently, LaI_3 has been regarded as an exceptional scintillator candidate among lanthanide halides.

Efforts have been devoted to improving the scintillation in LaI_3 . Inspired by the successful scintillation through doping Ce^{3+} in LaCl_3 [3,4] and LaBr_3 [5,6], in 2005, Bessiere

et al. introduced Ce^{3+} as a dopant into LaI_3 ; however, the scintillation was quenched above 100 K [13]. In 2015, Pushak *et al.* investigated luminescence in the $\text{NaI-LaI}_3\text{-Ce}$ system and observed that the luminescence intensity decreased significantly above ~ 18 K [18]. Actually, the loss of scintillation light is attributed to the proximity of the Ce^{3+} 5d level to the conduction band in LaI_3 [14], which prompted the exploration of alternative doping strategies. In 2018, Rutstrom *et al.* explored scintillation in Bi^{3+} -, Sb^{3+} -, and Eu^{2+} -doped LaI_3 , discovering the first room-temperature scintillation in $\text{LaI}_3\text{:Eu}^{2+}$ [19]. In 2021, Li *et al.* synthesized a luminescent LaI_3 -tetrahydrofuran complex that is excited by ultraviolet radiation [20]. However, LaI_3 still faces challenges, including low luminescence intensity and low efficiency in ligand searching, which highlight the need for alternative strategies to optimize its intrinsic characteristics.

Traditional pathways for exploring new scintillators involve single crystallization, codoping [21], nanocrystallization [22,23], and film processing [2,11]. However, these techniques encounter challenges, including the high costs associated with high-temperature annealing and difficulties in manufacturing large-area thin films [2,24]. In addition, as mentioned above, the lack of transferability of successful dopants from one compound to another increases the costs of trial and error. Hence, from an exploratory perspective, researchers have harnessed high pressure to tailor the properties of scintillation crystals [25]. Pressure, as an independent physical parameter, can effectively and purely modulate the intrinsic characteristics of compounds [26], particularly their band gap and lattice structures in scintillation crystals, such as YF_3 [27], LaGaO_3 [28], and $\text{Cs}_3\text{Sb}_2\text{Br}_9$ [29]. Regarding

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lanthanum halides, Gregorian *et al.* increased the scintillation intensity in LaCl_3 within a specific pressure range [30], and Gascón *et al.* achieved a reduction in the decay time of LaBr_3 by applying pressure [31]. Therefore, utilizing pressure to optimize the crucial characteristics of LaI_3 holds great potential for the development of scintillators.

In this work, we systematically investigated the high-pressure behavior of LaI_3 through synchrotron x-ray diffraction, Raman spectroscopy, ultraviolet-visible absorption spectroscopy, and impedance spectral measurements. We obtained the relationship between the band gap and pressure at room temperature ($dE_g/dP = -62.39 \text{ meV GPa}^{-1}$) and its metalization process, culminating in a metallic state at 37 GPa. The band gap closure pressure calculated by HSE hybrid functional calculations is 35 GPa, which is in agreement with experimental results. Unexpectedly, we observed a second-order isostructural phase transition in LaI_3 at 11 GPa under nonhydrostatic and (quasi)hydrostatic conditions, driven by changes in the electronic structure. Furthermore, we confirmed electronic conduction as the charge carrier under an alternating electric field. This research provides valuable insights into a pressure-driven approach for regulating the electrical properties and crystal structure of LaI_3 , further shedding light on the potential of pressure-tuned luminescent behavior of lanthanum halides.

II. METHODS

Lanthanum triiodide (Alfa Aesar, purity: 99.995+%) was loaded into symmetric diamond anvil cells in a glovebox filled with an Ar atmosphere containing O_2 and H_2O less than 0.01 ppm to prevent possible deliquescence or oxidation. The pressure values were calibrated by the frequency shift of the diamond Raman edge [32] and the fluorescence of the ruby R_1 emission line [33].

For the *in situ* x-ray diffraction (XRD) in Cell No. 1, the diamonds had culets with a diameter of 200 μm . LaI_3 was precompressed into a flake and loaded into a 90- μm -diameter sample chamber drilled by laser. The gasket was used by T301 stainless steel, and no pressure transmitting medium was used. For Cell No. 2, the diamonds had culets with a diameter of 200 μm and the sample chamber had a diameter of 100 μm . The gasket was made of rhenium (Re), and neon (Ne) was loaded as the pressure transmitting medium. XRD data were collected by a focused monochromatic x-ray beam ($36 \times 26 \mu\text{m}^2$) with a wavelength of $\lambda = 0.6199 \text{ \AA}$ at BL4W2 in Beijing Synchrotron Radiation Facility (BSRF) and at BL15U1 in Shanghai Synchrotron Radiation Facility (SSRF) ($3.1 \times 3.6 \mu\text{m}^2$). A MAR-3450 CCD in BSRF and a Mar165 CCD in SSRF were used as detectors, and the detector distance and other geometric parameters of the sample were calibrated using a CeO_2 standard. XRD images were integrated into two-dimensional diffraction patterns by using DIOPTAS [34]. Full profile analysis of the diffraction patterns and Rietveld refinements was conducted using GSAS-II packages [35].

For the Raman spectra measurements, the diamonds had culets with a diameter of 200 μm . LaI_3 was precompressed into a flake and loaded into a 90- μm -diameter sample chamber drilled by laser. The gasket was used by T301 stainless steel, and no pressure transmitting medium was used. Raman

spectra were collected using 532 nm exciting beam, and the Raman signals were collected using a $20\times$ Mitutoyo long working distance objective and dispersed by a 1200 mm^{-1} grating.

For the high-pressure electrical measurements, the diamonds had culets with a diameter of 80 μm , and sample chambers were drilled into a diameter of 60 μm . Insulating gaskets were prepared with a T301 stainless steel outer circumference coated with fine alumina powder mixed with epoxy as an insulator. Two Pt electrodes were adopted for impedance measurements, and no pressure transmitting medium was used. Impedance spectra were collected from 10 to 10^7 Hz with an amplitude of 1 V using a Solartron 1260 impedance analyzer equipped with a Solartron 1296 dielectric interface. A Faraday cage was installed outside the diamond anvil cell to shield the system from possible electromagnetic interference. The electrical transport measurements were conducted via a four-probe method using Pt electrodes. The temperature dependence of the electrical resistance was measured upon cooling and warming cycles with a slow temperature ratio (0.3 K min^{-1}). The data were taken upon warming as it yields a more accurate temperature reading.

For the *in situ* high-pressure ultraviolet-visible (UV-vis) absorption spectroscopy measurements, the sample of LaI_3 was precompressed into a flake and loaded in a 150- μm -diameter sample chamber using a T301 steel gasket. The diamonds had culets with a diameter of 280 μm , and NaCl was used as a background reference. UV-vis absorption spectra were performed by an UV-vis absorption spectrophotometer with a deuterium-halogen light source (180–1100 nm), and the response time was 200 ms.

Structural relaxations and electronic properties calculations were performed using the projector augmented wave method [36] in the Vienna Ab initio Simulation package (VASP) [37]. The exchange-correlation interaction was treated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [38]. The valence electrons considered for La and I atoms were $5s^2 5d^1 5p^6 6s^2$ and $5s^2 5p^5$, respectively. The cutoff energy for the expansion of the wave function in the plane wave basis was set to 800 eV, and Monkhorst-Pack k -point meshes with a grid spacing of $2\pi \times 0.20 \text{ \AA}^{-1}$ were chosen to ensure good total energy convergence. To overcome the band gap underestimation issue of the standard GGA-PBE functional, the Heyd-Scuseria-Ernzerh (HSE06) hybrid functional was employed for the precise electronic structure analysis, including the density of states and band structure for LaI_3 . The HSE06 scheme incorporates 25% exact Hartree-Fock exchange with 75% PBE exchange through the screened Coulomb potential approach, where the screening parameter (μ) is set to $0.2 \text{ \AA}^{-1}$.

III. RESULTS AND DISCUSSION

A. Structural characterizations under high pressure

At 0.9 GPa, the XRD pattern exhibits highly crystalline powder characteristics [Fig. 1(a)], and the lattice parameters of $Cmcm$ - LaI_3 ($a = 4.39 \text{ \AA}$, $b = 13.82 \text{ \AA}$, and $c = 9.95 \text{ \AA}$) are listed in Table I. This phase is characterized by a layered

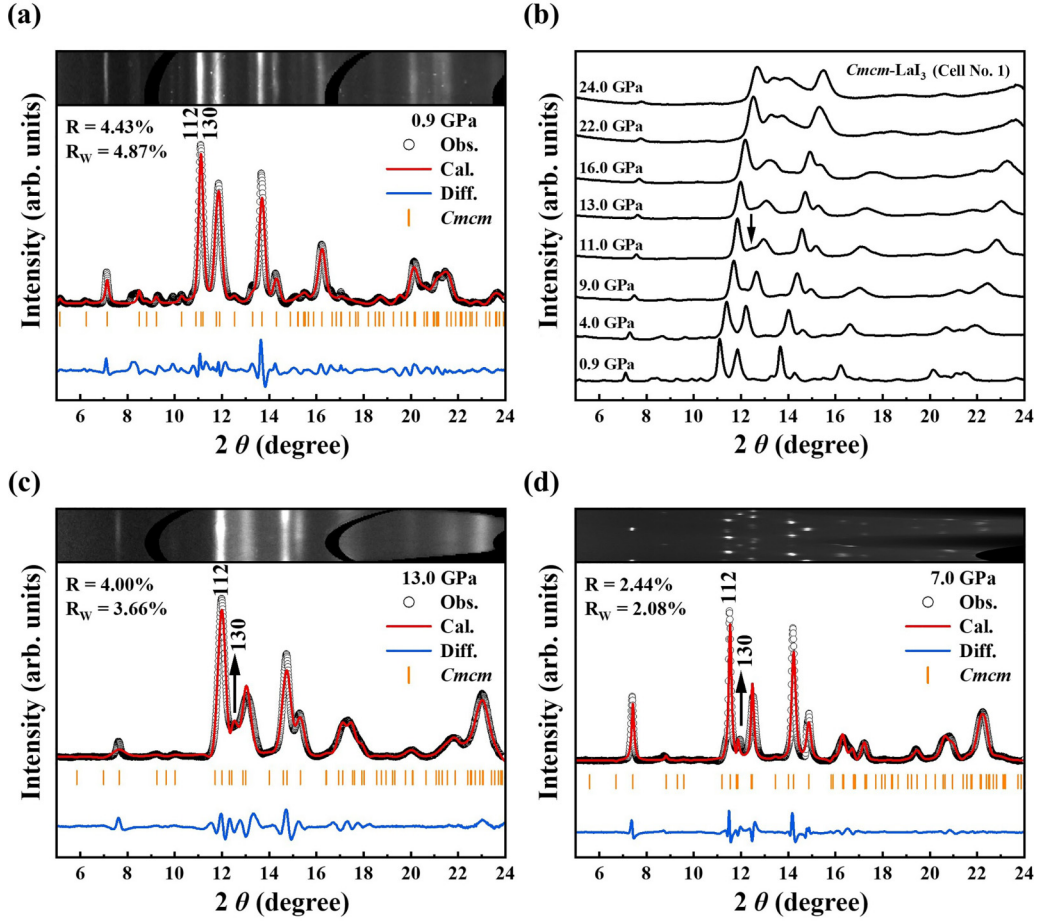


FIG. 1. Rietveld refinement results of Cell No. 1 *Cmc*- LiAl_3 at (a) 0.9 GPa and (c) 13.0 GPa, and Cell No. 2 at (d) 7.0 GPa. Red solid lines represent the results of the Rietveld refinements. The differences are shown as blue lines. Vertical sticks are positions of Bragg peaks. Raw XRD patterns of LiAl_3 at corresponding pressures are exhibited on top. (b) XRD patterns of Cell No. 1 LiAl_3 at various pressures. The black arrow at 11.0 GPa highlights the newly split peak.

PuBr_3 -type structure constructed from corner-sharing bi-capped trigonal prisms [Fig. 2(a)] [14]. In each eightfold La-I coordinated hendecahedron, I atoms occupy two inequivalent positions, and the hendecahedra form an alternating up-and-down configuration along the a - c plane within every single layer. The interlayer separation extends along the b -axis direction.

In Cell No. 1, without any pressure transmitting medium, as the pressure increases to 11 GPa, a new peak emerges

at $\sim 12.4^\circ$ and becomes more prominent at higher pressure, highlighted by the black arrow in Fig. 1(b). This suggests a possible structural transition. Actually, the Rietveld refinement at 13 GPa yields a well-refined result in the ambient *Cmc* structure [Fig. 1(c)], and the newly appeared peak could be attributed to the splitting of the (1 1 2) and (1 3 0) crystal planes. It is worth noting that nonhydrostatic conditions could also cause the splitting of the XRD peak. To rule out this factor, we used Ne as the gas pressure

TABLE I. Experimental structural parameters of *Cmc*- LiAl_3 at a representative pressure, space group (S.G.), lattice parameters, cell volume (V_0) at zero pressure, bulk modulus B_0 , and its pressure derivative B'_0 , Wyckoff positions, and the corresponding coordinates.

P (GPa)	S.G.	Lattice parameters ($\text{\AA}$)			V_0 ($\text{\AA}^3/\text{f.u.}$)	B_0 (GPa)	B'_0	Wyckoff positions			
		a	b	c					x	y	z
0.9	<i>Cmc</i>	4.39(2)	13.82(2)	9.95(2)	155.2	25.4	4.0	La (4c)	0	0.2466	0.2500
								I (4c)	0	0.9272	0.2500
								I (8f)	0	0.35572	0.0455
13.0	<i>Cmc</i>	4.05(4)	12.15(1)	9.30(2)	148.5	30.2	4.0	La (4c)	0	0.2078	0.2500
								I (4c)	0	0.9097	0.2500
								I (8f)	0	0.6443	0.0609

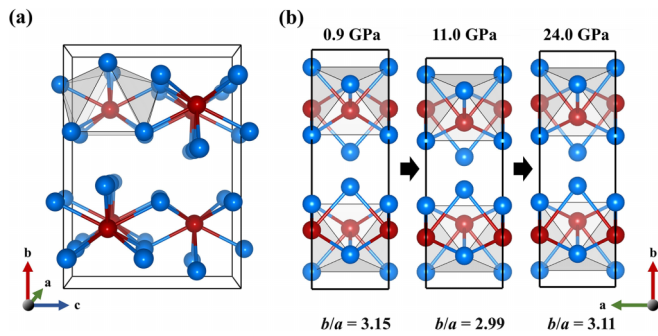


FIG. 2. (a) Perspective and (b) side views of layered $Cmc-LiAl_3$. Red and blue spheres are La and I atoms, respectively. The polyhedra demonstrate the eight-coordinated configurations. The ratios of the interlayer spacing (b axis) to the in-plane lattice constant (a axis) at representative pressures are labeled. For comparison, the a -axis lengths are visually normalized.

transmitting medium in Cell No. 2. Under (quasi)hydrostatic pressure conditions, the texture characteristics of the sample were well preserved, and the peak splitting of the (1 1 2) and (1 3 0) diffraction peaks was reproduced (Fig. S1 of the Supplemental Material [39]), confirming that this is an intrinsic pressure-induced feature [Fig. 1(d)].

To fully comprehend this structural evolution, extensive investigations on pressure-lattice parameters and pressure-volume relationships were conducted (Fig. 3). The pressure-induced evolution of lattice parameters exhibits anisotropy, which is commonly observed in layered compounds [40], as the lattice constant a decreases by 13.4%, b decreases by 14.5%, and c decreases by 8.4% from 0.9 to 24.0 GPa [Fig. 3(a)]. Moreover, below 11 GPa, the ratio of

interlayer distance to intralayer lattice constant (b/a) decreases [Fig. 2(b)], highlighting greater compressibility in the interlayer spacing. This is primarily because the interlayer interactions are governed by van der Waals forces, which are significantly weaker than the intralayer ionic bonds. Unexpectedly, above 11 GPa, the compression of the interlayer spacing b becomes noticeably weaker compared to that along the intralayer a axis, as the value of b/a abruptly switches from decreasing to increasing under nonhydrostatic and (quasi)hydrostatic conditions [Fig. 3(b)], coinciding with the pressure where the XRD peak splits. Actually, this phenomenon refers to an isostructural phase transition in which the symmetry remains unchanged but exhibits discontinuities in lattice parameters and volume (for first order) or in their first-order derivatives (for second order) at a critical pressure. This behavior is distinct from anisotropic compression, which shows a continuous lattice response over a finite pressure range. The isostructural phase transition has been extensively observed in a number of layered compounds under high pressure, including WS_2 [41], $FeSe$ [42], Ti_3AlC_2 [43], WSe_2 [44], and $PdPS$ [45]. Additionally, the relationship between Eulerian strain (f_E) and normalized pressure (F) could generally amplify subtle pressure-induced phase transitions [46]. As shown in Fig. S2 of the Supplemental Material [39], the data clearly exhibit two distinct regions, with two horizontal gray reference lines corresponding to $B'_0 = 4$. Positive and negative slopes imply $B'_0 > 4$ and $B'_0 < 4$, respectively. The values of bulk moduli are $B_0 = 25.1$ and 30.2 GPa. This analysis indicates a structural evolution in LaI_3 , which is not readily apparent in the P - V relationship. Notably, previous studies on lanthanide halides have not observed any pressure-induced isostructural phase transitions.

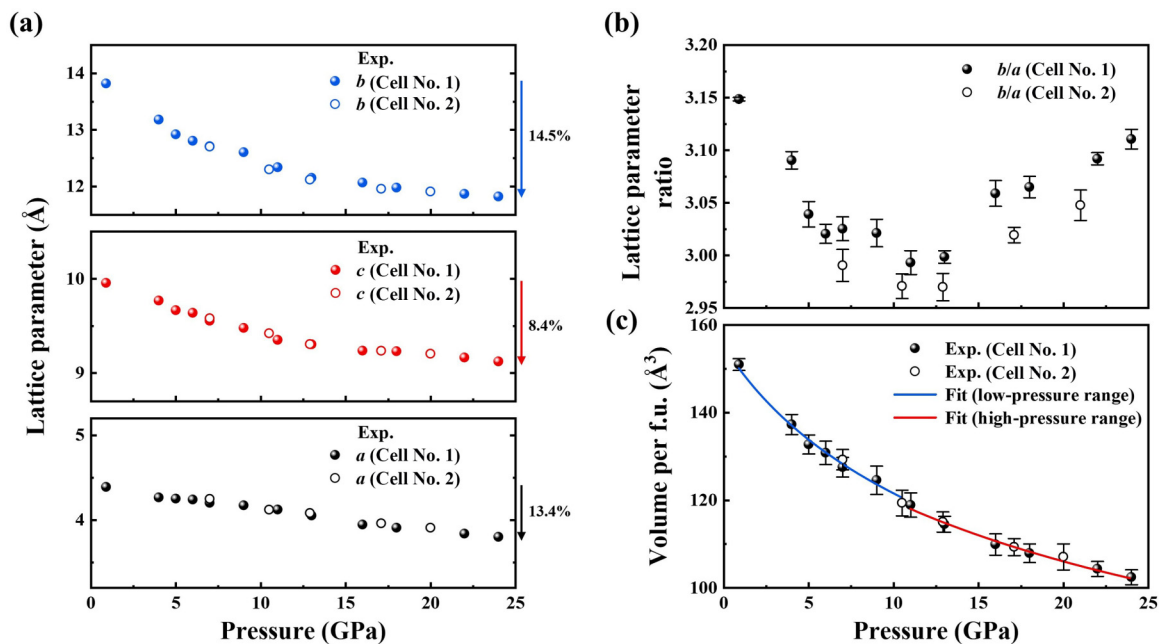


FIG. 3. (a) Evolutions of the lattice parameters in LaI_3 under high pressure. The percentage of each decrease is indicated on the right side, and the error bars are smaller than the size of the data points. (b) The ratio between the interlayer spacing (lattice parameter b) and the in-plane lattice direction (lattice parameter a) at different pressures. (c) Equations of states (EOSs) of $Cmc-LiAl_3$ fitted by experimental data.

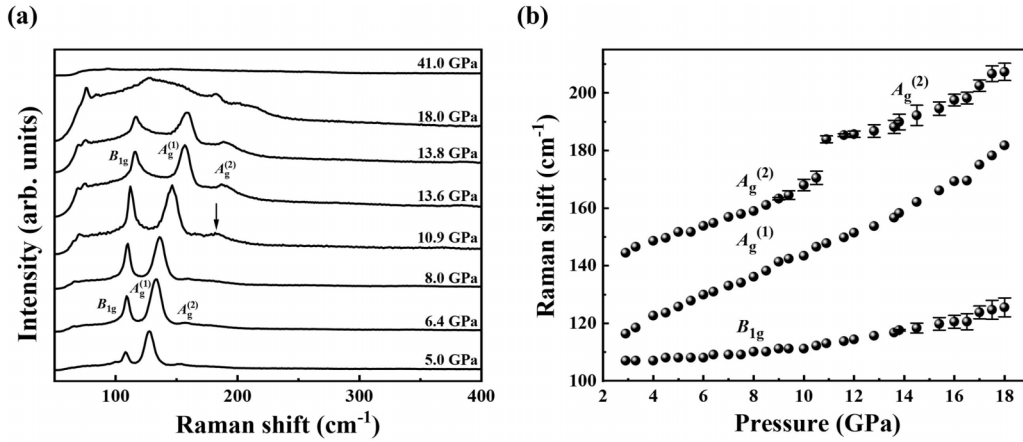


FIG. 4. (a) Representative high-pressure Raman spectra of LaI_3 upon compression at room temperature. The black arrow emphasizes the sudden increase of $A_g^{(2)}$ Raman vibrational mode at 10.9 GPa with the wave number of 183.9 cm^{-1} . (b) Pressure dependence of Raman shifts. Each Raman mode is labeled. Partial error bars are smaller than the size of the data points.

Furthermore, the volume compression behavior of LaI_3 can be described by fitting the third-order Birch-Murnaghan EOS:

$$P = \frac{3}{2}B_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4}(B_0' - 4) \times \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\}.$$

Actually, the bulk module (B_0) of LaI_3 before the isostructural phase transition ($B_0 = 25.1 \text{ GPa}$) is slightly smaller than that after the transition ($B_0 = 30.2 \text{ GPa}$), and both exhibit a continuous characteristic [Fig. 3(c)], verifying a second-order phase transition. This subtle phenomenon in the P - V relation is analogous to the isostructural phase transitions in H_2 [47], PdPS [45], BiMn_2O_5 [48], Sb_2S_3 [49], Os [50], and $\text{Na}_{1-x}\text{FeAs}$ [51]. Detailed structural information is listed in Table I. Besides, from a physical perspective, a higher bulk modulus indicates that LaI_3 adopts a more compact and stable structure under higher pressure.

B. Vibrational properties under high pressure

To comprehensively characterize the isostructural evolution in LaI_3 discussed above, we further conducted high-pressure Raman spectroscopic measurements at room temperature. Raman peaks of LaI_3 are assigned to one B_{1g} deformation mode, one $A_g^{(1)}$ hendecahedron breathing mode, and one $A_g^{(2)}$ bending mode (Fig. S3 of the Supplemental Material [39]). Upon compression, all Raman peaks exhibit a shift toward higher frequencies [Fig. 4(b)], suggesting a reduction in bond lengths. The variation in the intensity of the B_{1g} vibrational mode manifests a possible rearrangement of an electronic population [52], with the intensity peaking at 10.9 GPa. Meanwhile, at this pressure, the $A_g^{(2)}$ vibrational mode increases abruptly [highlighted by the arrow in Fig. 4(a) and Fig. S3(a) of the Supplemental Material [39]], consistent with the isostructural phase transition, which is similar to that observed in other compounds, including CeOCl [53], $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, and $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ [54]. Abrupt modifications

in electronic structure, such as changes in $\text{La } d$ orbital occupancy in this study, can lead to a redistribution of the electron cloud density around the ions, thereby altering interionic interactions. This redistribution may induce variations in local atomic distances and bond angles, which manifest as sudden shifts in optical phonon frequencies. As the pressure further increases to 41 GPa, the overall intensity of Raman signals becomes virtually undetectable, suggesting a possible process of pressure-induced metallization [55–59] [Fig. 4(a)]. The appearance of low-wave-number peaks (within 100 cm^{-1}) above 8 GPa is attributed to lattice vibrations and the increase of the low-frequency background may be attributed to electronic continuum scattering from conduction electrons.

C. Electrical properties under high pressure

The band gap of LaI_3 serves as a crucial factor in the electrical properties and scintillation. The value was previously calculated to be 3.3 eV with the HSE06 hybrid functional calculation [14], which agrees with the previous experiment [13]. Pressure provides an efficient tool for modifying the electrical properties of compounds. Therefore, in this study, we employed UV-vis absorption spectroscopy, impedance spectroscopy, and electrical transport measurements, combining DFT calculations to explore the electrical properties of LaI_3 under high pressure.

As depicted in Fig. 5(a), the band gap of LaI_3 declines linearly from 2.20 to 0.69 eV as pressure increases from 2 to 26 GPa with a negative pressure coefficient $dE_g/dP = -62.39 \text{ meV GPa}^{-1}$ by UV-vis absorption spectra. Moreover, the linear fit of the experimental data indicates a value of 0 eV at $\sim 37 \text{ GPa}$. The Tauc plot exhibits an obvious absorption edge in the UV-vis spectrum at 2.3 GPa (Fig. S4 of the Supplemental Material [39]), with the exponential n of 2 due to the indirect band gap [Fig. 5(b)] [60,61]. Moreover, the evolution of the band gap is generally accompanied by changes in optical properties, leading to observable variations in color. The blackening of a material indicates that the visible spectrum ($\sim 400\text{--}760 \text{ nm}$, corresponding to an energy range 1.6–3.1 eV) can no longer transmit through it. Thus, a

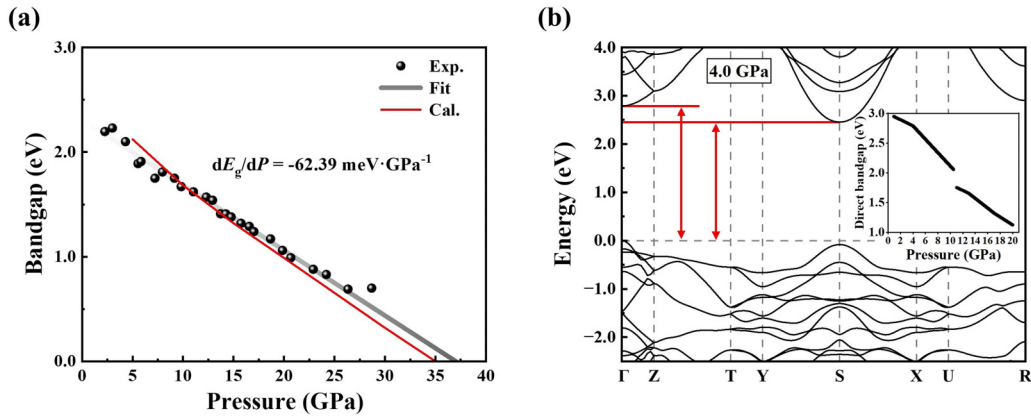


FIG. 5. (a) Band gap-pressure relationship of LaI_3 at room temperature. Black spheres represent the results of UV-vis experiments, the gray line represents the fit of experimental data, and the red line represents calculational results using the hybrid HSE06 functional. (b) In the band structure of LaI_3 at 4.0 GPa, two red vertical arrows indicate the Γ - Γ direct band gap and the Γ -S indirect band gap. The inset displays the values of the Γ - Γ direct band gap at different pressures.

semiconductor with a sufficiently small band gap may also appear black. In Fig. S5 of the Supplemental Material [39], it is evident that the color of LaI_3 undergoes a gradual transition from a transparent pale yellow to a deep red, ultimately culminating in an opaque black appearance, as pressure increases from 0.9 to 37.0 GPa.

As a reference, other lanthanide compounds containing f -state electrons, such as EuTe and SmTe , undergo isostructural phase transitions primarily driven by changes in oxidation states [62]. Such a transition appears unexpected in LaI_3 , where the f -state orbitals are unbound. To further elucidate the mechanism underlying the pressure-induced isostructural phase transition and the metallization in LaI_3 , we carried out first-principles calculations. Employing the HSE06 hybrid functional, we computed the evolution of the band structures and partial density of states under high pressure using structures obtained from XRD measurements, except for the one at 40 GPa (Figs. S6 and S7 of the Supplemental Material [39]). The valence band maximum is located at the Γ point and is predominantly composed of La_p orbitals, while the conduction band minimum occurs at the S point and is mainly dominated by La_d orbitals. Interestingly, the Γ - Γ direct band gap suddenly decreases at 11 GPa [Fig. 5(b), inset], corresponding to the isostructural phase transition. A direct band gap change at the Γ point, caused by changes in the electronic structure, also leads to an isostructural phase transition in PdPS [45]. Thus, we associate this isostructural phase transition at 11 GPa with changes in the electronic structure at the Γ point. As the pressure further increases, the calculated band gap gradually decreases to 0 eV at 35 GPa, consistent with the experimental data [Fig. 5(a)]. This closure is driven by the pressure-induced broadening of the La_d orbital states in the conduction band, leading to the insulator-to-metal transition in LaI_3 .

Furthermore, a structural evolution generally induces changes in electrical properties [63–65]. Thus, in order to determine the possible pressure-induced metallization, as well as the isostructural phase transition in LaI_3 discussed above, we conducted high-pressure impedance spectroscopy and electrical transport measurements.

Concerning the larger resistance in LaI_3 (20–35 k Ω) below 20 GPa, electrical impedance measurements serve as a suitable method in this pressure range. In this work, every impedance pattern is constructed by one obvious semicircle (Fig. S8 of the Supplemental Material [39]). Thus, under the utilization of an alternating current (AC) field, LaI_3 exhibits a typical electronic conductivity behavior [65]. This could be attributed to the similar radii of La^{3+} and I^- as well as the compact hendecahedron configurations, which restrict available ionic transport pathways. The data can be well fitted by an extensively adopted equivalent circuit comprising parallel R-CPE elements [Fig. S8(d) of the Supplemental Material [39]]. The algebraic discussion of the equivalent circuit is

$$Z = R_1 + \frac{1}{\frac{1}{R_2} + \frac{1}{Z_{Q1}}},$$

where R_1 and R_2 denote the resistance introduced by extrinsic factors and the transferring resistance of electrons through bulk LaI_3 , respectively, and Z_{Q1} represents the impedance of the constant phase element (CPE₁). In Fig. 6(a), within the pressure range 5–11 GPa, R_2 gradually decreases by 28.3%, exhibiting a trend observed in various electronic conductive compounds under high pressure [66,67]. Unexpectedly, the resistance increases at 11 GPa, corresponding to the pressure where the isostructural phase transition occurs. This increase in resistance suggests an electronic structural transition, rendering conductive electrons more localized under the AC field. As the pressure further increases to 19 GPa, a significant decrease in resistance indicates a typical pressure-induced metallization. On the other hand, by measuring the impedance spectra, we can analyze the dielectric constant of LaI_3 at different pressures (Fig. S9 of the Supplemental Material [39]). Its polarizability reaches the peak at 11 GPa, which also serves as evidence of the isostructural phase transition.

However, the impedance spectroscopy measurement method employed in this study is primarily suitable for high resistivity due to the weak electrical signal above 20 GPa [Fig. S8(c) of the Supplemental Material [39]]. Hence, alternative methods should be employed to measure the electrical

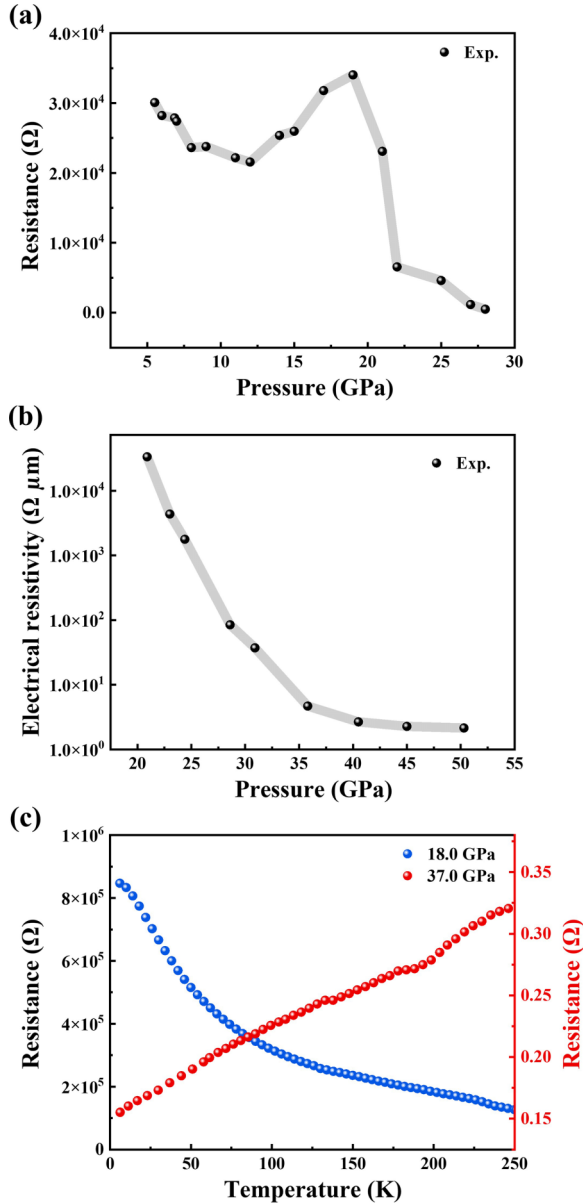


FIG. 6. (a) Resistance-pressure relationship from impedance spectrum measurements. (b) Electrical resistivity-pressure relation of LaI_3 at room temperature using the four-probe method. (c) Resistance-temperature relations of LaI_3 at 18.0 and 37.0 GPa.

properties of LaI_3 under low-resistance conditions. We conducted electrical transport measurements using the four-probe method (Fig. S5 of the Supplemental Material [39]) to determine the possible metallization of LaI_3 . As shown in Fig. 6(b), at room temperature, the pressure-induced narrowing of the

band gap results in a continuous decrease in electrical resistivity. At ~ 35 GPa, the resistance converges toward a minimum value, signifying a metallic state in LaI_3 . Furthermore, as described by the Debye model [68], the responses of resistance to temperature are distinct between metallic and nonmetallic states. In Fig. 6(c), the resistance data at 18 GPa exhibit typical semiconductor behavior. As the pressure increases to 37 GPa, the resistance data demonstrate a typical metallic behavior, consistent with the UV-vis experiments and calculations.

IV. CONCLUSIONS

In this work, we employed pressure to manipulate the structure of LaI_3 as well as its electrical properties. The results from the impedance spectra, UV-vis spectra, and electrical transport measurements, combined with DFT calculations, show that the band gap of LaI_3 linearly decreases under high pressure ($dE_g/dP = -62.39 \text{ meV GPa}^{-1}$), transitioning into a metallic state at 37 GPa. The metallization of LaI_3 is primarily attributed to the band gap closure rather than the structural phase transition. Unexpectedly, the results from the impedance spectra, Raman spectra, and XRD experiments indicate that Cmcm-LaI_3 undergoes a second-order isostructural phase transition at 11 GPa, driven by an electronic structural transition in which the direct band gap at the Γ point suddenly decreases. This research introduces a pressure-driven approach to regulate the band gap and crystal structure of LaI_3 , establishing a relationship between its band gap and pressure and highlighting the potential for scintillation applications in lanthanide halides.

ACKNOWLEDGMENTS

This research was supported by the Natural Science Foundation of China (Grants No. 12474010, No. 12474011, and No. 12374007). The XRD measurements were performed at the beamline BL4W2 of Beijing Synchrotron Radiation Facility and beamline BL15U1 (31124.02.SSRF.BL15U1) of Shanghai Synchrotron Radiation Facility. This work was also supported by the User Experiment Assist System of Shanghai Synchrotron Radiation Facility (31124.02.SSRF.LAB).

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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