Hot carrier relaxation in Cs$_2$Ti$_y$Br$_{6-y}$ ($y = 0$, 2 and 6) by a time-domain $ab$ initio study\textsuperscript{†}

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Cs$_2$Ti$_y$Br$_{6-y}$ is a potential light absorption material for all-inorganic lead free perovskite solar cells due to its suitable and tunable bandgap, high optical absorption coefficient and high environmental stability. However, solar cells fabricated based on Cs$_2$Ti$_y$Br$_{6-y}$ do not perform well, and the reasons for their low efficiency are still unclear. Herein, hot carrier relaxation processes in Cs$_2$Ti$_y$Br$_{6-y}$ ($y = 0$, 2 and 6) were investigated by a time-domain density functional theory combined with the non-adiabatic molecular dynamics method. It was found that the relaxation time of the hot carriers in Cs$_2$Ti$_y$Br$_{6-y}$ ranges from 2–3 ps, which indicates that the hot carriers within 10 nm from the Cs$_2$Ti$_y$Br$_{6-y}$/TiO$_2$ interface can be effectively extracted before their energy is lost completely. The carrier-phonon non-adiabatic coupling (NAC) analyses demonstrate that the longer hot electron relaxation time in Cs$_2$Ti$_y$Br$_4$ compared with that in Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$ originates from its weaker NAC strength. Furthermore, the electron–phonon interaction analyses indicate that the relaxation of hot electrons mainly comes from the coupling between the electrons distributed on the Ti–X bonds and the Ti–X vibrations, and that of hot holes can be attributed to the coupling between the electrons distributed on the X atoms and the distortions of [TiI$_y$Br$_{6-y}$].\textsuperscript{15} The simulation results indicate that Cs$_2$Ti$_2$Br$_4$ should be better than Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$ to act as a light absorption layer based on the hot carrier energy loss, and the hot electron relaxation time in Cs$_2$Ti$_y$Br$_{6-y}$ can be adjusted by tuning the proportion of the I element.

1. Introduction

Lead-based perovskite materials with the ABX$_3$ configuration have been extensively studied due to their excellent properties, such as high carrier diffusion length, high optical absorption and low exciton binding energy.\textsuperscript{16} Also, the conversion efficiency of lead-based perovskites solar cells have reached 25.2\% over the past decade.\textsuperscript{9,10} However, lead is a toxic heavy metal element, and this deficiency restricts the extensive usage of lead-based perovskite solar cells.\textsuperscript{11} Moreover, the presence of organic ions reduces the stability of 3D perovskite materials.\textsuperscript{12} Therefore, the development of new non-toxic, environmentally stable all inorganic perovskite materials is attracting increasing attention.\textsuperscript{13,14} Among the various inorganic materials, titanium-based all inorganic perovskite materials possess suitable and tunable band gaps, high optical absorption coefficients and superior environmental stability.\textsuperscript{15} Thus, they are promising candidates for the preparation of lead-free all-inorganic perovskite solar cells.\textsuperscript{16}

A series of Cs$_2$Ti$_y$Br$_{6-y}$ materials was successfully synthesized by Ju et al., which showed band gaps in the range of 1.1–1.8 eV, and highly stable films under heat, moisture and light.\textsuperscript{15} However, the performance of the fabricated perovskite solar cell using Cs$_2$TiBr$_6$ as the optical layer was far from expectation, where it possessed only 3.22\% power conversion efficiency. Furthermore, the open voltage in Cs$_2$TiBr$_6$-based solar cell is only 0.9 V, while the band gap of Cs$_2$TiBr$_6$ is 1.7 eV, and its short circuit current density and filling factor are relatively low, reaching only 5.69 mA cm$^{-2}$ and 5.64\%, respectively.\textsuperscript{17} To date, there are few theoretical studies on the reasons for the unsatisfactory performance of titanium-based all-inorganic perovskite solar cells. Through non-adiabatic molecular dynamics (NAMD) calculations, Qiao et al. ascribed the low circuit current in Cs$_2$TiBr$_6$-based solar cells to the much shorter carrier recombination time in Cs$_2$TiBr$_6$ than that in hybrid lead-based perovskite materials.\textsuperscript{18} Thus far, there is still no experimental or theoretical analysis from the aspect of hot carrier relaxation process to determine the reasons for the unsatisfactory performance of Cs$_2$Ti$_y$Br$_{6-y}$ ($y = 0$, 2 and 6)-based solar cells.

In this work, the hot carrier relaxation in Cs$_2$Ti$_y$Br$_{6-y}$ was investigated by time-domain density functional theory (DFT) combined with the NAMD method.\textsuperscript{19–23} The relaxation time of the hot carriers in Cs$_2$Ti$_y$Br$_{6-y}$ ($y = 0$, 2 and 6) were studied based on the carrier-phonon non-adiabatic couplings (NAC) analyses, and the effects of specific vibration modes and projected density of states (PDOS) on the

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NAC strength were discussed. Accordingly, results provide an understanding for hot carrier energy loss in the Cs₂TiI₆₋ₓBrₓ system and suggest a rational strategy to improve the performance of Cs₂TiI₆₋ₓBrₓ-based solar cells.

2. Computational details

The models of Cs₂TiBr₆, Cs₂TiI₆, and Cs₂TiI₂Br₄ are given in Fig. 1. Each of them contains 36 atoms, which was proven to be large enough for investigating the relaxation of hot carriers in perovskite materials.²⁴,²⁵ The lattice and atomic positions of Cs₂TiBr₆, Cs₂TiI₆Br₄ and Cs₂TiI₆ were optimized based on DFT methods, as implemented in the Vienna Ab initio Simulation Package (VASP).²⁶ The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used to represent the exchange-correlation functional. Ernzerhof (PBE) was used to represent the exchange-correlation effects, the DFT-U method was employed with U = 3 eV.²⁸ Grimme’s DFT-D3 correction implemented in VASP was used to account for van der Waals interactions.²⁹ A 4 × 4 × 4 k-point grid was adopted for geometric optimization until the residual forces on each atom were below 0.01 eV Å⁻¹, and a denser 8 × 8 × 8 k-point grid was employed for electronic structure calculation with a plane-wave energy cutoff of 520 eV.²⁷,²⁸ Spin–orbit coupling (SOC) was not considered in all of our calculations since it is proven to cause negligible impact on the crystal structure and band of titanium-based perovskite.¹⁸

Then, molecular dynamics (MD) calculations of the optimized structures were carried out using VASP. All the systems were heated to 300 K through repeated velocity rescaling in 3 ps canonical-ensemble (NVT) MD simulations. After the NVT-MD simulations, 5 ps adiabatic MD simulations were performed.¹⁵,²¹ Because each type of material possesses a direct bandgap and its band edge is located in the Γ-point, all the MD simulations were performed on the Γ-point with a 1 fs time step.¹⁵

Finally, NAMD simulations were performed based on the nuclear trajectory generated by the adiabatic MD simulations using the PYthon eXtension for Ab Initio Dynamics (PYXAID) code.²⁶,²⁷ To achieve statistical reliability, the NAMD results were averaged over 100 random geometries and 1000 stochastic realizations. More information about NAMD can be found elsewhere.²¹,²⁶–²⁸ The optimized unit cells with a fixed size were used in the MD simulations and the adiabatic MD simulations.

3. Results and discussions

3.1 Structural relaxation of Cs₂TiI₆₋ₓBrₓ (y = 0, 2 and 6)

Firstly, the optimized unit cells of Cs₂TiBr₆, Cs₂TiI₆Br₄, and Cs₂TiI₆ at 0 K are depicted in Fig. 1a, c, and e, respectively. The optimized lattice parameter for Cs₂TiBr₆ is a = 11.08 Å, which is close to the experimental value of a = 10.92 Å, and the lattice parameters of Cs₂TiI₆Br₄ are a = 11.07 Å and b = 11.77 Å, which are close to the experimental value of a = 11.25 Å. The lattice parameter of the optimized Cs₂TiI₆ is a = 11.66 Å, which is close to the experimental value of a = 11.67 Å.¹⁵ Then, we considered the change in crystal structure in the dynamic process. The crystal structures of Cs₂TiBr₆, Cs₂TiI₆Br₄, and Cs₂TiI₆ after 3 ps MD calculations are displayed in Fig. 1b, d, and f, respectively. The average bond length of Ti–Br in Cs₂TiBr₆ is 2.54 Å at 0 K and 2.53 Å at 300 K. The average bond length of Ti–I in Cs₂TiI₆ is 2.76 Å at 0 K and 2.76 Å at 300 K, and that of Ti–Br and Ti–I in Cs₂TiI₆Br₄ is 2.52 Å and 2.81 Å at 0 K, 2.50 Å and 2.83 Å at 300 K, respectively. Meanwhile, the crystal structures obviously changed with the torsion of the anion and displacement of the cation.

To reveal the structural change in the dynamic process further, the canonically averaged standard deviation of the position of each atom was calculated using the equation

\[ \sigma_i = \sqrt{\langle (\tilde{r}_i - \langle \tilde{r}_i \rangle)^2 \rangle}, \]

where \( \tilde{r}_i \) represents the location of atom i at time t along the 5 ps MD trajectories.¹⁷

The calculated values are presented in Table 1. By comparing the position deviation values of the three systems, we can find that the presence of I atoms in Cs₂TiI₆₋ₓBrₓ has a negligible influence on the vibration of the Ti and Cs atoms, where the values of \( \sigma_i \) for the Ti and Cs atoms decrease from 0.393 to 0.296 and 0.246 to 0.238, respectively. This can be ascribed to the fact that the radius of the I⁻ ion, 2.2 Å, is obviously larger than that of the Br⁻ ion, 1.94 Å,²⁵ which will hinder the motivation of the Ti and Cs atoms. More importantly, the vibration of the halogen elements, i.e., Br and I, exhibits the weakest intensity in

| Table 1 | Canonical average standard deviation of the atomic positions |
|---------|----------------------------------------------------------|
|         | Br | I   | Ti  | Cs  |
| Cs₂TiBr₆ | 0.267 | —   | 0.393 | 0.246 |
| Cs₂TiI₆Br₄ | 0.281 | 0.201 | 0.341 | 0.247 |
| Cs₂TiI₆ | —   | 0.365 | 0.296 | 0.238 |
Cs₂TiI₂Br₄. Since the intensity of the atomic vibration has a direct relation with the nuclear velocity, it will further affect the relaxation velocity of hot carriers through the carrier-phonon coupling.¹²,²²,³⁹ Thus, the details of the vibration-related carrier-phonon coupling are discussed in the next section.

3.2 Hot carrier relaxations in Cs₂TiₙBr₆₋ₙ (n = 0, 2 and 6)

Hot carrier relaxation is an important energy loss channel in perovskite solar cells.⁴⁰ It has demonstrated that extracting the hot carriers before they totally relax will be the core method for new generation high-efficiency solar cells.⁴¹,⁴² The hot carrier relaxation is an intraband charge dynamic process, which is inevitably affected by the density of states (DOS) of the valence band (VB) and the conduction band (CB).²¹,²⁵,⁴³ Fig. 2 shows the PDOS of each system. It can be observed that the halogen atoms mainly contribute to the VB of Cs₂TiₙBr₆₋ₙ, while the Ti and halogen atoms contribute to the CB. The conduction band minimum (CBM) of Cs₂TiₙBr₆₋ₙ arises from the Ti-3d orbitals. The band gaps for Cs₂TiBr₆, Cs₂TiI₂Br₄, and Cs₂TiI₆ are 1.8 eV, 1.4 eV, and 1.1 eV, respectively, which are consistent with the measured values.¹⁵ Specifically, the VB localize on the halogen atoms, and the CB distribute on the Ti atoms and the Ti-X bonds, while, the Cs atoms have no contribution on the band edges. The electrons distribution around the X and Ti atoms and the corresponding Ti-X vibrations should play a key role in the hot carrier relaxation in Cs₂TiₙBr₆₋ₙ.

During the hot carrier relaxation process, the energy of the hot electrons and hot holes is gradually lost interacting with phonons until they reach the CBM and VBM.⁴⁴ Thus, we performed NAMD simulations to study the hot carrier relaxation process in Cs₂TiₙBr₆₋ₙ. In all the NAMD simulations, the initial excitation energy was set to be 0.5 eV, which is large enough to contain the main orbitals close to the band edge, according to the energy distribution of the PDOS in Fig. 2. The population-weighted energy decay processes of the hot electrons and hot holes from the NAMD simulations are shown in Fig. 3. It can be seen that the hot electrons undergo slower relaxation than the hot holes obviously for both Cs₂TiBr₆ and Cs₂TiI₂Br₄. The hot electrons will relax to the CBM within 2–4 ps, while the hot holes only need ~1.5 ps to decay to the VBM. This can be attributed to the fact that hot holes are strongly bound around the halogen nuclei (Fig. 2), thus enabling fast energy transfer to the vibrating halogen atoms. In contrast, the hot electrons, which are weakly bonded by the nucleus since they are excited, have a slower cooling rate than hot electrons. In addition, the relaxation time of hot electrons in Cs₂TiₙBr₆ is longer than that in Cs₂TiBr₆ and Cs₂TiI₆. The electrons are still hot in Cs₂TiI₂Br₄ after 3.5 ps, but they will be completely relaxed within 2 ps in Cs₂TiBr₆ and Cs₂TiI₆. The longer hot electron relaxation time in Cs₂TiI₂Br₄ can be partially attributed to the weak vibration of its I atoms, as mentioned above.

To describe the relaxation process of hot carriers quantitatively, a single exponential function was used to fit the energy decay process of the hot carriers as follows.²²

![Fig. 2 PDOS diagrams of Cs₂TiₙBr₆₋ₙ. (a) PDOS diagram of Cs₂TiBr₆, (b) PDOS diagram of Cs₂Ti₂Br₄ and (c) PDOS diagram of Cs₂TiI₆.](image)

![Fig. 3 Hot carrier relaxation processes in Cs₂TiₙBr₆₋ₙ. Relaxation of hot carriers in the (a) CB orbitals of Cs₂TiBr₆, (b) VB orbitals of Cs₂TiBr₆, (c) CB orbitals of Cs₂Ti₂Br₄, (d) VB orbitals of Cs₂Ti₂Br₄, (e) CB orbitals of Cs₂TiI₆, and (f) VB orbitals of Cs₂TiI₆.](image)
The fitted relaxation time, \( \tau_i \), of hot electrons and hot holes is presented in Table 2.

Table 2 Fitted relaxation time, \( \tau_i \), of hot electrons and hot holes

| Orbital     | \( \tau_i = 0 \) (ps) | \( \tau_i = 2 \) (ps) | \( \tau_i = 6 \) (ps) |
|------------|------------------------|------------------------|------------------------|
| CBM+3      | 0.89                   | 1.42                   | 0.87                   |
| CBM+4      | 0.90                   | 1.21                   | 0.97                   |
| CBM+5      | 0.83                   | 1.68                   | 1.38                   |
| CBM+6      | 0.93                   | 1.57                   | 0.83                   |
| CBM+7      | 1.07                   | 1.73                   | 1.34                   |
| CBM+8      | 1.09                   | 2.49                   | 1.46                   |
| CBM+9      | 1.14                   | 2.15                   | 1.40                   |
| CBM+10     | 1.20                   | 2.12                   | —                      |
| CBM+11     | 1.34                   | —                      | —                      |
| VBM+3      | 0.66                   | 0.67                   | 0.67                   |
| VBM+4      | 0.72                   | 0.64                   | 1.06                   |
| VBM+5      | 0.58                   | 0.63                   | 0.86                   |
| VBM+6      | 0.96                   | 0.67                   | 0.90                   |
| VBM+7      | 0.83                   | 0.70                   | 1.05                   |
| VBM+8      | 0.94                   | 0.65                   | 1.16                   |
| VBM+9      | 0.94                   | 0.70                   | 1.21                   |

where \( \tau_i \) denotes the time required for the decay of the hot carrier energy to \( 1/e \) of the initial energy. The fitted results are listed in Table 2.

It can be observed that the delay time of a higher energy level is generally longer. This is because the carriers in the higher energy state have to pass through several energy levels before they relax to the band edge. The carrier relaxation time in Cs\(_2\)TiBr\(_4\), Cs\(_2\)Ti\(_2\)Br\(_4\), and Cs\(_2\)TiI\(_6\) is \( \sim 1.4 \) ps, \( \sim 2.2 \) ps, and \( \sim 1.4 \) ps for electrons, and \( \sim 0.9 \) ps, \( \sim 0.7 \) ps, and \( \sim 1.3 \) ps for holes, respectively. These values indicate that the hot carrier relaxation time can be manipulated by adjusting the proportion of I element in Cs\(_2\)TiI\(_{1-x}\)Br\(_x\). Combined with the experimental data, the diffusion coefficients of electrons and holes in Cs\(_2\)TiBr\(_4\) are \( d = 0.61 \) cm\(^2\)/s and \( 0.44 \) cm\(^2\)/s,\(^{17}\), and the characteristic diffusion distance of hot holes and hot electrons in Cs\(_2\)TiBr\(_4\) can be roughly evaluated by \( l = \sqrt{d\tau} \). The obtained values are \( \sim 9 \) nm and \( \sim 6 \) nm, respectively, which indicate that the hot electrons within 10 nm from the perovskite/ETL interface can be effectively extracted, as illustrated in Fig. 4. Considering the longer carrier relaxation time in Cs\(_2\)Ti\(_2\)Br\(_4\) than that in Cs\(_2\)TiBr\(_6\) and Cs\(_2\)TiI\(_6\), more hot carriers can be extracted by adjusting the proportion of I in Cs\(_2\)TiI\(_{1-x}\)Br\(_x\), which provides an effective way to manipulate hot carriers for different applications.

To understand the relaxation process better, the averaged carrier-phonon NAC in Cs\(_2\)TiI\(_{1-x}\)Br\(_x\) was calculated.\(^{22,24,45}\) The formula for the average carrier-phonon NAC is

\[
\langle \text{Im} (H_{\text{vb},ij}) \rangle = \frac{h}{T} \sum_{i=0}^{T-1} |d_{ij}(t)|, \tag{3}
\]

where \( d_{ij}(t) \) is the coupling vector between electronic states \( i \) and \( j \), which are defined as:

\[
d_{ij}(t) \equiv \langle \Phi_i(\vec{r}, t) | \nabla R | \Phi_j(\vec{r}, t) \rangle . \tag{4}
\]

The results of NAC are shown in Fig. 5. Clearly, the NAC value in the VB is much stronger than that in the CB. This is consistent with the above description that hot holes have larger relaxation rates than hot electrons in Cs\(_2\)TiI\(_{1-x}\)Br\(_x\). Then, it can be observed that the sub-diagonal terms show the greatest NAC values, while the NAC values for the other terms are very small. This indicates that strong non-adiabatic couplings mainly occur between adjacent orbits with a similar energy; therefore, the hot carrier relaxation should be a step-level relaxation process from the high-energy orbitals to the low-energy ones. In addition, the NAC values of Cs\(_2\)TiBr\(_4\) and Cs\(_2\)TiI\(_6\) on the CB state region (the upper-right corner) are larger compared with that of Cs\(_2\)TiI\(_2\)Br\(_4\) based on the results shown in Table 1, i.e., the weak vibration of the halide atoms in Cs\(_2\)TiI\(_2\)Br\(_4\). In contrast, the NAC values on the VB state region (the bottom-left corner) decrease monotonically with \( Y \) varying from 6 to 0 in Cs\(_2\)TiI\(_{1-x}\)Br\(_x\), which looks paradoxical with the decrease-then-increase vibration intensity of the halide atoms, as shown in Table 1. Thus, to investigate the contribution of atomic vibration (phonon) on the hot carrier relaxation further, we calculated the influence spectrum based on the optical response formalism with different energy levels.\(^{46-48}\)

The influence spectrum is the Fourier transformation (FT) of the energy gap fluctuation between the related transition and it represents the vibration modes that relate to the carrier.
relaxation process. The obtained influence spectrum for the relaxation processes of hot carriers for Cs$_2$TiI$_{12-y}$Br$_6$ are presented in Fig. 6. The Raman spectroscopy measurements demonstrate that the peaks with a wavenumber in the range of 50–100 cm$^{-1}$ correspond to the anion distortion of [TiBr$_6$]$_{2-}$, [Ti$_4$Br$_{12}$]$_{2-}$, and [Ti$_8$]$_3^{-}$; that in the range of 120–260 cm$^{-1}$ originate from the Ti-X bond vibrations$^{39-53}$ and that greater than 260 cm$^{-1}$ are associated with the high-order vibration modes$^{34,54}$ Considering that the instantaneous configurations rather than the steady ones of Cs$_2$TiI$_{12-y}$Br$_6$ were used in calculating the influence spectrum, the results we obtained may deviate slightly from the experimental measurements. Therefore, the vibrations in the influence spectrum are assigned as shown in Fig. 6.

Besides, from the influence spectrum for the adjacent-orbital relaxations of hot electrons in Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$ (Fig. 6a and e, respectively) it can be found that the hot electron relaxations in Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$ mainly depend on the Ti-X vibrations. These Ti-X vibrations are slightly affected by other vibration modes, and therefore, they own generally respectively.

The obtained influence spectrum for the carrier-phonon between various Cs$_2$TiI$_{12-y}$Br$_6$ were investigated by DFT theory combined with the NAMD method. Firstly, the structural relaxations of Cs$_2$TiI$_{12-y}$Br$_6$ at 300 K were studied. It was found that the crystals deform slightly at 300 K. Then, the relaxation processes of the hot carriers in various Cs$_2$TiI$_{12-y}$Br$_6$ were analysed. The relaxation time of hot electrons was found to be longer than that of hot holes. The hot electrons will take 2–4 ps to reach CBM, while the hot holes can completely relax to the VBM within 2 ps. The hot electron relaxation time in Cs$_2$TiI$_{12-y}$Br$_6$ is longer than that in Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$, ~2.2 ps, is longer than that in Cs$_2$TiI$_{12-y}$Br$_6$, ~1.4 ps, due to its weakest hot electron-related Ti-X vibrations. However, the hot hole relaxation time generally increases monotonically with an increase in the proportion of I element. The relaxation time of 2.2 ps indicates that the hot electrons within 10 nm from the perovskite/ETL interface can be effectively extracted. The NAC analyses confirm the variation trend of the hot carrier relaxation time in Cs$_2$TiI$_{12-y}$Br$_6$ with the proportion of I element. Finally, the results of the influence spectrum demonstrate that the hot electron relaxation processes are mainly correlated with the Ti-X vibrations, while the hot holes relaxation processes depend on the anion distortions strongly too. Thus, the hot carrier relaxation time in Cs$_2$TiI$_{12-y}$Br$_6$ can be adjusted by changing the proportion of I element.

4. Conclusions

In summary, the hot carrier relaxation processes in Cs$_2$Ti$_{12-y}$Br$_6$ were investigated by DFT theory combined with the NAMD method. Firstly, the structural relaxations of Cs$_2$Ti$_{12-y}$Br$_6$ at 300 K were studied. It was found that the crystals deform slightly at 300 K. Then, the relaxation processes of the hot carriers in various Cs$_2$Ti$_{12-y}$Br$_6$ were analysed. The relaxation time of hot electrons was found to be longer than that of hot holes. The hot electrons will take 2–4 ps to reach CBM, while the hot holes can completely relax to the VBM within 2 ps. The hot electron relaxation time in Cs$_2$Ti$_{12-y}$Br$_6$ is longer than that in Cs$_2$TiBr$_6$ and Cs$_2$TiI$_6$, ~2.2 ps, is longer than that in Cs$_2$Ti$_{12-y}$Br$_6$, ~1.4 ps, due to its weakest hot electron-related Ti-X vibrations. However, the hot hole relaxation time generally increases monotonically with an increase in the proportion of I element. The relaxation time of 2.2 ps indicates that the hot electrons within 10 nm from the perovskite/ETL interface can be effectively extracted. The NAC analyses confirm the variation trend of the hot carrier relaxation time in Cs$_2$Ti$_{12-y}$Br$_6$ with the proportion of I element. Finally, the results of the influence spectrum demonstrate that the hot electron relaxation processes are mainly correlated with the Ti-X vibrations, while the hot holes relaxation processes depend on the anion distortions strongly too. Thus, the hot carrier relaxation time in Cs$_2$Ti$_{12-y}$Br$_6$ can be adjusted by changing the proportion of I element.

Conflicts of interest

There are no conflicts to declare.
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