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Lead-free $Cs_3Bi_2Br_9$ Perovskite as Photocatalyst for Ring-Opening Reactions of Epoxides

Yitao Dai,[a] and Harun Tüysüz*[a]

Abstract: Herein, we present an innovative approach using stable, lead-free halide perovskite for solar-driven organic synthesis. The ring opening reaction of epoxides has been chosen as model systems for synthesis of value-added β-alkoxy alcohols, which require energy intensive process conditions and corrosive strong acids for conventional synthesis. The developed concept includes the *in-situ* preparation of $Cs_3Bi_2Br_9$ and its simultaneous application as photocatalyst for epoxides alcoholysis under visible light irradiation in air at 293 K, with exceptional high activity and selectivity ≥ 86 % for *β*-alkoxy alcohols and thia-compounds. The $Cs_3Bi_2Br_9$ photocatalyst exhibits good stability and recyclability. In contrast, the lead-based perovskite shows a conversion rate of only 1%. The origin of the unexpected catalytic behavior is attributed to the combination of the photocatalytic process and the presence of proper Lewis acidic centers on the surface of the bismuth halide perovskite photocatalyst.

All-inorganic halide perovskites with a general formula of ABX_3 (A = Rb, Cs; B = Ge, Pb, Sn; and X = Cl, Br, I) have attracted immense research interest due to their unique photovoltaic and optoelectronic properties.[1] This class of materials includes other derivative perovskites such as $Cs_3Bi_2X_9$[2], $Cs_3Fe_2Br_9$[3] and the double perovskite Cs_2AgBiX_6[4]. Halide perovskites have been explored for applications in various fields such as solar cells,[5] lasers[6] and phototransistors[7] and have also started to gain increasing attention in the field of heterogeneous catalysis. After the first report in 2016 of the photocatalytic production of hydrogen from HI using methylammonium lead iodide perovskite[8], several important reactions have been successfully catalyzed by halide perovskites under visible light irradiation.[9] For example, $CsPbBr_3$ was reported to efficiently reduce CO_2 to CO[9b], selective oxidation of benzyl alcohols to aldehydes can be realized by formamidinium lead bromide or $CsPbBr_3$ in the presence of TiO_2;[9c, 9d] meanwhile, it was also the subject of several recent studies investigating its dynamic charge transfer processes.[10] $CsPbI_3$ quantum dots with a narrow bandgap (1.8 eV) have been used to promote the photocatalytic polymerization of 2,2′,5′,2″-ter-3,4-ethylenedioxythiophene.[9a] Very recently, $APbBr_3$ (A = Cs or methylammonium) have been employed for the photocatalytic α-alkylation of aldehydes with the help of cocatalysts and base additives, which presented the high turnover number up to 52,000 under visible light irradiation.[11] Composite photocatalyst $NiO_x/FAPbBr_3/TiO_2$ could activate the C-H bonds of alkanes.[9e] Despite these promising systems, Pb-based perovskites are unattractive for toxicity reasons.[12] Sn-based perovskites are possible alternatives, but are unfortunately unstable in air.[13] In comparison, Bi-based all-inorganic halide perovskites can be promising candidates for photocatalysts, as they have low-toxicity and are air-stable.[2a, 2c, 4d, 14] To the best of our knowledge, the photocatalytic application of Bi-based perovskites in organic synthesis is still unknown.

The nucleophilic addition of alcohols to epoxides leads to the production of *β*-alkoxy alcohols, which can be used for the synthesis of anti-tumoral or immunosuppressive drugs.[15] Up to now, most effective heterogeneous systems reported to successfully catalyze epoxide alcoholysis reactions use corrosive strong acids (*e.g.*, triflic acid/silica[16]) or solid acids (*e.g.*, sulfated Zr-$HTiNbO_5$[17]), which can result in corrosion of equipment or acid leaching problems. Strong acid-free catalysts (*e.g.*, Fe(III) complex/SBA-15[18] and metal-organic frameworks such as UiO-66[19] and Zr-MOF[20]) require harsh reaction conditions (*e.g.*, high temperatures and long reaction time) to obtain good conversions, which can reduce the catalyst lifetime and present challenges for recyclability.[16] On the other hand, photocatalyst-enabled organic synthesis is considered a promising approach, as it can be carried out through the use of green and sustainable solar energy under mild conditions (*e.g.*, room temperature and ambient pressure).[21] For ring-opening reactions of epoxides, to our knowledge, no case has been reported. Although carbon quantum dots decorated with $-SO_3H$ groups (*via* a H_2SO_4 reflux) were shown to catalyze the reaction when irradiated with visible light[22], these materials displayed almost the same activity in dark and light irradiation conditions and can be considered reservoirs of strong acid, similar to the other reported sulfated catalytic systems.[17, 23] Halide perovskites can be prepared using anti-solvent precipitation method where the perovskite precursor salts are dissolved in dimethyl sulfoxide (DMSO) and then precipitated in a low-polarity solvent (*e.g.* alcohols)[2a, 2c]. Herein, we combine this perovskite synthesis approach with its application as a photocatalyst for epoxide alcoholysis in an integrated step as shown in Scheme S1. First, the *in-situ* synthesis of $Cs_3Bi_2Br_9$ perovskite is achieved by adding the precursors (CsBr and $BiBr_3$ dissolved in DMSO) directly into the target reaction solution containing an epoxide reactant and alcohol, the latter of which simultaneously acts as solvent, alcoholysis nucleophile, and anti-solvent to cause the perovskite particle formation (Scheme S1a). This one-pot approach with the integration of the photocatalyst synthesis and reaction evaluation provides several advantages, such as cost reduction, low environmental pollution, and facile operation conditions. Without any purification, separation, or post-treatment, the generated yellow suspension containing the $Cs_3Bi_2Br_9$ (Scheme S1b) is then directly irradiated by visible light in air at room temperature (293 K) to initiate the ring-opening reactions (Scheme S1c). This photocatalytic system displays high activity (1333 $\mu mol\ h^{-1}\ g_{cat}^{-1}$) and selectivity (≥ 86%) to produce 2-isopropoxy-2-phenylethanol from styrene oxide and isopropanol.

After the *in-situ* synthesis process, the obtained $Cs_3Bi_2Br_9$ was extracted for the following material characterizations. According to the powder X-ray diffraction (PXRD) pattern (Figure 1a), our $Cs_3Bi_2Br_9$ photocatalysts synthesized using the anti-solvent method[2a, 2c] matched very well with the references (PDF#70-0493 card), presenting high crystallinity and the trigonal *P*3*m*1 symmetry.[24] Transmission electron microscope (TEM) and scanning electron microscope (SEM) analyses revealed that the materials consisted of aggregated particles with a broad size range from 50 to 500 nm (Figure 1b and Figure S1). High resolution TEM (HRTEM) analysis (Figure 1c) revealed lattice fringes with interplanar spacing distances of 0.40 and 0.28 nm, which match quite well with the (102) and (202) lattice planes of crystalline $Cs_3Bi_2Br_9$.[24-25] Energy-dispersive X-ray spectroscopy (EDS) confirmed the chemical composition of the as-prepared sample had stoichiometric ratio Cs / Bi / Br = 3: 2: 9 (Figure S2 and Table S2) with homogeneous element distribution of Cs, Bi and Br (Figure 1d-g). The nitrogen sorption analysis confirmed that the as-prepared sample had a low surface area of 7 m^2/g due to the large particle sizes (Figure S4). The $Cs_3Bi_2Br_9$ sample had a direct bandgap of 2.7 eV for suitable visible light absorption (Figure 1h and Figure S8).

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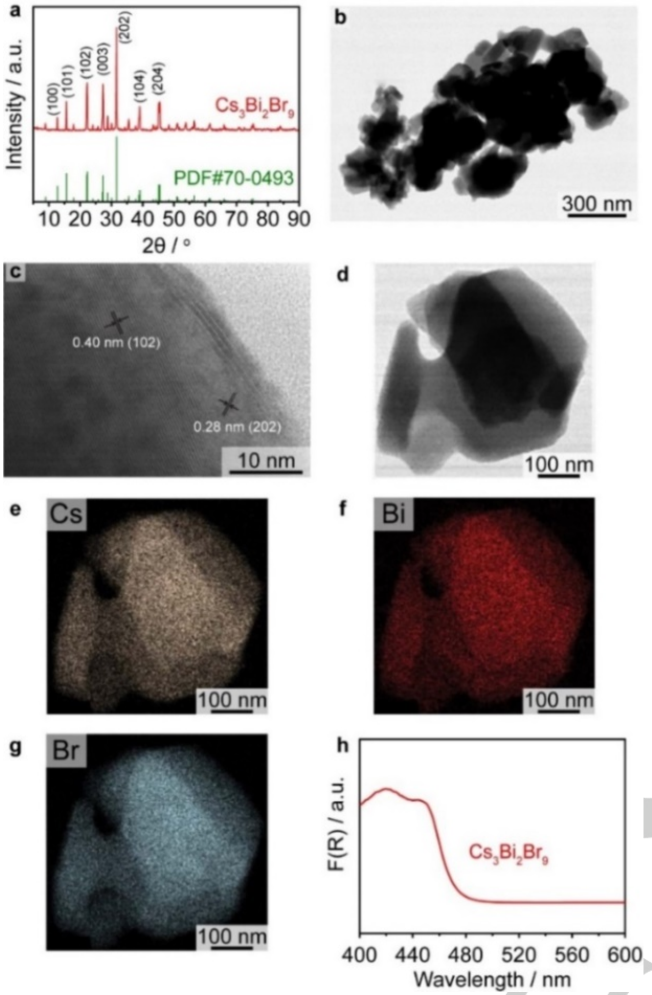
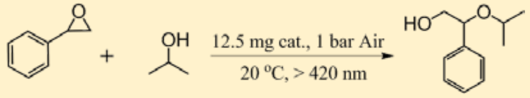


Figure 1. a, PXRD pattern with reference (PDF#70-0493). **b**, TEM image. **c**, HRTEM image. **d-g**, STEM image and element mapping. **h**, UV-Vis DRS profile of $Cs_3Bi_2Br_9$.

For the photocatalytic ring-opening of styrene oxide by isopropanol, control tests showed that negligible reaction took place (≤ 1% of conversion) in the absence of photocatalyst and light irradiation (Table 1, Entry 1 and 2). In contrast, when using $Cs_3Bi_2Br_9$ as a photocatalyst, almost full conversion (≥ 99%) and high yield (86%) for epoxide alcoholysis was observed after 6 h irradiation under visible light (≥ 420 nm) at room temperature in air (Table 1, Entry 3). When the reaction was performed under 1 sun irradiation, the high yield up to 88% could be obtained after 5 h. This promotion is mainly due to the partial UV light in the sunlight, which could generate the more energic photo-excited charges to accelerate the reactions. Even in the scaled test with the epoxide amount increased up to 1 mmol, the satisfactory activity (80% yield) could be reached under 1 sun irradiation at room temperature after 48 h. Notably, this facile photocatalytic system shows high regioselectivity to the *β*-alkoxy alcohol without the formation of any other alcohol regioisomers. The main by-products come from the oxidation of styrene oxide to benzaldehyde and isopropyl benzoate, meanwhile the oxidation of isopropanol to acetone was also observed. Furthermore, the $Cs_3Bi_2Br_9$ perovskite photocatalyst used milder reaction conditions but showed a comparable reaction rate (1333 μmol h^{-1} g_{cat}^{-1}) to reported thermal heterogeneous catalysts (Table S1) that also avoided the use of strong acids but required harsh reaction conditions (*e.g.*, elevated reaction temperature and long reaction time). In addition, other bismuth based photocatalysts (*e.g.*, $BiBr_3$ and Bi_2O_3) displayed poorer activity with conversion ≤ 13% (Table 1, Entry 4 and 6), while CsBr showed no conversion at all under the same reaction conditions (Table 1, Entry 5). Thus, it can be reasonably assumed that the possible active species for epoxide alcoholysis using the $Cs_3Bi_2Br_9$ photocatalyst are related to the Bi atoms in the perovskite. Moreover, when the Pb-based perovskite (prepared via *in-situ* anti-solvent method) was used as the photocatalyst, a conversion rate of only 1% was achieved (Table 1, Entry 7).

Table 1. Alcoholysis of styrene oxide by isopropanol: comparison of different photocatalysts.



Entry	Catalyst	Conversion (%)[a]	Yield (%)[a]
1	None[b]	<1	0
2	$Cs_3Bi_2Br_9$[c] (in dark)	1	<1
3	$Cs_3Bi_2Br_9$[c]	>99	86
		>99[d]	88
4	$BiBr_3$	13	12
5	CsBr	<1	0
6	Bi_2O_3	9	8
7	$CsPbBr_3$[e]	1	<1

Reaction conditions: 20 °C in air, 6 h irradiation under visible light (≥ 420 nm), 12.5 mg photocatalyst, 0.1 mmol styrene oxide, 5 mL isopropanol. [a]based on epoxide and determined by GC with toluene as internal standard. [b]no photocatalyst was added. [c]$Cs_3Bi_2Br_9$ was *in-situ* synthesized by adding the precursors into the starting reaction solution as shown in Scheme S1a-b. [d]1 sun irradiation for 5 h by use of solar simulator. [e]$CsPbBr_3$ was *in-situ* prepared by adding the precursors (CsBr and $PbBr_2$) into the starting reaction solution.

To further understand the $Cs_3Bi_2Br_9$ photocatalytic system, the ring-opening reaction of styrene oxide by isopropanol was systematically investigated as a model reaction. According to the recorded action spectrum obtained using monochromatic light irradiation (Figure 2a and Figure S5), the apparent quantum efficiencies (AQEs) of $Cs_3Bi_2Br_9$ for epoxide alcoholysis vary in a trend following the light adsorption profile, suggesting the utilization of light energy for the reaction. The highest AQE of 0.08% was obtained using monochromatic irradiation at 420 nm. When the irradiation energy is lower than the optical bandgap of $Cs_3Bi_2Br_9$ (2.7 eV), the AQE drops significantly to ~0.01%, as seen in the cases of 500 and 550 nm light irradiation. It should be mentioned that the AQE values shown here are underestimated due to the significant light scattering in a solid/liquid heterogeneous medium during illumination[26], and the actual number of photons absorbed by the photocatalyst were not determined.

As shown in Figure 2b, the time-dependent photocatalytic activity profile of the $Cs_3Bi_2Br_9$ catalyst indicates that the initial 2 h of irradiation serves as an activation period, as the conversion increased with longer irradiation time. Similar catalytic behavior was also observed when isopropanol was replaced by 1-butanol as the nucleophile under 14 h irradiation (Figure S6). The longer illumination time required to get higher conversion for the 1-butanol case is mainly attributed to the stronger steric effect, as the *in-situ* formed $Cs_3Bi_2Br_9$ prepared in 1-butanol has similar crystallinity and light adsorption ability as the photocatalyst prepared in isopropanol (Figure S8 and S9). The observed induction period can be ascribed to the initial adsorption of the alcohols on the catalyst surface and their reaction with the photogenerated charges to accumulate sufficient radicals that serve as active nucleophiles in the ring-opening reaction.[27] Additionally, the excess alcohol (as solvent) may also lead to the slower adsorption of the epoxide and its activation at catalyst surface, which could also cause this induction period behavior. It should be noted that due to the presence of DMSO (used as

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solvent to dissolve the perovskite precursors) in the reaction solution, some of the photocatalyst could have been re-dissolved (Table S3). However, these soluble species in the reaction solution had no significant effect on the ultimate photocatalytic performance. As shown in Figure 2b, removing the photocatalyst using hot filtration from the reaction mixture after 4 h of reaction did not generate significant further conversion (from 40% at 4 h to 43% at 6 h).

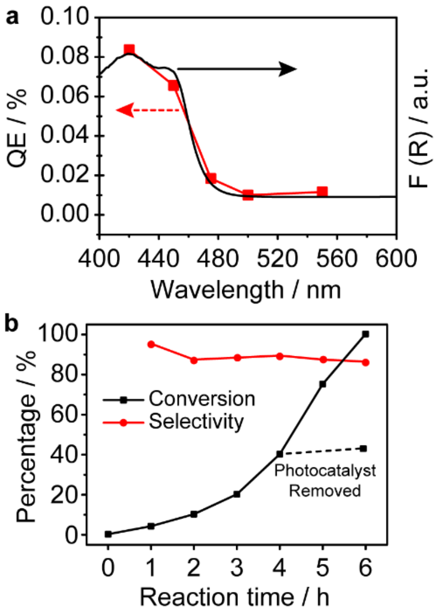


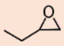
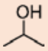
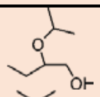
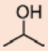
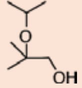
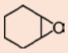
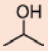
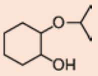
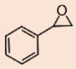
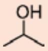
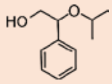
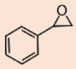
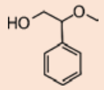
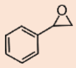
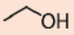
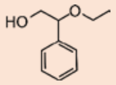
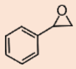
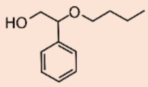
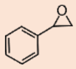
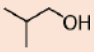
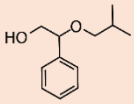
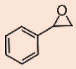
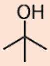
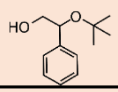
Figure 2. a, Action spectrum of $Cs_3Bi_2Br_9$ under monochromatic light irradiation at wavelengths of 420 nm, 450 nm, 475 nm, 500 nm and 550 nm. **b**, Time-dependent photocatalytic reaction over the $Cs_3Bi_2Br_9$ (≥420 nm) in air at 293 K for 6 h (-■- for conversion and -●- for selectivity). The dashed line shows the conversion in the absence of solid catalyst after hot filtration.

The general application scope of our *in-situ* synthesized $Cs_3Bi_2Br_9$ photocatalytic system is demonstrated through the ring-opening reactions of various epoxides by different alcohols. It should be noted that in most cases, the reactions displayed in Table 2 were performed under consistent reaction time (4h) to enable comparison, and that higher conversions could be possible with further optimization of reaction conditions.

As shown in Table 2, through 4 h visible light (≥ 420 nm) irradiation at room temperature in air, the *in-situ* formed $Cs_3Bi_2Br_9$ photocatalyst can be used to ring-open other epoxides, such as 1,2-epoxybutane, 2-methyl-1,2-epoxypropane, and cyclohexene oxide to produce the corresponding *β*-alkoxy alcohols (Table 2, Entries 1-3). These epoxide substrates were found to react more slowly than styrene oxide, likely due to their lower electron density and increased steric hindrance. For the cases of different alcohols (Table 2, Entries 4-11), higher catalyst precursor amounts were required for successful *in-situ* synthesis of the photocatalyst when using methanol and ethanol as solvents due to their strong polarity (Table 2, Entries 6-7); in these cases the lower conversions in comparison with the isopropanol example is mainly due to the dissolution of $Cs_3Bi_2Br_9$.[28] When 1-butanol was used a solvent (Table 2, Entry 8), much lower conversions (10%) were observed because of the steric effect from the long carbon chain. This hindrance is more obvious in the cases of 2-butanol and *tert*-butanol (Table 2, Entries 10-11). However, the longer light irradiation time can lead to high conversion even in these cases (Table 2, Entry 5 and 9).

In addition, this photocatalytic protocol can be extended to other nucleophiles such as thiol to produce thia-compound with a yield of up to 84% (Table S4), which confirms widespread applications of bismuth halide perovskite for more challenging coupling reactions.

Table 2. Photosynthesis of *β*-alkoxy alcohols *via* ring-opening reactions of epoxides over $Cs_3Bi_2Br_9$ under visible light irradiation.

Entry	Epoxide	Alcohol	Product	Time (h)	Con. (%)[a]	Sel. (%)[a]
1				4	28	95
2				4	23	94
3				4	14	95
4				4	40	90
5				6	≥99	86
6[b]		—OH		4	32	94
7[b]				4	33	93
8				4	10	94
9				14	86	94
10				4	8	94
11				4	2	95

Reaction conditions: 20 °C in air, under visible light (≥ 420 nm) illumination, 12.5 mg $Cs_3Bi_2Br_9$, 0.1 mmol epoxide, 5 mL alcohol. [a]Determined by GC using toluene as internal standard. [b]using 31.25 mg *in-situ* formed $Cs_3Bi_2Br_9$.

Based on related literature[19, 22], we hypothesized that the surface of our $Cs_3Bi_2Br_9$ photocatalyst contained the acid sites needed for epoxide activation. To investigate this, we performed UV-Vis diffuse reflectance spectroscopy (DRS) analysis with alizarin as the adsorbate, which has been reported to accurately assess the surface acidity of metal oxides and sulfides.[29] Pure uncoordinated alizarin displays absorbance at 2.856 eV, which is due to the intramolecular charge-transfer (IMCT) from the catechol moiety to the entire ring system as the lowest energy transition.[30] After the adsorption of alizarin onto the $Cs_3Bi_2Br_9$ perovskite surface, the IMCT band is clearly shifted to 2.42 eV (Figure 3a). This shift originates upon adsorption of the molecule onto the perovskite surface since the two original protons in alizarin are replaced by the metal cation (*e.g.* Bi in our case), which has lower degrees of electron withdrawal.[29] Based on the recorded acidity scale in the reported literature, the acidity of $Cs_3Bi_2Br_9$ is stronger than that for amphoteric ZnO (IMCT band at 2.38 eV) and weaker than that for Al_2O_3 (IMCT band at 2.48 eV).[29] Therefore, it can be concluded that weak Lewis acid sites exist on the $Cs_3Bi_2Br_9$ surface. In addition, we also observed a similar IMCT band shift when performing the same alizarin adsorption measurement on Bi_2O_3 (IMCT band at 2.44 eV, Figure S12a), which agrees with its acid-base properties as an amphoteric oxide.[31] This property may contribute to the photocatalytic activity of Bi_2O_3 for epoxide alcoholysis (Table 1, Entry 6), which is unfortunately limited by its wider bandgap (2.9 eV, Figure S12b) in contrast to $Cs_3Bi_2Br_9$. Similarly, the activity of $BiBr_3$ (Table 1, Entry 4) may also come from its mild Lewis acid nature.[32] In contrast, the $CsPbBr_3$ showed much weaker Lewis acidity with an IMCT band shift of 2.19 eV (Figure S13a), even though it has enhanced light absorption efficiency due to smaller bandgap (2.32 eV, Figure S13b). This also agrees well with the reported literatures.[9c, 29] Thus, weak Lewis acid sites on Pb-based perovskite could be the key point for its poor activity in ring-opening reactions.

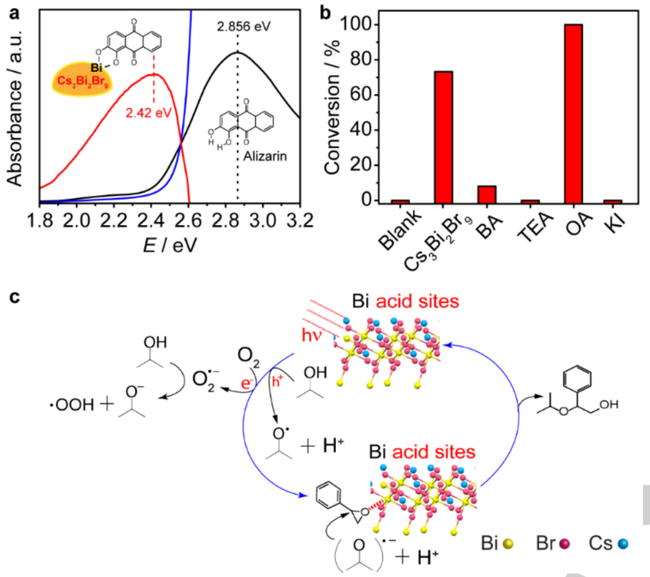


Figure 3. a, UV-Vis spectra of the sample $Cs_3Bi_2Br_9$ adsorbed with alizarin (red line), clean $Cs_3Bi_2Br_9$ (blue line) and pure alizarin (black line). **b**, Performance results of the control experiments with the addition of scavengers such as oxalic acid (OA), triethylamine (TEA), benzoquinone (BA) and KI under visible light irradiation for 5 hours. **c**, Proposed photocatalytic cycle for epoxide alcoholysis reaction over $Cs_3Bi_2Br_9$ with proper Lewis acids sites on surface (The yellow atoms are Bi, pink atoms are Br, and blue atoms are Cs).

To further investigate the effect of surface acid sites, we conducted additional experiments where various additives were added to the photoreactor (Figure 3b). After addition of an organic acid (oxalic acid, 0.3 mmol), the photocatalytic activity was obviously promoted with the conversion increased from 75% (in the case where only $Cs_3Bi_2Br_9$ photocatalyst was used) to 94% after 5 h of the reaction time. The presence of this organic acid could help the activation of the epoxide, which would in turn benefit the final ring-opening reaction. In contrast, when the same molar amount of an organic base, triethylamine, was added during the reaction, the photocatalytic system was totally deactivated. The poisoning from base addition can be ascribed to the occupation of surface acid sites of $Cs_3Bi_2Br_9$ by basic molecules. The significant influence of the acid-base reaction environment on the conversion strongly supports the vital role of $Cs_3Bi_2Br_9$ surface acid sites on the photocatalytic epoxide alcoholysis, which is usually driven by strong acid catalysts in the thermal catalytic approach.[16, 22] Furthermore, the addition of scavengers (benzoquinone as superoxide radical scavenger and KI as hole accepter) resulted in dramatically decreased conversions, suggesting the significant participation of $O_2^{\bullet-}$ and photogenerated holes.[33] The involvement of O_2 was also confirmed by the observed decreased activity (25% conversion) in anaerobic conditions (Ar atmosphere).

Considering the photocatalyst performance under different reaction conditions and the characterization described above, the mechanism for photocatalytic epoxide alcoholysis over $Cs_3Bi_2Br_9$ is proposed as shown in Figure 3c. First, under visible light irradiation, the photogenerated electrons and holes appear in the conduction band (CB) and valence band (VB) positions, respectively, of the $Cs_3Bi_2Br_9$ perovskite. Subsequently, the photogenerated holes and the superoxide anions ($O_2^{\bullet-}$) produced from O_2 reduction by the photogenerated electrons react with the alcohol (*e.g.,* isopropanol) to form alcohol radicals or anions, which serve as the active nucleophiles for the ring-opening reaction. Meanwhile, the Bi-based Lewis acid sites on the photocatalyst activate the epoxide (*e.g.,* styrene oxide) by coordinating the basic oxygen atom in the three-membered heterocyclic ring of epoxide.[34] Finally, the desired alcoholysis product is generated by the backside attack of the activated epoxide by the alcohol radicals or anions *via* the traditional nucleophilic substitution reaction pathway.[19]

In summary, through the integration of $Cs_3Bi_2Br_9$ halide perovskite synthesis and its photocatalytic evaluation in a one pot, an efficient approach has been established for the ring-opening reaction of various epoxides in different alcohols and thiols to enable synthesis of *β*-alkoxy alcohols and thia-compounds at room temperature and under visible light irradiation. This $Cs_3Bi_2Br_9$ photocatalyst system not only avoids the utilization of strong acids, but also displays high activity and good selectivity for epoxide alcoholysis. In comparison, the lead counterpart $CsPbBr_3$ shows the very poor activity with a conversion rate of 1%. According to the surface acidity characterization and control experiments, the high photocatalytic activity can be ascribed to the coupling effect between photocatalysis and proper Lewis acid sites on surface of bismuth-based material, which can help to activate the epoxides.

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Keywords: halide perovskite • epoxides • ring-opening reactions • visible light photocatalysis • Lewis acid

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Entry for the Table of Contents

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Photocatalytic ring-opening of epoxides over halide perovskite: The lead-free $Cs_3Bi_2Br_9$ is prepared in-*situ* and simultaneously used for the alcoholysis of various epoxides under visible light irradiation. This novel catalyst indicated excellent catalytic performances, good stability and recyclability. The origin of this unexpected catalytic behavior is ascribed to presence of proper acidic centers at the halide perovskite.

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Lead-free $Cs_3Bi_2Br_9$ Perovskite as Photocatalyst for Ring-Opening Reactions of Epoxides