$NaBiS_2$ as a next-generation photovoltaic absorber

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***Abstract* — I-V-VI$_2$ ternary chalcogenides were gaining more attention recently owing to their high air stability along with earth-abundant and nontoxic compounds. More interestingly, some of them have been predicted to be potential "perovskite-inspired materials" that can exhibit defect tolerance. In this work, we investigated the optoelectronic properties of cation-disordered NaBiS$_2$ nanocrystals, which have a steep absorption onset, with absorption coefficients >10^5 cm^{-1} just above its pseudo-direct bandgap of 1.4 eV. Surprisingly, an ultrafast photoconductivity decay and long-lived charge-carrier population almost independent of defect densities were simultaneously observed in NaBiS$_2$ nanocrystals. Through the density functional theory calculations, these unusual features are found to be highly associated with the non-bonding S *p* orbitals above the upper valence band, which can be further enhanced by cation inhomogeneity. Our work hence reveals the critical role of cation disorder on both absorption characteristics and charge-carrier kinetics of I-V-VI$_2$ ternary chalcogenides.**

I. Introduction

Over the past decade, lead-halide perovskites (LHPs) have emerged as a novel photovoltaic (PV) material with several remarkable optoelectronic properties. In addition to strong absorption coefficients and high carrier mobilities, their long minority carrier lifetimes (> 100 ns) in the presence of numerous defect states have enabled efficient LHP devices to be fabricated based on facile solution-processed methods at a low temperature, which is impossible for conventional Si-based PVs. Such a "defect tolerance" feature has been attributed to several factors, and the unusual electronic band structure along with the presence of ns^2 lone electron pairs [1] are believed to be the most crucial ones among all. Unfortunately, LHPs are still faced with great challenges on the lead toxicity and instability in ambient air, which significantly impede their industrialization. These challenges as well as our understandings on defect tolerance have motivated researchers to investigate other lead-free alternatives that may replicate success of LHPs, leading to the quest of the so-called "perovskite-inspired materials (PIMs)" in recent years.

Particularly, some I-V-VI$_2$ ternary chalcogenides (or ABZ$_2$ materials) have been predicted to be potential PIMs with low toxicity [2], and they are gaining more and more attention recently since one of the most promising ABZ$_2$ materials, AgBiS$_2$, has reached an efficiency over 9% in its solar cells [3]. However, most ABZ$_2$ materials including AgBiS$_2$ explored thus far have slow absorption onsets, and their charge-carrier transport is still rarely investigated. Herein, we comprehensively investigate the optoelectronic properties of cation-disordered NaBiS$_2$ nanocrystals (NCs), whose two cations can randomly occupy the same lattice sites owing to their similar ionic radii, similar to the case in AgBiS$_2$. Through the use of a series of spectroscopy techniques, we observed unusually strong absorption coefficients with a steep onset, ultrafast photoconductivity decay within a few ps, and extremely long-lived charge-carrier populations persisting for over 10 μs in NaBiS$_2$. We correlated these uncommon features with density functional theory (DFT) calculations in order to understand their origins, and cation disorder has been found to play a crucial role here as well. Finally, by intentionally introducing external defects through the post-annealing process, we also investigated the impacts of defects on charge-carrier kinetics of NaBiS$_2$ NCs and discussed another possibility of defect tolerance.

II. Main Experimental and Theoretical Results

NaBiS$_2$ NC films have been found to exhibit high air-stability for over 100 days and high absorption coefficients (α) from near-infrared (NIR) to ultra-violet (UV) region. As shown in Fig. 1, NaBiS$_2$ has shown α values exceeding 10^5 cm^{-1} at photon energy (hν) above its pseudo-direct bandgap of 1.4 eV, where only a minimal energy difference (0.01 eV) exists between its direct transition energy and indirect bandgap. These α values are higher than most solution-processed PV absorbers and also comparable to AgBiS$_2$, which has demonstrated an efficiency over 9% in its solar cells. Moreover, a much sharper absorption onset than AgBiS$_2$ was seen in NaBiS$_2$. All of these features make NaBiS$_2$ rather suitable for ultrathin PV application with a spectroscopic limited maximum efficiency (SLME) over 26% being estimated.

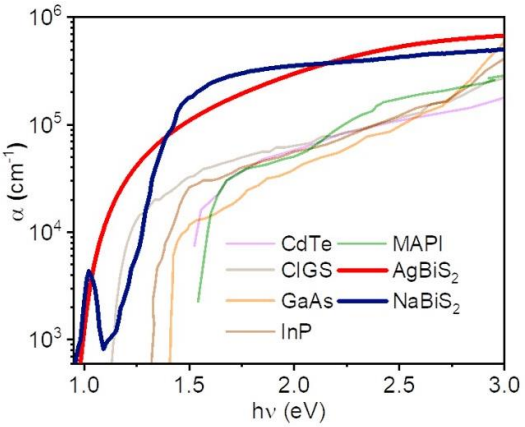

Fig. 1. Absorption coefficient α spectra of NaBiS$_2$ compared with other PV absorbers.

DFT calculations revealed that these unusual absorption characters arise from the lack of Na orbital contributions into the valence band (VB) due to the large energy difference between Na and S *p* orbitals. As a result, the VB edge of NaBiS$_2$ becomes very flat, leading to a large transition dipole moment resulting from the concentrated VB density of states (DOS), and hence the strong absorption strengths of NaBiS$_2$. At the same time, the flat VB edge also makes a small difference between the direct transition energy and indirect bandgap, which results in the pseudo-direct bandgap of

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$NaBiS_2$ and its sharp absorption onset similar to direct-bandgap materials. However, compared to $AgBiS_2$ with strong Ag *d* orbitals hybridization, $NaBiS_2$ has a much weaker anti-bonding strength at the VB, and the isolated S *p* orbitals can emerge just above the VB edge. These S *p* states are even flatter than the VB edge of $NaBiS_2$, and can therefore localize photoexcited holes easily.

More interestingly, these S *p* orbitals are found to be prevalent in Na-rich regions, especially those with one S atom coordinated by 5-6 Na atoms. Further enhanced by the strong carrier-phonon coupling of $NaBiS_2$, small hole polarons tend to be form in the vicinity of Na-rich regions. On the other hand, although electrons are more mobile compared to holes, large electron polarons are also predicted to be weakly localized around the Bi-rich regions. Consequently, electrons and holes are spatially separated in different cation segregation regions in $NaBiS_2$, as displayed in Fig. 2, leading to ultrafast photoconductivity decay and the absence of photoluminescence for this material.

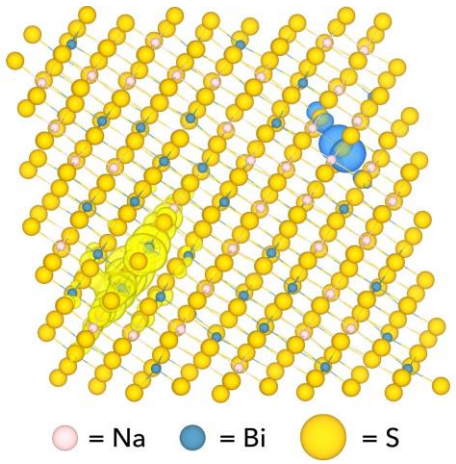

Fig. 2. Charge density isosurfaces of an electron-hole pair in a cation disordered $NaBiS_2$ supercell with sodium, bismuth, and sulphur atoms in pink, blue and yellow, respectively. The translucent yellow and blue surfaces represent electron and hole densities, respectively.

As evidenced by optical-pump-terahertz-probe (OPTP) and short-time transient absorption (TA) measurements, most mobile carriers were indeed found to be localized substantially within 1 ps. This ultrafast carrier kinetics could be described by the two-level mobility model, which has been applied to several materials showing obvious carrier localization features [4]. Surprisingly, despite the ultrafast decay, a very broadband signal persisting for over 10 µs was also observed from long-time TA measurements. Based on these results, we proposed that a large majority of carriers are localized into the S *p* states within ps timescale, while these strongly localized carriers could be also isolated from other external defects and relax very slowly till µs timescale. We then further investigated how defects could impact carrier kinetics of $NaBiS_2$ by introducing different degree of external defects through annealing at 100 °C for different time, which could remove the organic ligands attaching to NCs during synthesis and lead to NC fusion. As expected, we found that the carrier kinetics of $NaBiS_2$ in both short- and long-time scale was almost independent of the defect levels introduced, verifying our proposed model.

III. Conclusion

$NaBiS_2$ NC films have showed high absorption strengths and a sharper absorption onset compared to most ABZ_2 materials, both of which are suitable for ultrathin PV applications. From DFT calculations, these unusual absorption features are found to be highly related to the flat VB edge of $NaBiS_2$ arising from the lack of Na hybridization. At the same time, this special electronic band structure also facilitates the formation of S *p* states above the VB edge. It has been verified that the presence of S *p* states, strong carrier-phonon coupling along with cation segregation could lead to spatial carrier separation and ultrafast carrier localization. It has also been found these localized carriers could tolerate different defect levels introduced through annealing. Our work hence reveals that the elemental species in ABZ_2 materials might enable the great control over both the optical and carrier transport properties through the electronic structure, and carrier-phonon coupling is another critical factor that should be accounted for when searching for other promising ABZ_2 materials in the future.

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