Datum
20-06-2024

Dnr
2018-004357

Projektnr
46564-1

Energimyndighetens titel på projektet – svenska Högeffektiva solceller baserade på blyfria dubbel-perovskitlegeringar	
Energimyndighetens titel på projektet – engelska High-Efficiency Solar Cells Based on Alloyed Lead-Free Double Perovskites	
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Nyckelord: 5-7 st Double perovskites, solar cells, optoelectronics, alloying, thin films	

Förord

This project has been funded by the Swedish Energy Agency.

Innehållsförteckning

Sammanfattning

Solceller anses vara en av de mest lovande teknologierna för att möta det växande behovet av förnyelsebar energi. Blyhalidperovskitfilmer kan framställas från lösning och har visat utmärkt prestanda i fotovoltaiska tillämpningar under de senaste åren. Trots detta så är toxiciteten hos bly i perovskitmaterialen en nyckelutmaning som hindrar deras praktiska tillämpningar. Haliddubbelperovskiter är en helt ny generation av perovskitföreningar, där giftiga bivalenta Pb2+ katjoner ersätts av en kombination av icke-giftiga monovalenta och trivalenta katjoner. Dock begränsas dubbelperovskiter av ett stort bandgap (och därmed dålig ljusupptagningsförmåga). Detta projekt syftade till att lösa det kritiska bandgapproblemet hos dubbelperovskiter. Vi föreslog att

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använda legeringsstrategin och nya filmdeponeringstekniker för att erhålla dubbelperovskitfilmer med optimerat bandgap för högpresterande solceller baserade på dubbelperovskiter.

Under detta projekt har vi undersökt de inneboende begränsningarna hos ursprungliga dubbelperovskiter. Med hjälp av den grundläggande förståelsen legerade vi sedan olika element (inklusive Fe, Cu, Pd) i olika dubbelperovskiter och undersökte strukturen och bandgapet i detalj. Vår legeringsstrategi utökar avsevärt absorptionen av dubbelperovskiter bortom 1000 nm. Vi utforskade deras tillämpningar i både solceller och fotodetektorer. Dessutom utvecklade vi en ny kristallteknik för att förbättra absorptionen av dubbelperovskiter. Ytterligare förbättring av komponentprestanda kan förväntas genom materialdesign enligt vår legeringsstrategi med fokus på olika legeringsämnen.

Summary

Solar cells are considered as one of the most promising technologies to meet the growing demand for energy. Solution-processed lead halide perovskites have shown great success in photovoltaic applications over the past few years. Despite these exciting advances, the toxicity of lead in these materials is a key challenge hindering their practical applications. Halide double perovskites are an entirely new generation of compounds, where toxic bivalent Pb2+ cations are replaced by a combination of non-toxic monovalent and trivalent cations. However, double perovskites are limited by their large bandgap, resulting in poor light harvesting property. This project aimed to address the critical bandgap issue of double perovskites. We proposed to employ an alloying strategy and novel film deposition techniques to obtain double perovskite films with the optimised bandgap for high-performance solar cells.

During this project, we have investigated the intrinsic limitations of pristine double perovskites. Assisted by the fundamental understanding, we then alloyed different elements (including Fe, Cu, Pd) into different double perovskites, and investigated the structure and bandgap in details. Our alloying strategy significantly extends the absorption of double perovskites beyond 1000 nm. We explored their applications in both solar cells and also photodetectors. In addition, we developed a new crystal engineering technique to enhance the absorption of double perovskites. Further improvement of the device performance can be expected through continued material design efforts, focusing on different alloying elements in line with our alloying strategy.

Inledning/Bakgrund

Metal halide perovskites with the formula of ABX_3, where A is inorganic cesium or an organic cation, B site is Pb and X is a halide anion, have emerged as the

most promising materials for low-cost high-efficiency solar cells. These perovskites can be easily processed from solutions using low-cost raw materials. They have shown excellent semiconducting properties, such as strong and tunable light absorption, low exciton binding energy, low effective mass, long and balanced ambipolar carrier transport property. (1) As a result, the power conversion efficiencies (PCEs) of perovskite solar cells have quickly risen from 3.9% to over 20%, making it the fastest-advancing technology in the photovoltaic history. In spite of these great advances and exciting progress, current reliance on toxic Pb in perovskite solar cells represents a key issue hindering their large-scale commercialization.

The most obvious choice for lead-free perovskites is to substitute Pb^{2+} with another divalent cation. However, it has been demonstrated that only group IVA elements (e.g. germanium, Ge^{2+} or tin, Sn^{2+}) can form semiconducting ABX_3 perovskites. (2) Unfortunately, the resulting perovskites based on Sn^{2+}/Ge^{2+} are easily oxidized, resulting in film decomposition and device failure within seconds to minutes upon exposure to the air. Bismuth (Bi^{3+}) and antimony (Sb^{3+}) from the adjacent group can form a different perovskite structure ($A_3B_2X_9$) configuration with better environmental stability. However, high exciton binding energy and defect induced energetic disorder enhance charge recombination and make them unsuitable for solar cell applications.

Halide double perovskites with the formula of $A_2N^+M^{3+}X_6$, where toxic bivalent Pb^{2+} cations are replaced by a combination of non-toxic monovalent and trivalent cations, are a new generation of non-toxic and stable perovskites. (3) They also exhibit attractive properties suitable for solar cells, such as low exciton binding energy and long carrier lifetimes. In addition, they offer immense opportunities in terms of combinatorial chemistry. Double perovskites provide a promising approach to solve the toxicity issue of Pb-based perovskites. The challenge with these double perovskites is that they have a wide bandgap, resulting in poor light absorption properties. This project aimed to address this challenge by making use of the alloying strategy. The project lasted five years, from the beginning of 2019 till the end of 2023.

Genomförande

WP 1: Rationally screen alloyed double perovskites with suitable bandgaps through a synergistic approach, which combines first-principles calculations, single crystal synthesis and optoelectronic characterizations. Theoretical calculations are opening pathways to pre-screen the right alloys from a pool of candidate metal ions. Special attention was given to strong light absorption properties in the theoretical calculations. Factors such as direct or indirect bandgap, carrier mobility, and exciton binding energy were also considered. Based on the calculation results, the promising candidates were synthesized and characterized using advanced spectroscopic techniques, including photoluminescence (PL), PL decay, and PL mapping. Since synthesizing single crystals requires less experimental effort than films and is ideal for understanding

the material properties, we adopted the previously developed solution approaches for the synthesizing double perovskite single crystals.

WP 2. Prepare high-quality alloyed double perovskite films with correct compositions by employing three synthetic methods. The first method was the pressure-assisted annealing. The crystal lattice of double perovskites is sensitive to pressure, since the bandgap would be reduced with increasing pressure. The second method was the electrophoretic deposition. This method was successfully used in the processing of advanced coatings. The mechanism involved charged particles in a suspension being deposited onto an electrode under an applied electric field. The critical parameters, e.g. charged powder particles and dispersed colloidal solution, were carefully tuned. The third method is the vapor deposition. This approach was useful for materials with low solubility or incorrect compositions in films and was employed to fabricate uniform films for a range of materials, including lead-based perovskites.

WP 3. Fabricate high-efficiency double perovskite solar cells by coupling device physics and device engineering investigations. We optimized the film quality by controlling the crystallization process of the double perovskite films. We enhanced the transfer process from double perovskites to TiO_2 by Cl passivation. Energy alignment between double perovskites and carrier transport layers were carefully taken care of to ensure efficient charge extraction. The photovoltage losses due to non-radiative recombination in the solar cells were also quantified. Theoretical photocurrent value was calculated based on the carrier diffusion model and the external quantum efficiency to provide carrier diffusion information of devices. A good understanding of device physics was fed back to further improve the materials in WP1 and films in WP 2.

Three research groups led by the following PIs in this project: Feng Gao, Mats Fahlman, Sergei Simak.

Resultat

1, We uncovered evidence of strong deformation potential in pristine double perovskites. The Fröhlich and deformation potentials synergistically lead to ultrafast self-trapping of free carriers forming polarons highly localized on a few units of the lattice within a few picoseconds.
2, We take the benchmark double perovskite Cs2AgInCl6 as an example to reveal the atomic-level structure of double perovskite alloys Cs2AgIn1−xFexCl6 (x = 0–1) by employing solid-state nuclear magnetic resonance.
3, We observed magnetic properties of Fe-alloyed double perovskites. This result provides a new approach for spintronics based on optoelectronic lead-free double perovskites.
4, We observed extension of the absorption in Cu-alloyed double perovskites, and detected optoelectronic response from these additional absorption, providing a new alloying strategy for extending the optoelectronic responses.
5, We significantly enhanced the absorption of double perovskites simply by changing the crystal preparation temperature.

6, We observed extension of the absorption in Pd-alloyed double perovskites to over 1000 nm.
7, We found that the temperature sensitivity of the bandgap of $Cs_2NaFeCl_6$ crystal is as high as 2.52 $meVK^{-1}$ and the bandgap change from 6.8 to 423 K is 0.51 eV, significantly exceeding the values reported in lead-based perovskites and many conventional group-IV and III–V semiconductors.

Diskussion

The distribution of chemical composition in double perovskite alloys is very important and hence requires careful control. Alloying is very promising for enhancing the absorption and photovoltaic performance of lead-free double perovskites. In addition to alloying, other crystal engineering strategies could also be useful to solve the large bandgap issue in pristine double perovskites. With further efforts along the direction of bandgap engineering, high power conversion efficiencies can be expected from solar cells made with double perovskites; this will require further development of both materials and devices.

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Bilagor

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