Lead-Free Perovskite Narrow-Bandgap Oxide Semiconductors of Rare-Earth Manganates

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ABSTRACT: Tremendous success has been achieved in photovoltaic (PV) applications, but PV-generated electricity still cannot compete with traditional power in terms of price. Chemically stable and nontoxic all-oxide solar cells made from earth-abundant resources fulfill the requirements for low-cost manufacturing under ambient conditions and thus are promising as the next-generation approach to solar cells. However, the main obstacles to developing all-oxide solar cells are the spectral absorbers. Besides photovoltaics, novel chemically stable, nontoxic, and earth-abundant narrow-bandgap semiconductors are desired for photochemical applications in photodetectors, photoelectrodes, or photocatalysts. Herein, we report novel lead-free perovskite narrow-bandgap rare-earth semiconductors, YMnO₃, HoMnO₃, ErMnO₃, and YbMnO₃, which were identified by screening a family of perovskite rare-earth manganates, RMnO₃ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb). The sharp edge observed in their absorption spectra indicates the existence of band gaps, further confirmed with laser Raman fluorescence spectra. Good periodic on–off photoelectronic response was observed in 8 of the 12 members (i.e., R = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb). Among them, YbMnO₃ is approved as an n-type semiconductor with a direct band gap near 1.35 eV, whose theoretical Shockley–Queisser efficiency is approximately 33.7% for single-p–n-junction solar cells. This work sheds light on exploring stable oxide semiconductors with a narrow band gap for future applications.

INTRODUCTION

Tremendous success has been achieved in photovoltaic (PV) applications, with the total solar energy installation capacity reaching 509.3 GW worldwide in 2018. However, the price of PV-generated electricity in most locations still cannot compete with that of conventional electricity. Therefore, novel PV cells are needed to further reduce the cost of PV systems. A higher power conversion efficiency (PCE) is crucial for reducing PV system costs, and great progress has been made on this front. The PCE of emerging perovskite solar cells has soared from 20.1 to 23.3% over the past few years; the efficiency of some commercially available solar cell modules is greater than 20%. Besides the cost of the solar cells, other expenses such as packing and installation costs account for a considerable fraction of the PV system cost. Metal oxides (MOs) are chemically and thermally stable, nontoxic, earth-abundant, and environmentally friendly, thus fulfilling the requirements for low-cost manufacturing under ambient conditions. Therefore, solar cells that are entirely based on MOs are very promising for next-generation PV techniques.

Some MOs have been applied in PV cells and modules, but they are mainly used as transparent conducting electrodes. Examples include indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and aluminum-doped zinc oxide (AZO). Moreover, studies on historically used narrow-bandgap oxides for PV applications, such as Cu₂O, Co₃O₄, PbO₂, and ZnO, have been ongoing. By employing the latest engineering approaches for fabricating devices, great progress has been made regarding materials such as Cu₂O, which is the oldest narrow-bandgap semiconductor and has a direct band gap close to 1.9–2.1 eV. Recently, an efficiency of 8.1% was achieved with a MgF₂/Al-doped ZnO/Zn₂O₃Ge₆O₁₉O/Cu₂O:Na heterojunction solar cell. Based on these findings, we are confident that future research regarding solar cells will evolve toward the ultimate goal of an all-oxide material system. Nevertheless, the key component for developing all-oxide solar cells is searching for novel MO absorbers.

On the one hand, much effort on utilizing lead-free perovskites, particularly with organic–inorganic hybrid halides, for solar cells has been made and additional studies are ongoing; on the other hand, full-inorganic rare-earth
semiconductors exhibit interesting properties. Rare-earth manganates, with the general formula RMnO₃, are a family of interesting compounds that exhibit ferroelectric, ferromagnetic, antiferromagnetic, and colossal magnetoresistance properties. Accordingly, they have been applied in memory devices, sensors, gyrotrons, and optical devices and have even been used as combustion catalysts. RMnO₃ crystallizes with a distorted perovskite structure, which can be classified into two groups: the orthorhombic structure for larger rare-earth elements (La–Dy) and the hexagonal structure for smaller rare-earth elements (Sc, Y, Ho–Lu). Recently, RMnO₃ has attracted attention for PV applications. Jang et al. examined the switchable PV effect in YMnO₃ and LuMnO₃ thin films and observed PCE values 1–3 orders of magnitude greater than those of the classic ferroelectric photovoltaics (FPVs), undoped Pb(Zr,Ti)O₃, and BiFeO₃ under standard AM 1.5 G illumination. Huang et al. predicted the strong light absorption of TbMnO₃ in the solar-spectrum range using first-principles methods based on the density functional theory (DFT), which theoretically results in the maximum solar conversion efficiency of up to 33%.

FPVs are an interesting research field in solar cells. The non-centrosymmetry of ferroelectric materials that possess spontaneous electric polarization provides an inherent force to drive exciton separation and carrier extraction, differing from the photogenerated electron–hole pairs separated by the built-in electric field inside traditional p–n-junction solar cells, and the open-circuit voltages could be a few orders of magnitude greater than the band gap of the ferroelectric materials. Recently, a PCE of 8.1% under AM 1.5 G irradiation has been achieved with ferroelectric Bi₂FeCrO₆ solar cells.

Besides photovoltaics, novel chemically stable and nontoxic narrow-bandgap semiconductors are specifically needed in a wide variety of photoelectrochemical applications; for example, they are used as photoelectrodes in photocatalysts for solar water-splitting, photodetectors, and photoelectronic devices. Aiming at these applications, a family of perovskite rare-earth manganates, RMnO₃ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb), is examined in this work.

## RESULTS AND DISCUSSION

To explore the synthesis of RMnO₃ powders, the solid-state reaction was performed at 1000, 1200, and 1300 °C for 4 h. As indicated by the X-ray diffraction (XRD) patterns shown in Figure S1, the products synthesized at 1000 °C in ambient air mainly consisted of rare-earth oxides. As the temperature was increased to 1200 °C, the characteristic diffraction peaks of rare-earth oxides decreased and peaks corresponding to rare-earth manganates as the main phases appeared, as shown in Figure S1. As the temperature was further increased to 1300 °C, the minor residual rare-earth oxides PrO₂, NdO₂, SmO₂, and ErO₂ that had not been consumed in reactions could still be discriminated. Considerable amounts of Y₂O₃ and Er₂O₃ were present as residual starting materials in the nominal YMnO₃ and ErMnO₃ compounds, respectively. Moreover, an anomaly was observed for the LaMnO₃ and GdMnO₃ phases, whose content increased as the temperature was increased from 1000 to 1200 °C but decreased again as the temperature was increased from 1200 to 1300 °C due to the variation in the La₂O₃ and Gd₂O₃ contents. However, when CeO₂ and MnO₂ were reacted, the XRD patterns of the products indicated that the starting material CeO₂ was primarily present and minor Mn₃O₄ was formed as the temperature increased to 1200 or 1300 °C. For more details about the dependence of the structural transformation on temperature, please refer to Figure S1.

Figure 1 presents XRD patterns of the 12 RMnO₃ powders synthesized at 1200 °C for 4 h in an air atmosphere, in which two sets of diffraction patterns could be discriminated, with the exception of the CeO₂ raw material. Namely, the manganates of La, Pr, Nd, Sm, Gd, Tb, Dy, Y, Ho, Er, Yb, respectively, powders synthesized by a solid-state reaction at 1200 °C for 4 h in ambient air, in which the orthorhombic (La, Pr, Nd, Sm, Gd)MnO₃ and the nominal-composition CeMnO₃ with CeO₂ indexed are presented in (a) and the orthorhombic (Tb, Dy)MnO₃ and the hexagonal (Y, Ho, Er, Yb) MO₃ systems are presented in (b).

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c00138)

**Figure 1.** XRD patterns of RMnO₃ (R = Ce, La, Pr, Nd, Sm, Gd, Tb, Dy, Y, Ho, Er, Yb) powders synthesized by a solid-state reaction at 1200 °C for 4 h in ambient air, in which the orthorhombic (La, Pr, Nd, Sm, Gd)MnO₃ and the nominal-composition CeMnO₃ with CeO₂ indexed are presented in (a) and the orthorhombic (Tb, Dy)MnO₃ and the hexagonal (Y, Ho, Er, Yb) MO₃ systems are presented in (b).
in LaMnO₃, PrMnO₃, NdMnO₃, SmMnO₃, GdMnO₃, TbMnO₃, and DyMnO₃. It is possible that the carriers in YbMnO₃ are different from those in the other compounds. The electrochemical workstation adopted in our measurement shuts off automatically if the forward voltage is greater than 13 V, thus terminating the measurements of the photon-excited voltage of YMnO₃, CeMnO₃, ErMnO₃, and HoMnO₃ as observed in Figure S4a. When the voltage is too high, the photogenerated current is accordingly very weak, as shown in Figure S4b. Therefore, the photogenerated voltage may be very high, or it is possible that these compounds do not conduct at all.

Absorption, including the wavelength range and intensity, is the key factor determining whether a material is an applicable absorber for solar cells. Herein, the absorption spectra of the samples were collected to obtain this information. Figure 3a,b presents UV–vis–near-infrared (NIR) absorption spectra of the RMnO₃ powders synthesized at 1200 °C. No sharp edge is present in the absorption spectra of the RMnO₃ compounds, indicating that they absorb light over a wide range of wavelengths.
observed in the absorption spectra of orthorhombic La–Dy manganates displayed in Figure 3a, which is in accordance with the calculated value of $E_g$ of approximately 0, as summarized in Table 1. This result indicates that there is no band gap in these compounds. By contrast, absorption bands with sharp edges were observed in the spectra of the hexagonal Y and Ho–Yb manganates in Figure 3b. The cutoff wavelength of the absorption spectra at approximately 1000 nm indicates that the band gap is close to 1.24 eV. The absorption spectra of the 12 samples each synthesized at 1000, 1200, and 1300 °C, respectively, in ambient air are displayed in Figure S5. Figure S6a presents the absorption spectra of the 12 samples synthesized at 1200 °C, by plotting the spectra in Figure 3a,b together under the same horizontal and vertical scales. Besides, we should bear in mind that the concave region at 1800–2100 nm in Figures 3 and S5–S7 for all absorption spectra is caused by the Shimadzu UV-3600 spectrophotometer adopted here rather than by the intrinsic absorption of samples.

The band gap can be further evaluated based on Tauc plots using the relationship $\alpha h \nu \propto (E_g - h \nu)^{1/n}$, where $\alpha$ is the coefficient of optical absorption, $h \nu$ is the energy of photons, $E_g$ is the band gap, and $n = 2$ for direct transitions and $n = 1/2$ for indirect transitions; these plots indicate that a direct band gap near 1.35 eV (Figure 3c) and an indirect band gap near 1.27 eV (Figure S6b) were obtained for these four samples. After data transformation, however, no tangential line could be discriminated in Figure S6b. On comparing the spectral configuration of Figure 3c with that of Figure S6b, we can come to the conclusion that hexagonal YMnO3, HoMnO3, ErMnO3, and YbMnO3 have direct band gaps. Moreover, a band gap near 1.35 eV is consistent with the value of approximately 1.4 eV for hexagonal TbMnO3 theoretically predicted by Huang et al.29 It should be noted that the orthorhombic TmMnO3, rather than the hexagonal structure model of TbMnO3 adopted by Huang et al.,29 was obtained in this work. For Tauc plots of the absorption spectra of orthorhombic LaMnO3, CeMnO3, PrMnO3, NdMnO3, SmMnO3, GdMnO3, TbMnO3, and DyMnO3 obtained using the relationships $\alpha h \nu \propto (E_g - h \nu)^{2}$ and $\alpha h \nu \propto (E_g - h \nu)^{1/2}$, please refer to Figure S6c,d, in which the smooth decrease in the intensity with the photon energy further suggests that there are no band gaps in these compounds. In contrast to the band gaps of the inorganic lead halide perovskite CsPbBr3 (2.21 eV),41 the organic–inorganic hybrid lead-free halide perovskite (C6H5NH3)BiI4 (2.14 eV),19 and the phenethylammonium (PEA) bismuth halides (PEA)3Bi2I9/(PEA)3Bi2Br9/(PEA)3Bi2Cl9 (2.23/2.66/3.28 eV, respectively),42 the band gap of hexagonal YMnO3, HoMnO3, ErMnO3, and YbMnO3 of about 1.35 eV is closer to that of methylammonium (CH3NH3+ or MA) lead iodide MAPbI3 (1.64 eV) and formamidinium (NH2CH=NCH2+ or FA) FAPbI3 (1.55 eV).43
Table 2. Semiconductor Parameters of Volume Resistivity, Volume Hall Coefficient, Bulk Carrier Concentration, and Mobility 

| Compound     | Resistivity (Ω·cm) | Hall Coefficient (cm³·C⁻¹) | Carrier Concentration (cm⁻³) | Mobility (cm²·V⁻¹·s⁻¹) |
|--------------|-------------------|---------------------------|-----------------------------|-------------------------|
| YbMnO₃       | 2.669 × 10⁸       | −3.1589 × 10⁷             | 1.976 × 10¹⁰               | 11.83                   |
| HoMnO₃       | 9.4739 × 10⁸     | 1.387 × 10⁶              | 4.501 × 10¹²               | 0.1464                  |
| ErMnO₃       | 6.0439 × 10⁸     | 1.627 × 10⁶              | 3.836 × 10⁹               | 26.92                   |
| YbMnO₃       | 2.7119 × 10⁹     | −2.139 × 10⁷             | 2.918 × 10¹¹               | 7.890                   |

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carrier concentration is in the range of $10^{11}$ to $10^{18}$.

YbMnO$_3$ are n-type semiconductors. As shown in Table 2, the resistivity is in the range of $10^6$ to $10^7$·Ω·cm, and YbMnO$_3$ can be described in Figure 3f.

mobilities in the range of $0.1464 - 2.692$ cm$^2$/V·s.

Hexagonal YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and YbMnO$_3$ are on par with the experimental parameters ($10^8$ to $10^9$ cm$^2$/V·s) of MAPbI$_3$ single crystals reported by Bakr et al., and the theoretical potential values with the band gaps estimated in Figure 3c, the band and band-edge positions of YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and YbMnO$_3$ can be described in Figure 6c.

The absorption of incident light by a compound is determined by its composition, the chemical state of each element, and, ultimately, the electron transitions occurring in the ions. To reveal the mechanism and the compositions, chemical states of RMnO$_3$ pellets were investigated with X-ray photoelectron spectroscopy (XPS) analysis by choosing YbMnO$_3$ as a representative example. All expected elements were identified from the XPS survey, as shown in Figure 4a. The elemental ratio of Yb to Mn was found to be $\sim 1:1$. Five peaks at 184.6, 188.1, 192.4, 198.8, and 205.9 eV in Figure 4b, which are denoted a, b, c, d, and e, respectively, are fitted from the Yb 4d XPS spectrum, and they are attributed to Yb$^{3+}$.

The one-shoulder neighbor to Yb$^{3+}$ at 181.9 eV may be caused by Yb$^{4+}$, but this peak is by far very weak. By combining this spectrum with the Yb 4p XPS spectrum shown in Figure 4c, we can conclude that a small amount of Yb$^{4+}$ exists in YbMnO$_3$. Figure 4c shows that the Yb in YbMnO$_3$ exhibits spin-orbital splitting of Yb 4p with 4p$_{1/2}$ and 4p$_{3/2}$ peaks at 32.6 and 26.1 eV, respectively, corresponding to Yb$^{3+}$. Analysis of the peak splitting is an approach to determine the oxidation state. Typically, the $\Delta E$ of Mn 3s for MnO (Mn$^{2+}$) is 6.0 eV, that of Mn$_2$O$_3$ (Mn$^{3+}$) is $\geq 5.3$ eV, and that of MnO$_2$ (Mn$^{4+}$) is 4.7 eV. However, the magnitude of Mn 3s splitting was found to be $\sim 5.1$ eV in Figure 4d, indicating that the main oxidation state of Mn in YbMnO$_3$ is $\sim +3$, accompanied by a few compounds in the $+4$ oxidation state. From the point of view of charge balance, minor Yb$^{2+}$ might exist to balance with Mn$^{4+}$.

The Mn 2p XPS spectrum was also acquired. As shown in Figure S9, the spin-orbital splitting of Mn 2p with 2p$_{1/2}$ and 2p$_{3/2}$ peaks at 653.4 and 642.1 eV, respectively, was observed.
but the MnO satellite (∼647 eV) feature was not. This conclusion further confirms the existence of +3 as the main oxidation state of Mn and excludes the +2 oxidation state.

$YbMnO_3$ crystallizes in a hexagonal system with space group $P_6_3/m$ (185) and cell parameters of $a = 6.073(1)$ and $c = 11.349(3)$. In the crystal lattice of $YbMnO_3$, there are two $Yb$ sites and one Mn site. $Yb_1$ and $Yb_2$ are both sevenfold-coordinated, as shown in Figure 5a. Mn is coordinated with five neighboring O atoms, which build a pentahedron around Mn, as shown in Figure 5b. As Mn is fivefold-coordinated, the 3d orbital will split into high-energy singlet, $a_g (3z^2 - r^2)$, and low-energy parallel doublet, $e_g (xy/x^2 - y^2$ and $yz/zx)$, states.29

The projection of the unit cell along the $b$ and $c$ axes is displayed in Figure 5c,d, respectively. Therefore, the three-dimensional structure of $YbMnO_3$ could be considered staggered by the layers of Mn–SO pentahedra and Yb ions (as Figure 5c).

Based on this structural model, the electronic band structure (BS), density of states (DOS), and partial DOS (PDOS) of $YbMnO_3$ were calculated using a virtual cell approximation based on first principles. The calculated band gap is 0 (Figure 6a), which is in accordance with the data summarized in Table 1 but less than the aforementioned experimental value. It is common for theoretically calculated values to be less than the experimental band gap due to the underestimation of band gaps in DFT.60 However, the calculations can still provide useful information about the BS. The DOS and PDOS in Figure 6b clearly show that the VB mainly consists of the O 2p

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Figure 5. Three-dimensional crystal structure of $YbMnO_3$ and atom coordination. (a, b) Coordination around the Yb and Mn centers, respectively; (c, d) three-dimensional crystal structure of $YbMnO_3$ viewed along the $b$ and $c$ axes, respectively.

Figure 6. Electronic band structure, VB spectrum, and electron transitions. (a, b) BS and DOS of $YbMnO_3$ around the Fermi level; (c) VB spectra of $YbMnO_3$ and $ErMnO_3$; (d) mechanism of photoexcited charge carriers.
and Yb 4f orbitals and a small part of the Mn 3d orbitals, whereas the CB mainly consists of the Mn 3d orbitals. However, regarding the valence band maximum (VBM), Figure 6b shows that the uppermost edge comprises Yb 4f, the next one is O 2p, and the third one is Mn 3d. To verify the theoretical predictions, the VBM spectrum of YbMnO₃ was measured and compared with the VB spectrum of ErMnO₃ to reveal the effects of the Yb and Mn elements on the BS. In Figure 6c, two main peaks in regions located at 4–9 and 9–12 eV are assigned to the multiplet structures of Yb⁵⁷, which arise from the resonant photoemission in the 4d–4f excitation region. A bar diagram showing the multiplet structures of Yb⁵⁷ calculated by Cox and Schmidt-May can be found in refs S7 and S8 consistent with the resonant photoemission of the Yb 4f states presented in Figure 6c. Upon replacing Yb with Er, the VB spectrum changes completely within 4–12 eV, but the uppermost VB (i.e., VBM) in the region of 0–4 eV does not, suggesting that the VBM should consist of O 2p or Mn 3d orbitals rather than Yb 4f orbitals. The comparison of the VB spectrum of YbMnO₃ with that of ErMnO₃ confirms not only that the VB of YbMnO₃ mainly consists of Yb 4f orbitals, in accordance with the PDOS presented in Figure 6b, but also the contribution of O 2p or Mn 3d orbitals to the VBM. The difference in the absorption spectrum of YbMnO₃ from those of MnO₂ and Mn₂O₃, as displayed in Figure 3e, reveals that the hybridized states of O 2p and Mn 3d play a significant role in shaping the BS. Based on the available data from XPS, the smallest binding energies for the elements Yb and Mn are 2.0 eV for Yb 4f and 2.8 eV for Mn 3d, respectively, which are consistent with the lower edge of the d and f orbitals in Figure 6b. The smallest binding energy of O is approximately 7.0 eV for O 2p. Nevertheless, the O 2p states spread throughout the VB, which will overlap with the Mn 3d and Yb 4f states due to hybridization. Thus, the BS of YbMnO₃ could be described as shown in Figure S10, and the mechanisms of the absorption and fluorescence spectra displayed in Figure 3b,e could be well explained using this scheme. In Figure 3b, absorption band A is attributed to the charge transfer from O 2p to Mn 3d; bands B and C are attributed to electron transitions from the bonding states xy and x²−y², respectively, to the antibonding 3z²−r² state of Mn 3d; and bands D and E are attributed to electron transitions from the bonding states yz and zx, respectively, to the antibonding 3z²−r² state of Mn 3d. Upon excitation with a 633 nm laser light, as shown in Figure 3e, electrons from the Mn 3d (xy, x²−y²) states were pumped to the CB, which comprises the 3z²−r² state of Mn 3d. With electrons returning to the VB and the (xy, x²−y²) states of Mn 3d, light with peak wavelengths at 878 nm (L center) and 760 nm (H center) was emitted, respectively. The radiance of YbMnO₃, HoMnO₃, and ErMnO₃, which peaks at 878 nm, was much weaker than that of YbMnO₃ due to the strong hybridization of Yb 4f with O 2p. In addition, the high-energy H-center emission peak shifts from 760 nm to higher energy (658 nm) with an increase in the atomic number from Y, Ho, and Er to Yb, possibly caused by the effect of the lanthanide radius contraction with the change in the crystal field on Mn 3d orbital splitting.

Based on the above analyses, we reason out that the generation of charge carriers to produce the photon response shown in Figure 2a,b is caused by the transition from the occupied mixed states of O 2p, Yb 4f and Mn 3dₓ²−r² to unoccupied 3dₓ²−r² states. Intrinsically, this transition could be considered the Mn 3d–3d transition, but the ground state of Mn 3d hybridizes with a considerable amount of the high-energy Yb 4f state through O 2p. The electron transitions that are responsible for the generation of charge carriers are illustrated in Figure 6d.

Finally, we provide a short discussion. To achieve a high PCE, the photogenerated charge carriers, that is, excitons, must be able to move over long distances with long lifetimes before annihilation. Accordingly, the nuclei of atoms must exert a weak force on the charge carriers, the outer s, p, or f orbitals of which should be fully filled by electrons. Moreover, the outermost electrons should be readily excited to form excitons. According to these standards, Pb is an excellent element for PV absorbers due to its [Xe]6s²6p⁶ configuration, and its efficacy has been demonstrated in organohalide–perovskite solar cells. Yb has an electronic configuration very similar to that of Pb, as shown in Figure S11. Thus, replacing Pb with Yb promisingly opens a new route toward developing narrow-bandgap semiconductors for all-oxide solar cells.

### CONCLUSIONS

Four novel lead-free perovskite narrow-bandgap semiconductors, YMnO₃, HoMnO₃, ErMnO₃, and YbMnO₃, were screened from a family of rare-earth manganates RMnO₃ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, and Yb). The results demonstrate that the hexagonal manganates of YMnO₃, HoMnO₃, ErMnO₃, and YbMnO₃ have narrow band gaps, whereas the orthorhombic manganates of LaMnO₃, PrMnO₃, NdMnO₃, SmMnO₃, GdMnO₃, TbMnO₃, DyMnO₃, and YbMnO₃ have no band gaps. Through the solid-state reactions between rare-earth oxides and MnO₂ powder, the orthorhombic manganates of La, Pr, Nd, Sm, Gd, and Tb and the hexagonal manganates of Y, Ho, Er, and Yb were obtained, but CeMnO₃ was not obtained. Eight of the 12 members, that is, LaMnO₃, PrMnO₃, NdMnO₃, SmMnO₃, GdMnO₃, TbMnO₃, DyMnO₃, and YbMnO₃, exhibited a photon response. Nevertheless, no sharp onset was observed from the absorption spectra of orthorhombic LaMnO₃, PrMnO₃, NdMnO₃, SmMnO₃, GdMnO₃, TbMnO₃, and DyMnO₃. The hexagonal YMnO₃ and YbMnO₃ are n-type semiconductors, whereas HoMnO₃ and ErMnO₃ are p-type semiconductors. The hexagonal manganates of Y, Ho, Er, and Yb have similar band gaps; yet, the surface potentials of YMnO₃, HoMnO₃, ErMnO₃, and YbMnO₃ are approximately −4.87, −4.69, −4.36, and −4.71 eV, respectively. Among these family members, YbMnO₃ has a direct band gap of approximately 1.35 eV, whose theoretical Shockley–Queisser efficiency is approximately 33.7% for single- p–n-junction solar cells, exhibiting excellent potential as an absorber for next-generation all-oxide solar cells. The top VB of YbMnO₃ consists of the Yb 4f orbital, which hybridizes with Mn 3d through O 2p, whereas the bottom of the CB consists of the Mn 3d orbital. The charge carriers that generate the PV effect are mainly produced by the transition from the occupied mixed states of O 2p, Yb 4f, and Mn 3dₓ²−r² to the unoccupied 3dₓ²−r² states. This result represents a substantial step toward the exploration of chemically stable and nontoxic narrow-bandgap semiconductors potentially for applications of all-oxide solar cells, photodetectors, photodetectors, or photoelectric devices.
Among the 17 rare-earth elements, 12 were selected in this study. First, powders of RMnO$_3$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb) were synthesized in a solid-state reaction of MnO$_2$ with rare-earth oxides by mixing them together at a stoichiometric ratio of 1:1 for R to Mn and firing them under ambient air at 1000, 1200, or 1300 °C for 4 h. Then, the powders were pressed into disks with diameters of 11 mm and thicknesses of approximately 0.1–0.2 mm. To prevent grain particles from growing too large, the powders that were synthesized at 1000 °C for 2 h were used as precursors to fabricate pellets by mixing with approximately 5% poly(vinyl acetate) as a binder for granulation, pressing under 5 MPa, and sintering at 1350 °C for 24 h in an Ar atmosphere to obtain sufficient densification for photon response measurements. Next, one side of the pellets was sputtered with ITO and the other side was sputtered with gold to serve as electrodes. After being sintered, the surface profile of the pellets was examined with SEM (JSM-6490LV, JEOL). The crystal structures of the RMnO$_3$ powders and pellets were investigated using an X'Pert PRO MPD X-ray diffractometer (PANalytical B.V., Almelo, the Netherlands). Absorption spectra of the powders were recorded with a Shimadzu UV-3600 UV–vis–NIR spectrophotometer equipped with an integrating sphere for the measurement of solid powders. Fluorescence spectra of the powders fired at 1300 °C were first collected using an FLS 920 spectrometer at 77 K, which was cooled with liquid nitrogen, but no spectra were acquired. Then, the fluorescence spectra were recorded using the pellets with a laser confocal Raman spectrometer (LabRAM high Evolution Systems, HORIBA France SAS) pumped with a 633 nm laser at room temperature. XPS and UPS VB spectra of the pellets were measured using a Kratos Axis Ultra equipped with an X-ray source (α-K$_{α}$ $\alpha$=21.2 eV) for UPS. The photon source ($\alpha$=1486.6 eV) for XPS. The XPS and UPS spectra were calibrated with respect to the C 1s signal (284.8 eV). All XPS/UPS samples were analyzed using XPS PEAK4.1 software, through which the atomic ratio was derived by computing the area under the peaks. The photon response was measured using a multichannel scanning electrochemical workstation (Uniscan 370 Princeton Applied Research Scanning Electrochemical Microscopy (SCEM) Workstation). The Hall coefficient, resistivity, carrier concentration, and carrier mobility were tested using a Hall effect measurement system (ET9000, East Changing, China). The surface potential was measured using a Kelvin Probe, equipped with the Perdew–Burke–Ernzerhof (PBE) functional and norm-conserving pseudopotentials was selected as the exchange–correlation functional. When running the geometry optimization, the maximum force and energy tolerances were set as 0.03 eV Å$^{-1}$ and 1.0 $\times$ 10$^{-5}$ eV atom$^{-1}$, respectively, and the maximum displacement was set as 1.0 $\times$ 10$^{-3}$ Å. A 500 eV cutoff energy and a 1 $\times$ 3 $\times$ 3 k-point sampling set were used for convergence.

XRD patterns and absorption spectra of RMnO$_3$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb) powders synthesized at variable temperatures in ambient air; band gaps of RMnO$_3$ (R = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb) evaluated with the Tauc plots using the relationships $\alpha h\nu$ $\propto$ $(E_g - h\nu)^2$ and $\alpha h\nu$ $\propto$ $(E_g - h\nu)^{1/2}$ for direct and indirect transitions, respectively; comparison of XRD patterns between YbMnO$_3$ powder and YbMnO$_3$ pellet; coaction of thermal heating and light irradiation on the photon response of pellets; comparison between the absorption and fluorescence spectra of YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and YbMnO$_3$ pellets; SEM pictures of the surface profile of YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and YbMnO$_3$ pellets; Mn 2p XPS spectrum in YbMnO$_3$; absorption and emission mechanisms of YbMnO$_3$; and comparisons of the electronic configuration of Yb with Pb (PDF)

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L.C. conceived the original idea of this work and put it into practice. The manuscript was written through the contributions of all authors. Each author has commented and approved the final version of the paper.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
ITO, indium tin oxide; FTO, fluorine-doped tin oxide; RMnO3, rare-earth manganates; XRD, X-ray diffraction; UV−Vis−NIR, ultraviolet−visible−near infrared; XPS, X-ray photoelectron spectroscopy; UPS, ultraviolet photoelectron spectroscopy; DFT, density functional theory; BS, band structure; VB, valence band; CB, conduction band; VBM, valence band maximum; DOS, density of states; PDOS, partial density of states

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