Broadband-sensitized upconversion of ATiO$_3$:Er,Ni
(A = Mg, Ca, Sr, Ba)

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Upconverters that utilize two or more low energy photons to generate a single high energy photon are promising materials for solar energy conversion. Herein, we present a broadband-sensitive upconverter to utilize broad solar spectrum ranging from 1060 to 1650 nm which is not utilized by present crystalline Si (c-Si) solar cells. Our calculation shows that the broadband-sensitive upconverters designed can increase the efficiency of c-Si solar cell by $\sim$4.8\%, considering the present value of $\sim$25\% in the optimized c-Si solar cell. We used octahedrally oxygen-coordinated Ni$^{2+}$ ions to harvest 1060–1500 nm photons and transferred the absorbed energies to the Er$^{3+}$ ions. Those photons along with the 1450–1650 nm photons absorbed by the Er$^{3+}$ ions themselves are upconverted to 980 nm, which is efficiently utilized by c-Si solar cells. We optimized the efficiency of the broadband-sensitive upconverters by monitoring host cations and active-ions ($\text{Ni}^{2+}$ and $\text{Er}^{3+}$) concentrations. Absorption and Stokes emission band positions of Ni$^{2+}$ changed remarkably depending on the A-site cations in the ATiO$_3$ (A = Mg, Ca, Sr, Ba) hosts making difference in the Ni$^{2+}$ to Er$^{3+}$ energy transfer efficiencies and hence the overall upconversion (UC) emission intensities. Further, absorption and emission intensities of the Ni$^{2+}$ and Er$^{3+}$ ions largely pronounced in the CaTiO$_3$ host compared to the CaZrO$_3$ due to more distorted nature of the CaTiO$_3$ lattice. Intense Ni$^{2+}$ emission with larger Stokes shift favored efficient Ni-to-Er energy transfer in the forward direction with minimum-energy back transfer making more intense Er$^{3+}$ UC emission in the CaTiO$_3$:Er$^{3+}$,Ni$^{2+}$ upconverter. Thus, to realize efficient broadband-sensitive UC, it is essential to design a host material with low symmetry lattice to confirm higher emission efficiency of Er$^{3+}$ and controlled Ni$^{2+}$ absorption and emission bands to suppress the energy back transfer while maintaining efficient energy transfer in the forward direction.

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Key-words : Broadband-sensitive upconversion, Ni$^{2+}$-sensitization, (Ca/Sr/Ba)TiO$_3$-perovskites, Energy transfer, c-Si solar cells

1. Introduction

Utilization of solar radiation by engineered materials is one of the hot topics of research for the sustainable technology. The mainstream of the research is going on engineering materials that can convert sunlight into electricity via the photovoltaic effect, although there is huge interest for photochemical hydrogen production and photocatalytic decomposition of contaminations using solar radiation.$^{1,2}$ Crystalline silicon (c-Si) is the most notable material used for photovoltaics which generates carriers (electrons and holes) through absorption of photons from the sun light. However, only photons with energies higher than the band gap of such semiconductor materials can generate carriers. Incident photons with energies lower than the band gap of semiconductor (1.1 eV for c-Si) are not absorbed and hence not utilized, limiting the maximum conversion efficiency of single junction solar cells to $\sim$33\% (Shockley-Queisser limit). Thus, the unused infrared radiation provides an important opportunity for enhancing the efficiency of current solar cells for renewable energy generation.$^{3,9}$

Upconverters that utilize two or more low energy photons below the bandgap of semiconductors to generate a single high energy photon are promising materials for solar energy conversion.$^{4,5}$ Further, an upconverter layer can be placed at the back of the solar cell and by converting part of the transmitted NIR photons to wavelengths that can be absorbed by solar cells, it is easy to optimize solar cells and upconverters separately. Large number of reports on upconverters applied to current photovoltaic devices is available recently.$^{6,7}$ Among them, Er$^{3+}$-doped upconverters that absorb photons at around 1500 nm and emit at 980 nm which are suitable for c-Si solar cells, a mainstream of present solar cells, have taken great interest.$^{7,9}$ However, due to the narrow absorption band width of Er$^{3+}$ (1450–1600 nm), only a fraction of the solar spectrum is upconverted making an incremental improvement of solar cell efficiency.$^{10,11}$ To broaden the sensitivity range, we have successfully demonstrated a wide absorption range of 1060–1600 nm using a combination of Ni$^{2+}$ sensitizers and Er$^{3+}$ emitters that can transfer the absorbed energies to the c-Si solar cell absorption range.$^{12,13}$ Six coordinated Ni$^{2+}$ ions absorbed 1060–1450 nm photons and transfer the absorbed energies to the Er$^{3+}$ ions. Thus, the Er$^{3+}$ ions upconvert to 980 nm along with the photons absorbed by themselves at the 1450–1600 nm ranges.

The overall efficiency of the broadband-sensitive upconverter consisting of Ni$^{2+}$ sensitizers and Er$^{3+}$ emitters depends on the Ni$^{2+}$ absorption extent and Ni$\rightarrow$Er energy transfer efficiency besides upconversion (UC) efficiency of the Er$^{3+}$ itself. The energy bands of Ni$^{2+}$ ions (d$^\text{4}$ electronic configuration) are highly susceptible to the neighboring environment in the crystal lattice. Thus absorption and emission band positions and their intensities can be well tuned according to the host cations. Recently, we have successfully tuned the Ni$^{2+}$ absorption and emission band positions and their intensities in the AZrO$_3$:Er,Ni (A = Ca, Sr, Ba) upconverters by manipulating A-site cations.$^{14}$ Substitution of A-site cations with bigger or smaller cations lowered the symmetry around the central Er$^{3+}$ ions and intensified the UC emission. At the same time, significant change in the Ni–O bond...
length was observed which affected the Ni$^{2+}$ absorption and emission band positions and Ni→Er ET efficiencies. Thus, highly efficient UC emission was realized in the CaZrO$_3$:Er,Ni compared to the SrZrO$_3$:Er,Ni and BaZrO$_3$:Er,Ni upconverters.\(^{34}\)

Herein, we aim to further improve the UC performance by substituting Zr-site with Ti$^{4+}$ ions and selecting suitable A-site cations. Lowering the symmetry around the central RE$^{3+}$ ions remarkably improves the UC emission efficiency.\(^{15-17}\) Ionic radius of Ti$^{4+}$ (0.60 Å) is much smaller than that of Zr$^{4+}$ (0.72 Å).\(^{18}\) Thus, the TiO$_6$ octahedra are more tilted (distorted) that lowers the symmetry around the central Er$^{3+}$ ions in the CaTiO$_3$ than in the CaZrO$_3$, leading to more efficient Er$^{3+}$ emission. Further, due to changes in Ni–O bond lengths, the Ni$^{2+}$ absorption intensity and band positions are also affected, which definitely affects the Ni→Er ET efficiencies. Thus, in this report we carried out detailed investigation on the effect of the B-site ions (B = Ti, Zr) for the Ni$^{2+}$ absorption, energy transfer between the Ni$^{2+}$ and Er$^{3+}$, Er$^{3+}$ emission efficiency, and overall broadband-sensitive UC efficiency, as well as that of the A-site ions (A = Mg, Ca, Sr, Ba), and eventually achieved further improved UC efficiency. Based on these experimental results, we derived guidelines for design of the most efficient broadband-sensitive upconverter.

2. Experimental

2.1 Synthesis of Er, Ni-codoped samples

We synthesized powder samples of MgTiO$_3$, CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ doped with 10 mol % Er, and 0.2 mol % Ni. To compensate the charge imbalance caused by the aliovalent Er$^{3+}$ doping at the A$^{3+}$ sites (Mg, Ca, Sr, Ba) 10 mol % Li was simultaneously codoped. 0.4 mol % Nb were codoped for the charge compensation caused by Ni$^{2+}$ doping at the Ti$^{4+}$ sites. CaZrO$_3$ samples codoped with equivalent amount of Er and Ni to that of ATiO$_3$ was also prepared for comparison. The solid state reaction method was employed to synthesize the compound oxide powders. Predetermined amounts of the oxides or carbonates (Kojundo Kagaku, Japan) were well mixed with the help of small rollers were again mixed well and heat-treated at 1300°C for 6 h in air for reaction and crystallization. To reduce the Ni$^{3+}$ if any present during high temperature sintering, the final powders were reduced at 800°C for 3 h by flowing 10% H$_2$/90% N$_2$.

The crystalline structure was identified by X-ray diffraction (XRD) using Cu kα line and a θ–2θ method. Scanning Electron Microscope (SEM) measurements were carried out using a Hitachi SU3500 scanning electron microscope.

2.2 Optical measurements

We prepared samples with a sandwich structure of quartz glass/UC-powder/quartz glass for optical measurements. The thickness of the powder layer was maintained 0.5 mm to assure complete absorption/scattering of the incident photons. Diffuse reflectance spectrum of each sample was recorded using an integrating sphere. Absorption spectra of Ni$^{2+}$ and Er$^{3+}$ were expressed in terms of Kubelka–Munk function. Stokes and UC emission spectra were measured under CW LD illumination at 1180 and 1490 nm. To evaluate the energy transfer rates, time-resolved measurements of the emission intensities were carried out using an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser (7 ns pulse duration). Si and InGaAs photodiodes and suitable bandpass filters were used to collect emitted photons, and the output signal was accumulated using a storage oscilloscope.

3. Results and discussion

3.1 Structure analyses

XRD patterns of the Er, Li, Ni, Nb codoped samples of ATiO$_3$ (A = Mg, Ca, Sr, Ba) are presented in Fig. 1. All the samples are of single phase and well crystallized as indicated by the sharp XRD peaks. No distinguished impurity phases were detected indicating all the doped aliovalent ions (Er$^{3+}$, Li$^{2+}$, Ni$^{2+}$, and Nb$^{5+}$) occupied the perovskite lattice sites. The ideal ABO$_3$ perovskite crystallizes as a cubic structure where the A-site cations form 12-fold cuboctahedrons and B-site cations occupy the center of octahedrons (a 6-fold coordination). However, decreasing the size of the A-site ions, the BO$_6$ octahedrons gradually tilt to accommodate in the dodecahedral cavity which remarkably reduces the symmetry of the crystal.\(^{19}\) We observed perfect cubic structure in the SrTiO$_3$ which reduced to orthorhombic in the CaTiO$_3$ and more distorted rhombohedral in the MgTiO$_3$. On the other hand BaTiO$_3$ favored tetragonal structure due to quite bigger size of Ba as well effect of other additives. The lattice parameters, cell volumes, and crystal symmetries for the Er$^{3+}$, Ni$^{2+}$ codoped (Mg/Ca/Sr/Ba)TiO$_3$ upconverters are summarized in Table 1.

3.2 Morphological analyses

Figures 2(a)–2(d) show the SEM micrographs of the Er, Ni codoped samples of ATiO$_3$ (A = Mg, Ca, Sr, Ba), respectively. Each sample consisted of well crystallized particles with sharp edges and clear boundaries. However, their shape and grain size varied remarkably depending on the host cations. The MgTiO$_3$ sample exhibited irregular particles with quite bigger particles size ranging between 2 to 10 μm. The CaTiO$_3$ particles were more regular and within narrow size distribution ranging between 2 to 5 μm. The SrTiO$_3$ sample exhibited regular cubic shape particles connected with each other and exhibited further narrower size distribution that ranges between 1 to 2 μm. On the other
hand, BaTiO$_3$ particles are quite small in the submicron ranges ($\sim$500 nm diameter) and exhibited spherical shapes with homogeneous size distribution.

3.3 Absorption and UC emission properties

Absorption spectra of the Ni, Er codoped ATiO$_3$ (A = Mg, Ca, Sr, Ba) samples in the NIR range are presented in Fig. 3. Absorption peaks located around 1500 and 970 nm were assigned to the $f$-$f$ transitions of Er$^{3+}$ ions, namely, transitions from the ground state ($^4I_{15/2}$) to the first excited state ($^4I_{13/2}$) and second excited state ($^4I_{11/2}$), respectively.6,20) Rather broad and comparatively weak absorption bands between the two Er$^{3+}$ absorption peaks was originated from the $3A_2(3F)$ ground state to the $3T_2(3F)$ excited state transition of the six coordinated Ni$^{2+}$ ions located at the center of the TiO$_6$ octahedra in the ATiO$_3$ hosts.21) The Ni$^{2+}$ ions absorption band positions ranged from 1000 to 1500 nm in the CaTiO$_3$ and SrTiO$_3$ samples while they were extended to longer than 1600 nm in the MgTiO$_3$ and BaTiO$_3$ samples. However, there was no change on the absorption peak positions of the Er$^{3+}$ ions with variable A-site cations except slight changes in the peak shape and intensity. It clearly suggests that the Ni$^{2+}$ absorption bands position can be well tuned by varying the A-site cations while maintaining the Er$^{3+}$ absorption peak position unchanged.

UC emission spectra of the ATiO$_3$:Er$^{3+}$,Ni$^{2+}$ (A = Mg, Ca, Sr, Ba) samples excited at 1490 nm (direct Er$^{3+}$ excitation) and 1180 nm (through indirect Ni$^{2+}$ excitation) are presented in Figs. 4(a) and 4(b), respectively. Strong UC emission at around 980 nm, typical for the Er$^{3+}$ ions, was observed in all the samples under both the Er$^{3+}$ and Ni$^{2+}$ excitations. Under the 1180 nm excitation, the excitation light is absorbed by the Ni$^{2+}$ ions, the absorbed energies are transferred to the nearby Er$^{3+}$ ions followed by the Er$^{3+}$ UC emission. Clear and strong UC emission under the Ni$^{2+}$ excitation, similar to that of direct Er$^{3+}$ excitation, suggests that the energy absorbed by the Ni$^{2+}$ ions transferred to the Er$^{3+}$ ions followed by the Er$^{3+}$ UC emission. The detail of the Ni$^{2+}$ → Er$^{3+}$ energy transfer phenomena will be discussed later.

Excitation power dependent UC intensity plots presented in Fig. 5 suggest that the UC is two photon process under the direct Er$^{3+}$ excitation (at 1490 nm) as well as indirect Ni$^{2+}$ excitation (at 1180 nm). However, the UC intensity was strongly dependent on the excitation wavelengths. Direct Er-excited UC intensities were more than twofold intense compared to the indirect Ni$^{2+}$ excitation under similar excitation power densities. The main reason of such difference might be the difference of absorbance at different wavelengths. Figure 3 clearly shows that the Ni$^{2+}$ absorbance at 1180 nm is quite weak compared to the Er$^{3+}$ absorbance at 1490 nm. The UC emission intensities depend quadratically on the absorbance. Thus, the stronger UC emission is expected when excited at 1490 nm. Further, the UC emission intensities are

![Fig. 2. SEM images of the ATiO$_3$:Er,Ni samples; (a) = Mg, (b) = Ca, (c) = Sr, and (d) = Ba prepared by solid state reaction at 1300°C for 6h in air ambient.](image1)

![Fig. 3. Absorption spectra of the Ni, Er codoped ATiO$_3$ samples (A = Mg, Ca, Sr, Ba) in the NIR range.](image2)

![Fig. 4. UC emission spectra of the ATiO$_3$:Er$^{3+}$,Ni$^{2+}$ (A = Mg, Ca, Sr, Ba) samples under (a) 1490 nm and (b) 1180 nm CW laser excitations.](image3)
strungly dependent on the host cations exhibiting the order CaTiO₃ > SrTiO₃ > MgTiO₃ > BaTiO₃ under the 1490 nm excitation. The order was more pronounced under the 1180 nm excitation. The detail of the host ions dependent UC emission variation will be discussed in the consecutive section. In conclusion, the CaTiO₃:Er³⁺,Ni²⁺ is the most efficient broadband-sensitive upconverter under both the 1490 and 1180 nm excitations.

3.4 Host ions dependent Er³⁺ UC

Figure 6 summarizes the Er³⁺ UC emission intensities for the Er, Ni codoped ATiO₃ (A = Mg, Ca, Sr, Ba) upconverters and control samples (Er-only doped) under the 1490 and 1180 nm excitations. For the Er-only doped samples, the UC emission intensities are in the order of MgTiO₃ > CaTiO₃ > SrTiO₃ > BaTiO₃ and can be explained on the basis of crystal symmetries around the central Er³⁺ ions in those hosts. Although all the ATiO₃ exhibit perovskite type crystal structures, they have different space group symmetries. As seen by the XRD patterns in Fig. 1, SrTiO₃ exhibits perfect cubic structure (highest symmetry around the central Er³⁺ ions), the symmetry is lowered to the tetragonal in BaTiO₃, to orthorhombic in CaTiO₃ and more distorted rhombohedral in MgTiO₃. It is well reported that f-f transitions of rare-earth ions is more pronounced in the lower symmetry sites exhibiting higher emission efficiency.¹⁰),¹³),²²),²³)

Thus, Er³⁺ ions located at the lower symmetry Mg²⁺ and Ca²⁺ sites should exhibit more intense UC emission than those at the higher symmetry Sr²⁺ and Ba²⁺ sites and very similar trend was observed for the Er³⁺-only doped ATiO₃:Er upconverters as shown in Fig. 6. Although the symmetry of BaTiO₃ is lower than that of SrTiO₃, the UC emission of the Ba sample is weaker. The Ca sample exhibits most intense UC emission for both Er-only doped and Er, Ni codoped samples. The difference caused by Ni codoping is dramatic decrease for the Mg samples. The order Ca > Sr > Ba does not change. Thus, besides Er³⁺ UC emission efficiency, the Ni → Er energy transfer and Ni→→Er energy back transfer efficiencies should play significant roles for the overall broadband-sensitive UC efficiencies of the Er, Ni codoped samples and corresponding discussion is presented in the following section.

3.5 Host ions dependent energy transfer between Ni²⁺ and Er³⁺

Strong UC emission of the ATiO₃: Ni²⁺, Er³⁺ (A = Mg, Ca, Sr, Ba) samples under the Ni²⁺ excitation at 1180 nm similar to the direct Er³⁺ excitation at 1490 nm suggests that the energy absorbed by the Ni²⁺ ions transferred to the Er³⁺ ions followed by Er³⁺ UC. To confirm the energy transfer from the Ni²⁺ to the Er³⁺ in the ATiO₃:Ni²⁺, Er³⁺ (A = Mg, Ca, Sr, Ba) samples, Stokes emission spectra excited at 1180 nm (Ni²⁺ excitation) were recorded as shown in Fig. 7. The Ni²⁺-only doped control samples (ATiO₃:0.2 mol% Ni²⁺) exhibited broad emission bands ranging from 1200 to 1600 nm similar to the previous reports,²¹) except an extremely broad emission band for the MgTiO₃ sample. Deconvolution of the measured spectrum of the MgTiO₃:Ni²⁺ sample by multi-peak fitting found that the spectrum consisted of two peaks, one from ~1250–1500 nm and the other ~1300 nm to longer than 1600 nm. Existence of two types of Ni²⁺ ions in the MgTiO₃ host might be the origin of the two emission bands. By introducing 10 mol% Er (ATiO₃:0.2 mol% Ni²⁺, 10 mol% Er³⁺), the Ni²⁺ emission bands around 1200–1600 nm quenched and emission bands around 1450–1600 nm, corresponding to the Er³⁺, appeared. However, the extent of quenching (calculated from the ratio of integrated emission intensities over 1250–1450 nm for the Ni, Er-codoped and Ni-only doped samples) differed remarkably depending on the host cations. The Ni²⁺ emission was perfectly quenched in the CaTiO₃, whereas it was quenched by more than 80% in the SrTiO₃ and ~70% in the BaTiO₃. For the MgTiO₃, the quenching was only around 50%. It suggests that the energy transfer from the Ni²⁺ sensitizers to the Er³⁺ emitters is close to unity in the CaTiO₃ sample while it is very low for the MgTiO₃ sample, being intermediate for the SrTiO₃ and BaTiO₃. Further, the Ni²⁺ emission bands were suppressed in the whole range (1200–1600 nm) irrespective of the overlapped region with that of the Er³⁺ absorption bands. It suggests that the Ni²⁺ to Er³⁺ energy transfer process is a nonradiative one.²¹) If reabsorption of the Ni²⁺ emission by the Er³⁺ were the dominant
mechanism of the energy transfer, the Ni$^{2+}$ emission would remain unaffected outside the Er$^{3+}$ absorption band of 1450–1600 nm.

The energy transfer efficiencies from Ni$^{2+}$ to Er$^{3+}$ were calculated from the measured time decay profiles of the Ni$^{2+}$ emissions in the Ni-only doped and Ni, Er codoped samples excited by the 1200 nm pulse. Figure 8(a) shows the results of the Ni$^{2+}$ emissions at 1400 nm (collected through a bandpass filter with a 50 nm window centered at 1400 nm) for the Ni-only doped samples (no Er) compared with those for the Er, Ni codoped samples in Fig. 8(b). The decay profiles of the Ni$^{2+}$ emission for the Ni-only doped samples are fitted using two-exponential functions as expressed in Eq. (1), and the Ni$^{2+}$ lifetimes ($\tau_{\text{Ni}}$) are determined by Eq. (2)\textsuperscript{25-27}

$$I_{\text{Ni,Er}}(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2),$$

$$\tau_{\text{Ni}} = (a_1 \tau_1^2 + a_2 \tau_2^2)/(a_1 \tau_1 + a_2 \tau_2)$$

where, $\tau_1$ and $\tau_2$ are the fast and slow decay times and $a_1$ and $a_2$ are the amplitudes. The $\tau_{\text{Ni}}$ values of the Ni$^{2+}$ emission for these samples are summarized in Table 2.

For the Er, Ni codoped samples, the decay rate was higher and completed within microseconds. It suggested that the excited state energies of Ni$^{2+}$ donors transfer rapidly to the Er$^{3+}$ acceptors. The energy transfer from the Ni$^{2+}$ donors to the Er$^{3+}$ acceptors can be expressed as in Eq. (3) if the energy migration among the donors is significant\textsuperscript{24,28,29} whereas it is expressed as in Eq. (4) if the migration is negligibly weak\textsuperscript{20,30-32}

$$I_{\text{Ni,E}r,\text{Er}}(t) = \exp(-w_{\text{Ni,Er}})I_{\text{Ni,only}}(t)$$

$$I_{\text{Ni,E}r,\text{N}i}(t) = \exp(-\gamma_{\text{Ni,E}r,\text{Ni}} \sqrt{t})I_{\text{Ni,only}}(t)$$

In the present case, the experimental data are well fitted by Eq. (4) using a fitting parameter $\gamma_{\text{Ni,E}r,\text{Ni}}$ in Eq. (3), with the previously determined $I_{\text{Ni}}(t)$ for each sample. This is consistent with the facts that the Ni concentration is quite low (0.2 mol %) to get pairing for energy migration among Ni ions and the energy transfer is rapid completing within sub-milliseconds. Using these two equations in Eqs. (1) and (4), the energy transfer efficiency $\eta_{\text{Ni,E}r}$ is expressed as follows,

$$\eta_{\text{Ni,E}r} = 1 - \int_0^\infty dt I_{\text{Ni,Er,codepo}}(t) \left[ \int_0^t dt I_{\text{Ni,Er}}(t) \right]$$

Table 2 also summarizes the resultant values for various samples. The $\eta_{\text{Ni,E}r}$ values in the order CaTiO$_3$ > SrTiO$_3$ > BaTiO$_3$ > MgTiO$_3$. It is clear that almost all the energy absorbed by the Ni$^{2+}$ ions transferred to the Er$^{3+}$ ions in the CaTiO$_3$ sample while only a fraction of the energy transferred in other samples. It might be the reason that the Ni$^{2+}$ emission were still detected even after sufficient amount of Er$^{3+}$ doping for the Mg sample. For the BaTiO$_3$; Er,Ni sample, despite sufficiently high (>86%) Ni→Er ET value, significant Ni$^{2+}$ emission peak was still detected and could not be explained on the Ni→Er ET alone.

In fact, the energies transferred from the Ni$^{2+}$ sensitizers to the Er$^{3+}$ emitters can return back to the Ni$^{2+}$ centers if the Ni$^{2+}$ absorption bands overlap with the Er$^{3+}$ emission bands which affects the Ni$^{2+}$ and Er$^{3+}$ steady state emission intensities significantly. To quantify the energy back transfer from the Er$^{3+}$ to the Ni$^{2+}$ (Ni→Er), we measured the emission spectra of the Er$^{3+}$ in

![Fig. 7. Stokes emission spectra of the Ni in the Ni-only doped ATiO$_3$ (A = Mg, Ca, Sr, Ba) samples compared to the Er, Ni codoped ones when excited at 1180 nm. Black dashed line in Fig. 7(a) is the deconvolution of the Ni$^{2+}$ emission peak. A long pass filter with a cut-off wavelength at 1250 nm was used to eliminate the excitation light at 1180 nm. Abrupt decrease of signal at around 1580 nm is due to the low sensitivity of the detector.](image)

![Fig. 8. Time evolution of the Ni$^{2+}$ emission at 1400 nm of the (a) Ni-only doped samples and (b) Ni, Er-codoped samples under the 1200 nm pulsed excitation. Solid black lines are the results of fitting using Eqs. (1) and (4).](image)

| Hosts | $\tau_{\text{Ni}}$ (ms) | $\eta_{\text{Ni,E}r}$ (%) | $\eta_{\text{Ni,Ni}}$ (%) |
|-------|-----------------|-----------------|-----------------|
| MgTiO$_3$ | 0.15 | 37 | 82 |
| CaTiO$_3$ | 0.79 | 97 | 9 |
| SrTiO$_3$ | 0.90 | 88 | 18 |
| BaTiO$_3$ | 0.19 | 86 | 71 |

Table 2. Lifetime of the Ni$^{2+}$ emission ($\tau_{\text{Ni}}$) in the Ni-only doped samples (no Er), and Ni-to-Er forward ($\eta_{\text{Ni,E}r}$) and backward ($\eta_{\text{Ni,Ni}}$) energy transfer efficiencies for the Er, Ni codoped samples

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the Er-only doped and Er, Ni-codoped samples and results are presented in Fig. 9. For the CaTiO₃ sample, the Er³⁺ emission peak intensity at ~1550 nm was suppressed by less than 10%, indicating negligible Ni–Er energy back transfer. It was reduced by ~18% in the SrTiO₃, whereas the reductions were ~71% for the BaTiO₃ and ~82% for the MgTiO₃ samples. It suggests that major fraction of the energies transferred from the Ni²⁺ sensitizers to the Er³⁺ emitters again came back to the Ni²⁺ in the BaTiO₃ and MgTiO₃ samples. This is the reason of detecting significant Ni²⁺ emission band in those samples even after sufficient amount of Er³⁺ codoping. It has been well reported that larger the spectral overlap between the donor (Er³⁺) emission band with the acceptor (Ni²⁺) absorption band, higher energy back transfer is expected.²⁰,²⁵ As seen in Fig. 3, the absorption band of Ni²⁺ extended to longer than 1600 nm in MgTiO₃ and BaTiO₃ samples, although the Er³⁺ emission band position remained almost constant. The detail of the Ni²⁺ absorption and emission band positions according to the host cations have been discussed in our previous reports.¹²,¹⁴ Stronger overlap of Er³⁺ emission bands with the Ni²⁺ absorption bands in the MgTiO₃ and BaTiO₃ samples exhibited larger Ni–Er energy back transfer values and deteriorated the Er³⁺ UC emission intensities. We also conducted the time-resolved measurements of the Er³⁺ Stokes emission at 1550 nm after the pulsed excitation at 1490 nm for the Er-only and Er, Ni-codoped samples, however, the Ni-emission was included at 1550 nm because of the extended Ni²⁺ absorption bands to longer than 1550 nm in some samples (see Fig. 3) and it was quite difficult to extract the Er-only contribution in the Er, Ni codoped samples. Thus, we determined the energy back transfer efficiencies (Ƞₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑ euler) using Stokes emission intensities.

Figure 10 compares the UC emission intensities of the optimized CaTiO₃:Er³⁺,Ni²⁺ upconverter with the previously reported CaZrO₃:Er³⁺,Ni²⁺ upconverter under the 1180 and 1490 nm excitations. The UC intensities excited at 1180 and 1490 nm are normalized separately. It clearly suggests that the newly developed CaTiO₃:Er³⁺,Ni²⁺ upconverter is more than 3 folds efficient than the CaZrO₃:Er³⁺,Ni²⁺ one when directly excited at the Er³⁺ absorption band (1490 nm). It is well known that the Er³⁺ absorption and emission intensities are pronounced in the hosts with more distorted lattice.²²,³³ As discussed earlier, CaTiO₃ has more distorted lattice compared to the CaZrO₃. As a result, Er³⁺ ions exhibited more pronounced absorptions at ~970 and 1500 nm [Fig. 10(b)]. More strained nature of the CaTiO₃ host is further supported by the peak broadening of f–f transitions (Er³⁺ ion) around 1500 nm. Clear Stark splitting of the 4I_{15/2}→4I_{13/2} transition (Er³⁺ ion) was observed in the CaZrO₃ exhibiting two peaks at 1470 and 1530 nm, which was merged to single broadened peak in the CaTiO₃. Increased absorption at 1500 nm obviously intensified the UC emission at 980 nm. The UC emission intensity at 980 nm is further improved due to higher 4I_{15/2}→4I_{11/2} transition probabilities of Er³⁺ in the CaTiO₃ with more distorted lattice. The difference is more pronounced for the Ni²⁺ excitation at 1180 nm that exceeds by 7 folds. At the Ni²⁺ absorption band (1180 nm), the increase of absorbance is incremental. Thus, the large difference of the UC emission intensity should have originated from the higher Ni–Er ET in the CaTiO₃:Er³⁺,Ni²⁺ (~97%) compared to the ~86% in the CaZrO₃:Er³⁺,Ni²⁺.¹⁵ Further, the Ni–Er energy back transfer is minimum for the CaTiO₃:Er³⁺,Ni²⁺ (~9%) compared to ~31% in the CaZrO₃:Er³⁺,Ni²⁺. The difference originated due to suitable Ni²⁺ absorption band locations in the CaTiO₃ which is not overlapped with the Er³⁺ emission band at 1550 nm. On the contrary, substantial overlap was observed for the CaZrO₃ sample making larger Ni–Er energy back transfer. Thus for the design of efficient broadband-sensitive upconverters, efficient Er³⁺ and Ni²⁺ emissions, and higher Ni–Er energy transfer with minimal energy back transfer...
are desired. This is possible by selecting proper host with lowest symmetry (e.g., CaTiO$_3$) to realize highest Er-UC efficiency while maintaining narrow Ni-emission bands and larger Stokes shift to surpass the backward energy transfer maintaining sufficient forward energy transfer.

Figure 11 shows the broadband sensitivity of the most efficient CaTiO$_3$:Er,Ni upconverter. It is clear that photons of solar radiation in the range of ~1060–1650 nm can be upconverted to ~980 nm which is just below the c-Si absorption range and can be efficiently harvested by the c-Si solar cell. If all the photons ranging from 1060 to 1650 nm are perfectly upconverted, the improvement in the short-circuit current density ($J_{SC}$) is ~8.1 mA/cm$^2$ under AM1.5G 1 sun illumination. At present, the optimal c-Si solar cell conversion efficiency is ~25% with $J_{SC}$ ~40 mA/cm$^2$. Assuming perfect UC, the newly developed CaTiO$_3$:Ni$^{2+}$,Er$^{3+}$ broadband-sensitive upconverter can improve the conversion efficiency by ~4.8% for the c-Si solar cells. However, to realize such increased c-Si solar cell efficiency, further improved Ni$^{2+}$ absorption and Er$^{3+}$ UC emission efficiency are essential.

4. Conclusion

In this study, we synthesized a series of ATiO$_3$:Er$^{3+}$,Ni$^{2+}$ (A = Mg, Ca, Sr, Ba) upconverters and carried out their structural and optical characteristics. Absorption and emission band positions of the Ni$^{2+}$ sensitizers in the ATiO$_3$:Er$^{3+}$,Ni$^{2+}$ upconverters determine the energy transfer between the Ni$^{2+}$ and Er$^{3+}$ and resultant Ni$^{2+}$-sensitized broadband-sensitive UC efficiencies. The Ni$^{2+}$ absorption and emission band positions and hence the Ni$^{2+}$ to Er$^{3+}$ forth and backward energy transfer efficiencies can be well tuned by properly selecting the host cations in the ABO$_3$-type perovskites. Among them, CaTiO$_3$:Er$^{3+}$,Ni$^{2+}$ exhibited most intense broadband-sensitive UC emission due to efficient Ni$^{2+}$→Er$^{3+}$ energy transfer efficiency reaching near to unity with minimal Ni→Er energy back transfer. The UC emission intensity was further improved due to higher Er$^{3+}$ UC efficiency owing to the lower crystal symmetry. Although MgTiO$_3$:Er$^{3+}$ possesses high Er$^{3+}$ UC emission efficiency, MgTiO$_3$:Er$^{3+}$,Ni$^{2+}$ exhibited poor broadband-sensitive UC due to smaller Ni→Er forward and larger Ni→Er energy transfer efficiencies. Higher symmetry of Er$^{3+}$ ions in the (Ba/Sr)TiO$_3$ hosts lowered the UC emissions in the (Sr/Ba)TiO$_3$:Er$^{3+}$,Ni$^{2+}$. Thus, for the efficient broadband-sensitive UC to realize, a host material containing low symmetry sites to achieve efficient Er$^{3+}$ emission and controlled absorption and emission bands of Ni$^{2+}$ to suppress the energy back transfer while maintaining efficient energy transfer in the forward direction is essential. The broadband-sensitive upconverter can be used to harvest wide solar radiation ranging from 1060 to 1650 nm which is not utilized by present c-Si solar cells. Assuming ideal UC, the upconverter can increase the conversion efficiency of present c-Si solar cell by 4.8% (assuming present value ~25%).

Acknowledgements This work was partially supported by Advanced Low Carbon Technology Research and Development Program (ALCA), Japan Science and Technology Agency.

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