

INFLUENCE OF HYGROSCOPY ON THE OPTICAL PROPERTIES OF THE UP-CONVERTER $\text{BaCl}_2:\text{Er}^{3+}$

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ABSTRACT: A conventional silicon solar cell transmits about 20% of the solar spectrum. A way to reduce these transmission losses is up-conversion, where low energy photons are coupled together to form a photon with energy sufficient to create an electron-hole-pair in the solar cell. An up-converter applied to the rear of a bifacial solar cell therefore leads to a spectral response at wavelengths beyond the conventional absorption range of the solar cell.

For the application to crystalline silicon solar cells the most promising up-converters are host materials doped with trivalent erbium (Er^{3+}), where both the up-conversion efficiency and excitation range are strongly dependent on the properties of the host material. Beside sodium yttrium fluoride doped with trivalent erbium ($\text{NaYF}_4:\text{Er}^{3+}$), which to date is the most efficient up-converter under excitation at about 1500 nm, barium chloride doped with trivalent erbium ($\text{BaCl}_2:\text{Er}^{3+}$) is proposed to be an efficient up-converter due to advantageous phononic properties [1]. A drawback of chloride materials is hygroscopy, the property to attract water from surrounding air. Within this paper the influence of the hygroscopic properties of barium chloride on the optical properties and the consequence on the up-conversion performance of $\text{BaCl}_2:\text{Er}^{3+}$ are investigated.

Keywords: Up-conversion, Third Generation

1 INTRODUCTION

Up-conversion is an approach to reduce transmission losses by converting photons of the solar spectrum with energy less than the band gap of the solar cell into photons, which are able to generate electron hole pairs within the solar cell. In form of an extra layer on the rear of a bifacial solar cell such an up-converter increases the amount of photons accessible by the solar cell (see Figure 1a). The general theoretical potential of this concept was calculated by Trupke *et al.* [2] and with focus on silicon solar cells including the properties of available up-converters by Strümpel *et al.* [3]. Experimentally the successful application of an up-converter to a silicon solar cell has been demonstrated by Shalav *et al.* [4].

There is a wide variety of materials showing up-conversion, where for the application to silicon solar cells erbium doped materials are most promising [5]. This is due to the electronic structure of these ions, which leads to the excitation of the up-conversion process at about 1500 nm, which corresponds to energies lower than the band gap of silicon at 1.12 eV at 300 K ($\lambda_{\text{bandgap}} = 1100 \text{ nm}$), while the resulting emissions are at 980 nm and shorter wavelengths, which is within the

absorption range of silicon. The energy levels of trivalent erbium are schematically drawn in Figure 1b, including the possible excitations under absorption at about 1500 nm (upward arrows) and the resulting emissions (downward arrows).

Due to the shielding of the energy levels, which are responsible for the optical transitions, by outer shells in the erbium ion, the approximate location of the excitation and emission wavelengths are largely independent on the host material, whereas the exact excitation and emission wavelengths and the efficiency of the up-conversion process strongly depend on the properties of the host material. This influence can be ascribed to two main effects.

The first is Stark splitting, which means the splitting of the energy levels due to the electric field caused by the host material ions surrounding the erbium ion. This determines the exact location (in the range of tens of nm) and the shape and broadness of the excitation range. As illustrated in Figure 2, this effect leads to a much broader excitation range for the host material yttrium fluoride (YF_3) than for BaCl_2 [1]. The broadness of the energy levels is not only important regarding the amount of photons accessible in principle for the up-conversion process. In fact the overlap of energy levels is enhanced

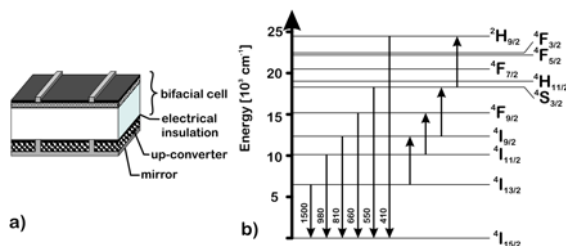


Figure 1: a) Arrangement of an up-converter applied to the rear of a bifacial solar cell, b) energy level diagram of trivalent erbium. The upward arrows indicate possible excitations at about 1500 nm. The emissions as a result of the up-conversion process (downward arrows) are all within the absorption range of silicon.

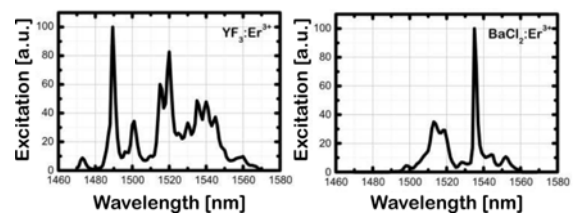


Figure 2: Excitation spectra of $\text{YF}_3:\text{Er}^{3+}$ and $\text{BaCl}_2:\text{Er}^{3+}$ under emission at 550 nm [1]. Due to stronger Stark splitting (the splitting of the energy level of the active ion due to the electric field of the surrounding host material ions) the excitation range of the fluoride is much broader than of the chloride.

by extended energy levels, which supports energy transfer mechanisms on which several up-conversion mechanisms are based. This enhances the probability of these up-conversion processes.

The second influence of the host material arises from the phononic properties. On one hand the probability of phonon assisted energy transfer mechanisms is enhanced when suitable phonons are present, but on the other hand also loss mechanisms (e.g. cross relaxation) are supported.

This demonstrates the complex dependency of the up-conversion properties on the host material. The most efficient up-converter under excitation at about 1500 nm known to date is erbium doped sodium yttrium fluoride ($\text{NaYF}_4:\text{Er}^{3+}$), which is assigned to a very low phonon energy compared to other fluorides [6]. Generally chlorides are expected to have more advantageous phononic properties as shown by investigations of Ohwaki and Wang [1]. They compared YF_3 and BaCl_2 doped with trivalent erbium and found much higher up-conversion efficiencies for BaCl_2 than for YF_3 , even if the broadness of the excitation range is smaller for BaCl_2 . Therefore chlorides seem to be very promising regarding an application as up-converter host material.

A drawback of these compounds for this application might be hygroscopy, the effect of absorbing water when exposed to humidity. The results of the hydration of anhydrous BaCl_2 are either a stable form of hydrated barium chloride as the dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) or incomplete hydration products such as mono and half-hydrates or even compounds with unknown water contents ($\text{BaCl}_2 \cdot x\text{H}_2\text{O}$) [7]. Dihydrates can be prepared reproducibly from aqueous solution [8] or by controlled back hydration [7]. Hydrated barium chloride can be dehydrated by heating to temperatures between 80 and 180°C or higher [9].

The discussion of the complex influence of the host material properties on the up-conversion performance prepares the ground for the assumption that hygroscopy of barium chloride strongly influences the up-conversion performance.

2 EXPERIMENTAL SETUP

2.1 Preparation of the Up-converters

To produce the erbium doped barium chloride based up-converters, barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and erbium chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$) were dried at 180°C for several hours for dehydration. The dried powders were carefully mixed and sintered at about 1000°C for one hour under N_2 -atmosphere.

$\text{NaYF}_4:\text{Er}^{3+}$ (20%) was processed by T. Nann at FMF Freiburg.

The powder-shaped up-converters were put in solid shape using the transparent binder Zapon lacquer. Due to a high amount of volatile organics in the binder, after drying the percentage of binder in the sample is below 6 weight%.

2.2 Measurement setup

The up-converter samples were attached to the rear of a bifacial silicon solar cell using a refractive oil to

enhance the optical contact. The details of the solar cell design and the processing can be found in [10].

The excitation spectra in the infrared part of the spectrum (1470 – 1590 nm) were taken using a setup provided by University of New South Wales (UNSW) and described in detail in [11]. The excitation source was a Santec laser with a spot diameter of about 0.8 mm and 3 mW excitation power.

Reflection measurements were performed using a Cary 5e spectrophotometer with an integrating sphere.

3 EXPERIMENTAL RESULTS

In Figure 3 the comparison of the excitation and the absorption spectra of the two different up-converters $\text{BaCl}_2:\text{Er}^{3+}$ and $\text{NaYF}_4:\text{Er}^{3+}$ are shown. The excitation spectra were taken by measuring the short circuit current of a bifacial silicon solar cell with the corresponding up-converter applied to the rear. For $\text{NaYF}_4:\text{Er}^{3+}$ both spectra agree very well, while for $\text{BaCl}_2:\text{Er}^{3+}$ the absorption is much broader than the excitation spectrum. From this it can be concluded that a high amount of photons is absorbed without contributing to the up-conversion process, which implies that the up-conversion is disturbed by parasitic absorption.

To determine the reason for this parasitic absorption reflection measurements on heat treated samples of pure BaCl_2 (without erbium) were performed. The results of the reflection measurements are shown in Figure 4. The two main absorptions found experimentally are given in Table I. It is highly likely that the absorptions occurring around 1500 nm are due to the combination of the symmetric (ν_{symm}) and asymmetric (ν_{asymm}) vibrational modes of two crystallographically non-equivalent water molecules in hydrated BaCl_2 . Explicit measurements of combination $\nu_{\text{symm}} + \nu_{\text{asymm}}$ were not found in the literature for BaCl_2 , but for the very similar compound $\text{NaBr}_2 \cdot 2\text{H}_2\text{O}$ the absorption at 1440 nm was clearly assigned to the ($\nu_{\text{symm}} + \nu_{\text{asymm}}$)-band [12]. For the single vibrations in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ several experimental figures were found in the literature. A very detailed description of the vibrations of these water molecules is given by Kondyurin *et al.* [13], where also corrections of misinterpretation in earlier publications are made. The wavenumbers of the vibrations found experimentally by

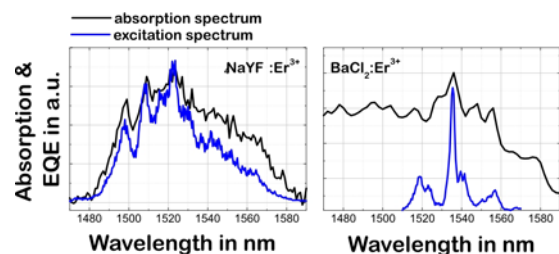


Figure 3: Comparison of the excitation and the absorption spectra of $\text{NaYF}_4:\text{Er}^{3+}$ and $\text{BaCl}_2:\text{Er}^{3+}$. For $\text{NaYF}_4:\text{Er}^{3+}$ both spectra agree very well, while for $\text{BaCl}_2:\text{Er}^{3+}$ this is not the case. Obviously the host material absorbs photons, which do not contribute to the up-conversion process.

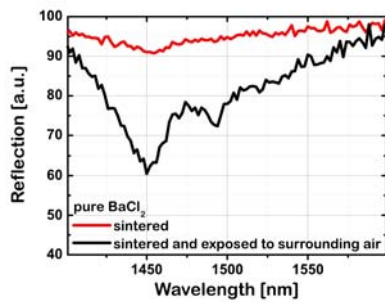


Figure 4: Comparison of the reflection of un-doped barium chloride after sintering at about 1000°C (red line) and after exposing the sample to surrounding air for about 1 week. Due to the exposing to surrounding air absorptions at 1450 and 1494 nm occur.

Kondyurin *et al.* (and relevant for our purposes) are given in Table I, together with the location of the combination of the two modes ($\nu_{\text{symm}} + \nu_{\text{asymm}}$) estimated from this data. The difference between the exact positions of the absorption found in our experiments and calculated from literature might be caused by differences in the hydration state. Lutz *et al.* [7] showed that for mono- and half-hydrates a shift to higher wavenumbers takes place, which equals a shift to shorter wavelengths. In this publication no distinction between crystallographically inequivalent water molecule positions is mentioned.

4 CONCLUSION

It has been shown that the incorporation of water molecules due to hygroscopy in barium chloride is leading to absorption at wavelengths that interfere with the up-conversion excitation range of trivalent erbium. The absorptions can be assigned to the combination of the symmetric and asymmetric vibrational modes of the incorporated water molecules. This parasitic absorption very likely detaches photons from the up-conversion process and lowers therefore the up-conversion efficiency of $\text{BaCl}_2:\text{Er}^{3+}$ when hydrated. Dehydration by sintering the compound can reduce the parasitic absorption. Regarding the application of $\text{BaCl}_2:\text{Er}^{3+}$ as an up-converter to solar cells, it is absolutely necessary to ensure an airtight application directly after heat treatment.

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Table I: Positions of the absorption of pure barium chloride with unknown hydration state around 1500 nm. For comparison the wavenumbers found in literature for the single vibrations - symmetric ν_{symm} and asymmetric ν_{asymm} - of the two crystallographically non-equivalent water molecules (I and II) in the barium chloride dihydrate $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and in the half- and mono-hydrate are given. The positions of the infrared absorption for the combination of both vibrations $\nu_{\text{symm}} + \nu_{\text{asymm}}$ are calculated from these data. The occurrence of two different absorptions found in this investigation might be due to two different crystallographically non-equivalent water molecules as described in [13].

	Position of absorption			Ref.
	ν_{symm} [cm^{-1}]	ν_{asymm} [cm^{-1}]	$\nu_{\text{symm}} + \nu_{\text{asymm}}$ [nm]	
this investigation				
$\text{BaCl}_2 \cdot x\text{H}_2\text{O}$			1450 & 1494	
Literature data				
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O-I}$	3330	3383	1490	[13]
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O-II}$	3330	3459	1473	[13]
$\text{BaCl}_2 \cdot 1/2\text{H}_2\text{O}$	3550	3399	1439	[7]
$\text{BaCl}_2 \cdot 1\text{H}_2\text{O}$	3545	3446	1430	[7]

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