The paper discusses the potential of several Yb-doped scheelite-like double tungstate crystals for sunlight down-conversion. Four hosts NaY(WO$_4$)$_2$, NaY$_{1/2}$Gd$_{1/2}$(WO$_4$)$_2$, NaY$_{2/3}$Gd$_{1/3}$(WO$_4$)$_2$, and NaY(Mo$_{1/2}$W$_{1/2}$O$_4$)$_2$ with the same 10% at. Yb doping level were comparatively investigated. Besides that, the effect of increase the Yb concentration from 10 at.% to 15 at.% was checked in case of NaY(WO$_4$)$_2$ crystal host. The efficient ytterbium 900-nm broadband emission was obtained under ultraviolet excitation, despite the absence of Yb absorption lines in this range. This happens due to non-radiative energy transfer from donor centers of the hosts to Yb active ions. This absorption wavelengths range of the host can be tuned by changing the crystal chemical composition. The obtained results indicate that the family of Yb-doped scheelite-like double tungstates is a suitable candidate for developing down-converter materials for solar energy applications.

**Keywords:** sunlight down-conversion; photovoltaics; ytterbium; coatings; glass-ceramics.

**1 Introduction**

Solar energy is the cleanest and most abundant renewable energy source. However, it is a low-intensity resource and its efficient exploitation is challenging. Conventional single-junction semiconductor solar cells effectively convert photons of energy only close to the semiconductor band gap ($E_g$). Photons with lower energy cannot be absorbed by the material and their energy is totally wasted. As a result, only about 48% of the sunlight irradiance is exploited to generate electrons. Moreover, although photons with energy higher than $E_g$ are absorbed with production of electron-hole pairs, each optical photon can produce only one such pair with the energy corresponding to $E_g$\[1\], while the excess energy is lost as heat in the device, see Fig. 1a.
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Figure 1: Schemes of the silicon solar cell operation: (a) the conventional cell; (b) the cell with quantum cutting

A conceptually simpler and cheaper approach to exceed these theoretical efficiency limits of semiconductors is the spectral modification of incident solar radiation. It requires only a basic component (the passive wavelength converting layer) to be added to conventional cells, allowing to fully exploit highly mature technologies of photovoltaics. Two types of spectral modifications
are possible. The first one is down-conversion (DC) (also referred as quantum cutting), where photons with energy more than twice higher than $E_g$ are converted into doubled (ideally) number of photons with energy close to $E_g$, see Fig. 1b. The second one is up-conversion (UC), where two or more sub-bandgap photons (which otherwise are lost) produce at least one photon with higher energy, well matched to the cell $E_g$.

These concepts shows significant promise. While the classical efficiency limit is around 31% for a crystalline silicon (c-Si) cell under nonconcentrated sunlight [1], detailed-balance calculations show that it could be improved to approximately 37% using one of the spectral modification ways described above [4,5] [2,3]. However, these efficiency levels can be reached only after development of the proper material(s), with spectral characteristics tailored to the cell band gap, having a good overlapping between its luminescence excitation spectrum and the emission spectrum of the Sun near the Earth surface, as well as providing high efficiency of quantum cutting process.

Rare-earth (RE) doped crystals have been widely studied for a long time as energy transfer materials. With the proper choice of host crystal, rare-earth dopant species and doping levels, they can show either UC or DC [4]. Renewable energy applications of such systems are of great interest [3,5-8], in particular, photovoltaics [9-18]. Ytterbium ion (Yb$^{3+}$) is the ideal candidate for use in c-Si solar cells DC. Yb$^{3+}$ has a single excited state lying about 10000 cm$^{-1}$ above the ground state and radiatively emitting at around 1 µm wavelength, where the spectral responsivity of c-Si is the highest. The absence of other energy levels prevents energy losses by unwanted excited state absorption and transfers and allows Yb$^{3+}$ exclusively accepting energy packages of 10000 cm$^{-1}$ from a donor. Efficient DC using Yb$^{3+}$ as acceptor requires a donor energy level above 20000 cm$^{-1}$ and an optimized ratio between donor and acceptor populations.

As for donor centers to Yb$^{3+}$, several concepts have been investigated to date: rare-earth ions with excited states within the 4f electronic shell (Er$^{3+}$, Tb$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, and others [19-22]), rare-earth ions with 4f–5d transitions (Eu$^{2+}$, Ce$^{3+}$, and Yb$^{2+}$ [23-26]), ions of d- and p-elements, in particular, Bi$^{3+}$[23,27,28]. All these schemes show their own drawbacks. In particular, (4f-4f)-transitions of rare-earths ions give discrete narrow-lines absorption spectra, therefore they are able to efficiently absorb only a small part of solar high energy photons. In addition, some of these donor ions (Er$^{3+}$, Ho$^{3+}$, etc.) can easily accept excited-state energy transfer back from ytterbium to their low-lying excited levels, then emitting themselves useless photons with an energy lower than the c-Si band gap [19,22]. An alternative approach is to exploit molecular complexes of the host itself as donor centers towards Yb. The crystals containing molybdate [MoO$_4$]$^{2-}$ and vanadate [VO$_4$]$^{3-}$ complexes have been investigated [29-32]. Since these complexes are the structural components of the hosts, the key condition for efficient nonradiative excited-state energy transfer, i.e. the almost direct contact between donor and acceptor, is naturally satisfied in such crystals. The published results have shown that this idea is rather promising [32].

The aim of the present work was to study novel compositions of Yb-doped hosts containing [WO$_4$]$^{2-}$ groups, and to compare them with earlier studied [MoO$_4$]$^{2-}$-containing crystals. The crystal hosts we synthesized belong to the family of scheelite-like double tungstates and double mixed tungstate-molybdates with a general formula NaT(XO$_4$)$_2$ (T = Gd, Y; X = Mo, W), and are typically characterized by innovative mixed compositions, as detailed in the following. Different Yb-doped scheelite-like hosts are actively studied as laser and Raman media [33-36]. Today, scheelite-like double molybdate and tungstate crystals doped with Yb ions begin to be studied as a promising materials for down-converters for c-Si solar cells as well [32]. In this framework, being the occurrence and the extent of DC phenomena strongly system-dependent, the exploration of new host chemical compositions is particularly important.
This class of molybdates and tungstates is characterized by a disordered structure due to the random distribution of the Na and T cations on every lattice sites. Yb replaces the T ion and experiences a distribution of crystal field strengths. The disorder is the reason of the additional inhomogeneous broadening of optical absorption and luminescence bands of Yb$^{3+}$ ions in these crystals. Broadened spectral bands bring a number of advantages from the point of view of the material applications as spectral shifters and converters, though the spectral broadening simplifies the acceptance of the excited state energy from donors. Moreover, it is also worth noting that scheelite-like tungstates and molybdates also have an important technological advantage for the proposed photovoltaic application, because they can be obtained not only in the form of single crystals, but also in the form of ceramics and glass-ceramics [52–54] [37-39]. This feature has a great importance for the practical use of these materials because it opens the possibility of scaling the dimensions of the layers deposed on silicon solar cells.

2 Results and discussion

The investigated samples are listed in Table 1. Four of them (S1..S4) are scheelite-like double tungstates. The fifth sample (S5) contains a Mo$^{6+}$ ion, partially substituting a W$^{6+}$ ion in the (WO$_4$)$^{2-}$ group, and can be indicated as a mixed molybdate-tungstate. All the samples except S4 had a nominal Yb concentration of 10 at.%. This concentration corresponds to the value where the mechanism of quantum cutting (DC with quantum yield larger than unity) was shown to start its manifestation overcoming the competing effect of concentration quenching in earlier studied scheelite-like molybdates [32].

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Formula</th>
<th>Nominal Yb concentration (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>NaY$<em>{1/2}$Gd$</em>{1/2}$(WO$_4$)$_2$</td>
<td>10</td>
</tr>
<tr>
<td>S2</td>
<td>NaY$<em>{2/3}$Gd$</em>{1/3}$(WO$_4$)$_2$</td>
<td>10</td>
</tr>
<tr>
<td>S3</td>
<td>NaY(WO$_4$)$_2$</td>
<td>10</td>
</tr>
<tr>
<td>S4</td>
<td>NaY(WO$_4$)$_2$</td>
<td>15</td>
</tr>
<tr>
<td>S5</td>
<td>NaY(Mo$<em>{1/2}$W$</em>{1/2}$O$_4$)$_2$</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1: List of investigated samples. Yb concentrations are in at.% with respect to the total amounts of trivalent ions in the crystal composition, and correspond to the initial melt compositions.

3.1 Absorption

Polarized Yb absorption spectra of different samples at RT are quite similar to each other. Figure 2 shows, as an example, the spectra for S3 sample. One can see the pronounced dichroism, typical for Yb ions in optically anisotropic hosts [40-43]. The main difference among samples lies in the absolute values of absorption coefficient of S4 sample, as expected due to its larger Yb concentration. Integrated areas of S4 absorption coefficients are about 45% and 46% larger than those of S3, respectively for π and σ polarizations, respectively. It means that, for these crystals, the ratio of actual doping levels is practically the same as the nominal one. Looking at the shapes of spectra, they consist of rather broad overlapping bands with a strong peak at 976 nm corresponding to the transition between the lowest Stark sublevels of the manifolds $^2$F$_{5/2}$ and $^2$F$_{7/2}$. FWHM of the whole $^2$F$_{7/2}$$\rightarrow$ $^2$F$_{5/2}$ transition band is about 50 nm for both polarizations.
Figure 2: Polarized absorption spectra of S3 at room temperature RT.

Figure 3: Comparison of polarized absorption spectra of all samples at RT. Enlarged plots on the right allow to appreciate the crystal-composition dependent spectral shift, which, however, at RT is partially hidden by the phonon broadening of the bands. The S4 ordinate axis can be read on the right of each plot, while the ordinate axis on the left of each plot refers to the other samples.
Figure 3 compares the RT polarized spectra of all samples. The differences in the shape of the spectra, including the small spectral shift (enlarged plots in Figure 3) is due to the different chemical composition of hosts.

The effects of changing hosts on the Yb$^{3+}$ spectral features are more evident at low temperature. Figure 4 shows the polarized IR absorption spectra at 100 K, for $\pi$ and $\sigma$ polarizations, respectively. It is possible to distinguish again three bands, corresponding to the three transitions between the lowest Stark sublevel of the $^2F_{7/2}$ ground state and all three Stark sublevel of the $^2F_{5/2}$ excited state. The narrow band centered at 976 nm is the $^2F_{7/2}(0) \rightarrow ^2F_{5/2}(0')$ transition. The other two bands are $^2F_{7/2}(0) \rightarrow ^2F_{5/2}(1')$, $\lambda = 970-952$ nm and $^2F_{7/2}(0) \rightarrow ^2F_{5/2}(2')$, $\lambda = 952-923$ nm. They are broader and more complex in shape and structure. Comparing the spectra, integrated areas of S4 absorption coefficients are 50% larger than those of S3, like for the RT spectra. There is also small shift between the corresponding peaks of different samples in both polarizations, in agreement with room-temperature findings, and no shift was observed between S3 and S4, as we could expect sharing them the same host.

![Figure 4: Polarized low-temperature absorption coefficient of the studied samples.](image)

![Figure 5: Absorption spectra of the studied samples in the range 300-400 nm.](image)
Figure 5 shows the absorption spectra at room-temperature for samples S1-S2-S3-S5 in the UV spectral range. The spectral features in this region are connected to the energy bandgap of the hosts. No polarization-dependent features were detected, thus in Fig. 5 only the π polarization is shown. S4 spectrum has not been plotted since it is practically identical to that of S3. The UV risefronts of absorption spectrum of gadolinium-containing samples S1 and S2 are slightly shifted towards smaller energies as compared with Gd-free tungstate crystals S3 and S4. Besides that, samples S1 and S2 show a small band peaked at about 312 nm, corresponding to the three energy levels \( ^6P_{3/2}, ^6P_{5/2} \) and \( ^6P_{7/2} \) of Gd\(^{3+} \). No differences connected to the different contents of Gd among the samples were detected within the uncertainty of our experimental apparatus. As for the molybdenum-containing sample S5, its spectrum is very strongly shifted towards longer wavelengths as compared with those of pure tungstates. In the visible range (400-700) nm, all samples are transparent.

### 3.2 Yb\(^{3+} \) luminescence under resonant excitation

The polarized emission spectra under the resonant IR excitation are shown in Figure 6. Again, it is possible to see the dichroism of Yb spectra. σ curves are more structured, with many overlapping peaks, while the π ones are smoother. In both polarizations there is a clear evidence of reabsorption at the dip at about 975 nm, especially in S4, which has a higher Yb concentration.

Note that, unlike the absorption, the fluorescence intensity of S4 sample does not increase substantially above that of S3, despite the higher Yb concentration. In fact, integrated fluorescence intensity of S4 is only about 4% larger than that of S3 in π polarization and about 8% larger in σ polarization. This is, first of all, probably due to some concentration quenching effect, reducing the emission intensity, similarly to what observed in scheelite-like molybdates [32], and many other Yb doped systems [22,24,30].

![Figure 6: Polarized Yb emission spectra of the studied samples under laser excitation at 969 nm.](image)

### 3.3 Yb\(^{3+} \) luminescence under non-resonant excitation

To evaluate the DC potential of samples, polarized emission spectra were also measured under ‘soft’ UV excitation, 300-400 nm. In fact, Yb does not have absorption bands in that
spectral region. Thus any Yb fluorescence at this excitation is possible only due to an energy transfer from inherent optically active centers of the hosts [44].

Considering the proposed solar energy application, we were interested in characterizing the material behavior under the whole broadband 300-390 nm host absorption (Figure 5), corresponding to a spectral range where c-Si solar cells have a very poor efficiency in photovoltaic conversion. Thus, using as excitation source the internal Xenon lamp of the spectrofluorometer and taking into account the fact that the excitation monochromator allowed to set at most 30 nm of excitation bandpass, we have performed three sets of measurements for every sample, for 315 nm, 345 nm, and 375 nm center excitation wavelengths to cover the whole range of interest. A final correction on measured spectra was necessary to take into account of the spectral intensity distribution of the excitation source.

![Graphs showing polarized Yb emission spectra](image)

**Figure 7:** Polarized Yb emission spectra of the samples under UV excitation. Each plot has been taken with 30 nm excitation band, peaked at the wavelengths indicated in red.

Polarized spectra under UV excitation are presented in Figure 7. An intense broadband luminescence was found in the region of Yb$^{3+}$ band. The spectral shape of this luminescence in both $\pi$ and $\sigma$ polarizations is very similar to that presented above under IR resonant excitation (Figure 6). This is an evidence of a nonradiative excited state-energy transfer (ESET) from inherent optically active centers of host crystals to Yb$^{3+}$ ions. Similar Yb$^{3+}$ luminescence under UV excitation has been earlier observed for Yb:CaMoO$_4$ [31, 45], Yb:NaGd(MoO$_4$)$_2$ and Yb:NaLa(MoO$_4$)$_2$ [32] and for some other Yb doped scheelite-like crystals, as well as for tungstates with monoclinic crystal structure [46].
One can see that, while S1-S4 samples are quite similar, S5 has a very different behavior and in its case, the fluorescence is much more efficient when excited in the range 330-390 nm, rather than in the 300-330 nm range.

For a quantitative comparison among samples, we considered the values of integrals of spectral fluorescence curves in the whole excitation range 300-390 nm (Figure 8). One can see that the mixed molybdate-tungstate crystal S5 shows the most promising behavior. This is linked to the peculiar characteristics of its excitation spectrum, shown in Figure 9, with a pronounced and broad peak at about 350 nm. The excitation maximum for S5 sample is essentially red-shifted as compared to S1-S4, and better overlaps with the considered spectral range of 300-390 nm. The same shift has been earlier observed also for some other Yb-doped scheelite-like molybdate crystals with respect to tungstates. Such red shift makes S5 the most promising sample for PV applications, because the fraction of sunlight in the range 350-400 nm essentially exceeds that in the range 300-350 nm.

The efficiency of ESET is nearly independent on the trivalent host ion (Gd$^{3+}$ and Y$^{3+}$). In fact, the difference between the Yb$^{3+}$ luminescence intensity between S1, S2 and S3 under UV excitation (Figure 7) is comparable with that under the resonant IR-excitation (Figure 6) and with the corresponding difference in the strengths of the absorption bands (Figure 4). The existing small differences are connected with composition-dependent local structural variation of the Ytterbium surrounding and slight differences in the actual Yb concentrations.

Finally, if we compare the total values, obtained as the sum on all polarizations, of the integrated Yb emission under UV excitation, for the samples S3 (10% at. doping level) and S4 (15% at.), we can see that S4 has a 31% higher emission than S3. This remarkable increase has to be compared with the integrals of the Yb emission under resonant excitation into the Yb band (spectra in Fig. 6). For the resonant IR excitation, the total S4 fluorescence was higher than that of S3 by about 6% only. As explained in Ref. 32 this behavior suggests the occurrence of DC with photon multiplication, i.e., quantum cutting.

Figure 8: Integrated Yb$^{3+}$ fluorescence of the samples under 300-390 nm excitation.
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Figure 9: UV excitation spectra for the polarized Yb emission. The spectra were acquired choosing a detection band of 58 nm centered on the peak wavelength of Yb fluorescence for each sample and indicated in legend.

The UV-excitation spectra for Yb$^{3+}$ emission are shown in Figure 9. A local excitation peak at about 312 nm can be recognized in the spectra of Gd-containing S1 and S2. This peak is in agreement with what observed in the absorption spectra (Figure 5) of the above crystals. This peak is the evidence that Gd$^{3+}$ ion acts in the UV excitation and the following ESET to Yb$^{3+}$ ions, although, Gd$^{3+}$ is, certainly, not the only kind of donor center, and, maybe, even not the most efficient one. Obviously, there are some additional center(s) of a different nature, which bring the major contribution as the donors into the ESET to Yb$^{3+}$ ions. In fact, the ESET to Yb$^{3+}$ ions efficiently runs also in the Gd-free S3, S4 and S5 samples. We suppose, these centers are related with some other host structural elements. Authors of the paper in Ref. 31 believe that autolocalized excitons in [MoO$_4$]$^{2-}$ functional groups play the role of the main donor active centres during ESET in molybdate crystals. However, Ref. 45 refutes this version.

3.4 Host luminescence under UV excitation

In addition to the Ytterbium IR luminescence, the samples also show very weak luminescence (by two orders of magnitude weaker than Yb emission) in the visible range under UV excitation. Polarized emission spectra in the visible region under UV pump are shown in Figure 10. This emission cannot arise from Yb ions. In fact, similar luminescence has been found earlier for NaGd(MoO$_4$)$_2$ [32] and some other scheelites [45], including Yb-free crystals. For CaWO$_4$ and CaMoO$_4$ crystals the strong luminescence in this spectral region is known for many years, and it is well studied [47,48]. As a rule, it is attributed to autolocalized excitons in tungstate and molybdate functional groups of the hosts-[29,49].

As expected, due to the differing S5 composition, with (WO$_4$)$_2^-$ groups, partially replaced by (MoO$_4$)$_2^-$ groups, the S5 luminescence spectrum in the visible is considerably different from those of S1-S4. On the other hand, unexpectedly, samples S1-S4, which are all characterized by (WO$_4$)$_2^-$ groups, show rather substantial differences in the spectra. Moreover, the highest differences are even shown between S3 and S4 samples, which only differ in the Yb doping level. This fact brings some doubts in the attribution of the observed visible luminescence to (WO$_4$)$_2^-$ or (Mo$_{1/2}$W$_{1/2}$O$_4$)$_2^-$ groups, as it was for simple CaWO$_4$ and CaMoO$_4$ crystals. At least, in our samples the mechanism of this luminescence is not so simple and evident, and requires a further clarification. Maybe, this luminescence is somehow related to the presence of some ionic impurities, as it could be also inferred from the small and narrow peaks emerging e.g. at about 560, 610, 615 nm on the white broadband emission curves in Figure 10. These hypothetical
impurities are in extremely low amounts, as they could not be detected by absorption measurements, they were likely excited, for the case of 310 nm pumping, by energy transfer from the hosts, and will be the subject of further investigations.

**Figure 10:** Emission of the hosts in the visible range.

Finally, to complete the characterization, we acquired the excitation spectra for emission in the visible range. Figure 11 shows the polarized excitation for the fluorescence at 500 nm (i.e. near the host emission peak), acquired with 3 nm spectral resolution on the excitation channel. It is possible to notice a strong peak at around 310 nm in the curves of S1 and S2, corresponding to the three energy levels $^6P_{3/2}$, $^6P_{5/2}$ and $^6P_{7/2}$ of Gd$^{3+}$, in agreement with the absorption spectra. It means that ESET from Gd$^{3+}$ for the host emission centers does run. Again, S5 shows fairly different characteristics, with a pronounced peak at about 330 nm and a smaller peak at about 380 nm.

**Figure 11:** Excitation spectra of host emission peaked at 500 nm (10 nm emission bandpass).

The comparison of Figures 9 and 11 shows that the UV excitation spectra of Ytterbium IR luminescence do not coincide with the host visible luminescence. It means that the host luminescence centers do not participate in ESET for Yb$^{3+}$. The same conclusion was previously been drawn for the series of Yb:NaGd(MoO$_4$)$_2$, Yb:NaLa(MoO$_4$)$_2$, Yb:CaWO$_4$ and Yb:CaMoO$_4$ crystals [45], on the basis of measurements the relative intensities of visible and Yb$^{3+}$
luminescence at various Yb concentrations, as well as based on luminescence decay kinetics measurements at UV excitation.

3 Conclusions and outlook

The Yb-doped double tungstates with different compositions and a sample of double mixed tungstate-molybdate were investigated to evaluate the material potential as light down-converters for photovoltaic applications. The role of Yb concentration was also studied for one of the tungstate hosts. The disordered structure of hosts, furtherly increased by an additional doping with Gd or Mo to prepare the solid solutions, allows the efficient energy transfer from the host to ytterbium ions, arising in the Yb\(^{3+}\) broadband emission at around 1 µm wavelength under excitation in the UV range from 300 to 390 nm, where Yb\(^{3+}\) itself has no absorption lines. The concentration-dependence of Yb emission intensity in NaY(WO\(_4\))\(_2\) seems to suggest the occurrence of DC with photon multiplication. The introduction of molybdenum into the crystal composition produces a strong red-shift of the host absorption in comparison with pure tungstates. The Yb\(^{3+}\) excitation bands of both molybdate and tungstate fractions are joined together, resulting in the formation of a very broad excitation band for DC. Consequently, the Mo-containing sample appears the most promising for PV applications. Our estimations show that further optimization of both ytterbium concentration and double tungstate composition could improve the efficiency of silicon solar cells approaching 35-40% by using these down-converters.

Meanwhile, the comparison of both the UV excitation spectra of the Yb luminescence, and the broadband visible luminescence of tungstate and molybdate molecular complexes revealed that these complexes do not participate in DC of the excited state energy onto Yb ions. This coincides with previous conclusions [45] made on the basis of other spectroscopic studies on some related Yb-doped crystals. The nature of the donor centers, transferring their excited state energy to Yb\(^{3+}\), as well as the mechanisms of this energy transfer, which could involve defects such as oxygen vacancies (V\(^{\circ}\)O), formation of autolocalized exciton on [YbO\(_5\)] cluster, the f-d transition on Yb\(^{3+}\) ion, as well as delocalized excitons, are requiring further studies. The important advantage of these materials is the extremely high absorption coefficient of the host that opens promising perspectives for the technological exploitation in future fully integrated designs, e.g. with the down-converting materials grown as thick (≈100 µm) films directly on silicon, thanks to the reduced lattice misfit [50,51] (see also Supplementary Material) or inserted, in form of micro- or nano-crystals within the cell anti-reflective glass. This study has demonstrated that the family of scheelite-like double tungstates and mixed tungstates-molybdates doped with ytterbium has considerable potential for photovoltaic DC applications. It is also worth to mention an interesting further application of these materials for Yb-doped solar-pumped lasers, to enable for a renewable magnesium-hydrogen energy cycle [52,53].

Additional Material
Evaluation of the potential of Scheelite-like double tungstates for future epilayers on silicon or for glass-ceramic layers

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References


Additional material for the manuscript:

**Yb-doped double tungstates for down-conversion applications**

Elisa Sani1*, Alfredo Brugioni1, Luca Mercatelli1, Daniela Parisi2, Evgeny V. Zharikov3, Denis A. Lis3, Kirill A. Subbotin3,4

1CNR-INO National Institute of Applied Optics, Largo E. Fermi 6, 50125 Firenze, Italy
2NEST Istituto Nanoscienze-CNR and Dipartimento di Fisica dell’Università di Pisa, Largo B. Pontecorvo 3, 56127 Pisa, Italy
3Prokhorov General Physics Institute of Russian Academy of Sciences, Vavilova st. 38, Moscow, 119991 Russia
4Mendeleev University of Chemical Technology of Russia, Miusskaya Square, 9, Moscow, 125047 Russia

*Corresponding author: email elisa.sani@ino.it

The batches for crystal growth were prepared by traditional solid-state reaction. The structures were identified by X-ray powder diffraction (XRD; CuKa=1.5406 Å; Rigaku/Dmax2500, Rigaku Corporation, Japan). The diffraction peaks of the samples are well indexed to the tetragonal scheelite-type NaGd(WO4)2 (JCPDS No.25-0829). No additional impurity peaks are detected, indicating the formation of pure tetragonal phase. The example of the XRD patterns for NaGd(WO4)2 is given in Fig. 1

![XRD patterns of NaGd(WO4)2](image)

**Figure 1:** The XRD patterns of NaGd(WO4)2 calcined at 700 °C for 24 hours. The figure also shows that all diffraction peaks well matched the standard data of JCPDS 25-0829 [NaGd(WO4)2].
Evaluation of the potential of Scheelite-like double tungstates for future epilayers on silicon

First of all, the possibility to realize the deposition of double tungstate epilayers on silicon substrate can be assessed by their lattice misfit. During heteroepitaxial growth of a film, a difference in lattice parameters (i.e. lattice misfit) between dissimilar materials usually causes a strain in the film. The accommodation of lattice misfit between an epitaxial film and substrate has been examined by Frank and van der Merwe [1-3]. They show that a misfit smaller than about 7 percent will be accommodated by uniform elastic strain (Fig. 2). Authors of Ref. 4 have extended this value up to 10 percent. After reaching of a critical thickness [5] it is energetically favorable for misfit to be shared between dislocations and strain (Fig. 3). The dislocations can substantially diminish the mismatch-induced strain. The layer thickness at which the formation of misfit dislocations is expected studied in many papers (see, for instance, Refs. 4-7). Depending upon the elastic modulus, failure strength in compression and tension, and the Burgers vector of the film material, the magnitude of allowable lattice misfit can vary over a wide range from one epitaxial system to another [4,5].

Figure 2: Coherent interface (strained). Notes: $a_{Si}$ is lattice parameter $a$ of silicon; $c_F$ and $a_F$ are lattice parameters of double tungstate film.
Figure 3: Semi-coherent interface with misfit dislocations (after reaching a critical thickness by film). Notations are the same as on Fig. 2.

<table>
<thead>
<tr>
<th></th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
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<tbody>
<tr>
<td>Silicon crystal [8]</td>
<td>5.431</td>
<td>--</td>
</tr>
<tr>
<td>NaY(WO$_4$)$_2$ [9]</td>
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Table 1: Lattice parameters of crystalline silicon and of representative double tungstates

Table 1 shows the lattice parameters of crystalline silicon and some double tungstates.

In order to see the prospects of heteroepitaxy of double tungstates on silicon, we will use in calculations the tougher restriction in 7 percent according to Refs. 1-3. It gives for silicon the following acceptable limit in lattice parameter of film: 5.431 x 0.93 = 5.051 Å. From Table 1 we can see that all presented there double tungstates are suitable for epitaxy on silicon using $a$ axis direction. If we look at lattice parameter $c$, one can see that it also could be interesting for epitaxy. Indeed, 5.431 x 1.07 = 5.811 Å. The creating the limit of lattice parameter twofold value is 5.811 x 2 = 11.622 Å. From Table 1 we can see that all the double tungstates have lower values, i.e. locate inside the limit. It means that all compositions have perfect fit (better than 7%) with silicon lattice, and epitaxial layers of our tungstates on silicon are quite possible for $a$-axis and even for $c$-axis.

Another important issue in realization of successful double tungstate epitaxy on silicon is the compliance of their thermal expansion coefficients. The best situation here would be not only closeness of these coefficients at room temperature but also the nearness of paces of thermal expansion change with temperature in order to prevent a cracking of epilayer. Unfortunately, the information about thermal expansion of double tungstates is very poor in contrast with silicon.
Possibly, the situation here is not as good as it is with lattice parameters. For instance, the thermal expansion coefficient of NaGd(WO$_4$)$_2$ is about 2.5 times higher compared to silicon ($6.7 \times 10^{-6}$ K$^{-1}$ [11] and $2.6 \times 10^{-6}$ K$^{-1}$ [12] correspondingly). The solution of this mismatch lies in isomorphic fit of suitable composition.

In addition, there is another option: instead of epitaxy we can just impose the crystalline or glass-ceramics layer (glassy layer with active micro or nano-crystals) of double tungstate on the top of silicon solar cell. In this case no any problem with dislocations will appear.

References


