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Up-Conversion Phosphors synthesis and application in solar converters

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Abstract
The present paper reports photo luminescence studies of $Ca_3Si_3O_8F_2$:Ce and $BaSrCeO_4$:Eu phosphors each doped with Ce, Eu 1, 1.5, and 2.5 molar percentage respectively. The samples were prepared using Standard Solid State Reaction method and ground the starting materials with appropriate stoichiometry into a fine powder using agate mortar and pestle, and fired at 1200°C for 3 hours in a muffle furnace. The photo Luminescence spectrum was recorded at room temperature. $Ca_3Si_3O_8F_2$:Ce when excited with 630 and 650nm broad peak with high intensity from 390-500 nm followed by bit yellow emission is observed. $BaSrCeO_4$:Eu when the phosphor is excited whit 254nm main emissions are around 595nm. The same phosphor is excited with 625nm the emission is around 595nm with higher intensity. The observed luminescence peaks are the allowed transitions of Ce and Eu. The luminescence observed in the studied phosphors may be cooperative up-conversion process. These phosphors can be considered as up-conversion materials in the solar cells for better efficiency.

1. INTRODUCTION

Up Conversion - transforming large wavelength photons into small wavelength photons. This is possible via excitation mechanisms which involve more than one absorbed photon per emitted photon. The drawback here is that it is a non-linear effect. In down conversion-suitable materials must efficiently absorb high energy photons and reemit more than one photon with sufficient energies. Its efficiency is high and hence widely used. Upconversion can only occur in materials in which multiphonon relaxation processes are not predominant, thus allowing more than one metastable excited state. In rare-earth compounds, the 4f or 5f electrons are efficiently shielded and thus not strongly involved in the metal-to-ligand bonding. As a consequence, electron-phonon coupling to f-f transitions is reduced, and multiphonon relaxation processes are less competitive. The phenomenon of upconversion is therefore most common and best studied in materials containing lanthanide ions. But there are also transition-metal systems and rare-earth / transition-metal combinations which show this phenomenon.

Applications :

1. Generation of visible light from GaAs diodes (970 nm)
2 .Diode-laser driven flat panel displays
3. IR-activated security marking without interference from sample autofluorescence
4. Detection of infrared radiation & IR quantum counters
5. Bio-imaging & Therapy
6. Light curable polymers in restorative surgery
7.Markers or labels in immunoassays & flow cytometry
8. Fibre-optic amplifiers
9. Solar Cells

Considerable amount of work has been done on this topic in single crystals. Only limited work has been done in the area of ceramic powder phosphor that shows efficient upconversion. The term upconversion is also sometimes used for other types of processing which generate shorter-wavelength photons. An example is the upconversion of IR photons to the visible spectral range by sum frequency generation in a nonlinear crystal (NLC; the materials may be LiIO3, LBO, or BBO). This can be used e.g. for photon counting at long wavelengths, where no suitable detectors are available. However, the fluorescence efficiency in this case is much less than that involving UC through multi-photon absorption involving intermediate real energy states

2. MAIN MECHANISM

1.Energy Transfer Upconversion (ETU)- also known as cooperative upconversion : The energy from one excited ion is transferred to another excited ion to create a doubly excited ion
2.Exited State Absorption (ESA): An already excited ion absorbs another photon

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UC phosphors are more sensitive to vibronic coupling between host and activator than that of Stokes shifted phosphors. This stems from the fact that UC involves two or more excited energy levels each of which should be long lived. One should chose the host material with low energy optical phonons. Fluorides, heavier halides or oxyhalides are good hosts for UC: A host lattice with suitable properties such as low absorption of visible light i.e commonly used are $NaYF_4$, and Y Al Garnet (YAG), Y_2O_3 and YAG containing activators and sensitizers.

Activators:
Ions that may be doubly exited. Activators often have a low absorbance for low energy photons eg. Erbium.

Sensitizers: Ions with a larger optical absorption window can transfer energy to an activator ion through an ETU process

Many of the halides are air sensitive as well as toxic, which has weakened its large scale industrial applications. Chalcogenides such as S, Se, Te etc. are also found to be potential candidates for up conversion though the phonon frequency is little higher than halides. Among Chalcogenides,rare earth oxysulfide possesses several excellent properties such as chemical stability, low toxicity and can be easily mass produced at low cost. It has average phonon energies of about 520 cm−1. Up conversion fluorescence may be strongly suppressed (quenched) by multi phonon transitions, as these can reduce the lifetimes of metastable levels. A second effect of vibronic coupling Host phonon energy levels influence emission spectra particularly in Er-doped phosphors. Stronger coupling increases red/green emission intensity ratio. Therefore NaYF4:Yb,Er give green emission while Y_2O_3:Yb,Er gives red emission
UC by energy transfer (APTE) in YF_3:Yb^{3+},Tm^{3+} in which the absorption of three 930 nm IR laser photons by Yb^{3+} ions and subsequent energy transfer to Tm^{3+}, thrice consecutively, causes the emission of a single blue photon at 430 nm from Tm^{3+}. Similarly YF_3:Yb^{3+},Er^{3+} converts IR light (2-photon absorption) into green (1-photon emission) light. For such absorption the f-f transitions of RE^{3+} with long life time are quite useful.

$NaYbF_4$:Sm nano-phosphors :Under 980 nm excitation, the annealed nano-phosphors emitted green, red, and broadband near-infrared UC fluorescence. In addition, the 475 nm cooperative UC fluorescence was observed by many workers.

The cooperative energy transfer of Yb–Yb pairs is the main UC mechanism when the Sm doping concentration is low,while energy transfer between Sm and Yb is thought to be the main UC mechanism when the Sm doping concentration is high.

$LaMgAl_{11}O_{19}$:Yb:Mn : Excitation at 975 nm with a diode laser resonant with the 2F7/2→2F5/2 Yb3+ transition induces a broad emission band centered at 514 nm and assigned to the 4T1→6A1 transition of tetrahedral Mn2+. It is interesting to note the upconversion luminescence can be seen by the naked eye up to 500 K. This finding is a promising step in order to use the Mn2+–Yb3+ system as a potential candidate for display phosphors by upconversion. As the excitation power density was high enough, the emission intensity of upconversion decreased due to thermal quenching. The thermal effect caused by the exposure of the 978-nm laser was reported.
Because UC phosphors are an unusual, expensive and rare substances and hence difficult to duplicate, they are good candidates for security applications, especially in areas where high-speed machine reading is required. Upconverting labels are inherently non-linear in that their efficiency depends on incident power density. Power density of the incident illumination does vary from sample to sample, for example because of variations in turbidity. Emission spectrum of typical upconverting phosphors can also depend markedly on power density of excitation.

In recent years, renewed interest has been directed toward up-conversion devices and materials. The interest is principally due to prospects for the realization of infrared up-conversion lasers pumped with laser diodes. The revival of interest for the up-conversion phenomenon is due to the advent of powerful and less costly that can be used as excitation sources and the appearance of new materials such as fluorine containing phosphors. The first report on an infrared up-conversion is BaY_2F_8 crystal doped with Ho^{3+} and Yb^{3+} .

3. EXPERIMENTAL

The present studied $Ca_3Si_3O_8F_2$:Ce and $BaSrCeO_4$:Eu phosphors each doped with Ce, Eu 1, 1.5, and 2.5 molar percentage are prepared. The samples were prepared using Standard Solid State Reaction method and ground the starting materials with appropriate stoichiometry into a fine powder using agate mortar and pestle, and fired at 1200°C for 3 hours in a muffle furnace. The photo Luminescence spectrum was recorded at room temperature.

4. RESULTS AND DISCUSSIONS

Calcium Silicates containing Fluorine $Ca_3Si_3O_8F_2$:Ce and $BaSrCeO_4$:Eu phosphors are found new up-conversion phosphors. The figure-2 shows the excitation and emission spectra of $Ca_3Si_3O_8F_2$:Ce. It is found from the excitation spectra two peaks are observed at 260 and 325nm and the corresponding curves 1, 2, 3 indicates the emission under 325, 630 and 650nm excitation respectively, broad peak with high intensity from 390-500 nm followed by bit yellow emission.

Figutre-3 is the PL of $BaSrCeO_4$:Eu. When the phosphor is excited whit 254nm main emissions are around 595nm. The same phosphor is excited with 625nm the emission is around 595nm with higher intensity. The observed luminescence in the studied phosphors is cooperative up-conversion process.

The upper-state lifetime in a solid-state gain medium, or more generally the lifetime of a metastable electronic state of a dopant ion in such a medium, can be strongly reduced by decay processes which involve the simultaneous emission of several phonons. Such a process is called a multi-phonon transition. Multiple phonons are typically required for such transitions because the energy of a single phonon is not sufficient to match the difference in level energies. It is known fact the Green/Blue or red visible up conversion luminescence from Tb^{3+} $^5D_3$, $^5D_4 \rightarrow {}^7F_J$, or Eu^{3+} $^5D_0 \rightarrow {}^7F_J$ transitions, respectively, has been observed upon Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$ excitation at 975 nm.

The rate of multi-phonon transitions decreases exponentially with increasing number of phonons required. As a consequence, a certain metastable state may exhibit a very strong reduction in its lifetime by multi-phonon emission if the host medium supports phonons with relatively high energy, whereas the same process may be negligible for a host medium with lower phonon energies. For that reason, many up-conversion phosphors work only with gain media which have small phonon energies, such as heavy metal ceramics, so that sufficient lifetimes of certain energy levels are achieved. In other cases, however, high enough phonon energies are important if these are required for facilitating certain non- radiative transitions, which are needed to depopulate the lower level.

Figure 1 is the Possible up conversion processes of Yb^{3+} sensitized Er^{3+} (or Ho^{3+}) in $La_2Mo_2O_9$:Yb,R and a schematic illustration of excitation and emission when excited with 980nm laser pulse.

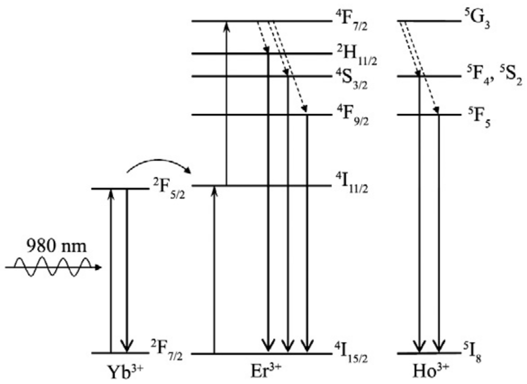

Fig.1: upconversion processes of Yb^{3+} sensitized Er^{3+} (or Ho^{3+}) in $La_2Mo_2O_9$:Yb,R and a schematic illustration of excitation and emission (*from Yen-Chi Chen-2011*)

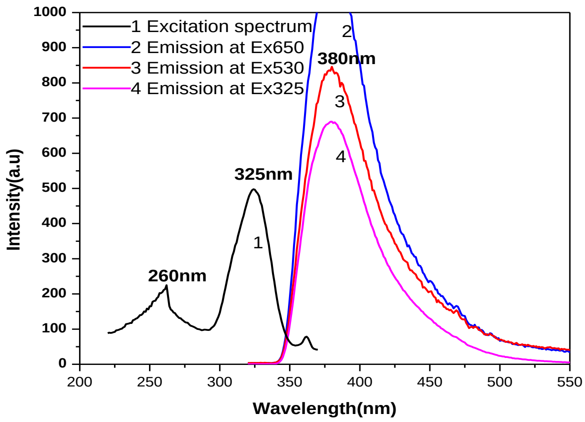

Fig.2: shows the excitation and emission spectra of $Ca_3Si_3O_8F_2$:Ce.

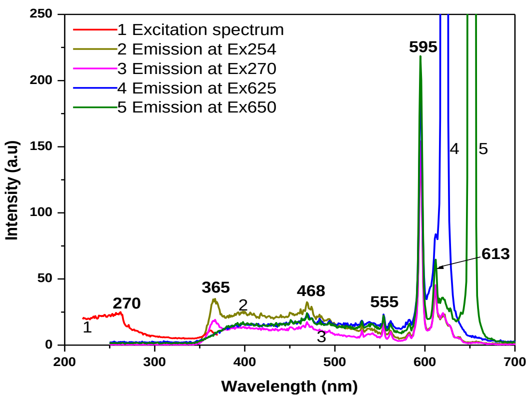

Fig.3: is the PL of $BaSrCeO_4$:Eu.

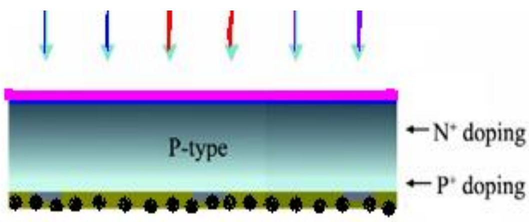

Fig. 4: UPC Phosphor embodied solar cell

Figure.4 is the schematic representation of upconversion phosphor embodied solar cell. The light falling on the solar cell which is transmitted to other end and falling on the phosphor, the phosphor absorbed the red component of the incident light and converted and emit in the violet-yellow region. This emitted light is absorbed by the PV cell which in turn creates the electron hole pairs in the PV cell leads increase its efficiency by 6-7% as reported. The investigation on the spectroscopy and excited state dynamics of these systems is extremely important in order to understand the up conversion processes observed in the present phosphor systems.

5. CONCLUSIONS

$Ca_3Si_3O_8F_2$:Ce when excited with 630 and 650nm broad peak with high intensity from 390-500 nm followed by bit yellow emission is observed. $BaSrCeO_4$:Eu when the phosphor is excited whit 254nm main emissions are around 595nm. The same phosphor is excited with 625nm the emission is around 595nm with higher intensity. The observed luminescence peaks are the allowed transitions of Ce and Eu. The luminescence observed in the studied phosphors may be cooperative up-conversion process. These phosphors can be considered as up-conversion materials in the solar cells for better efficiency.

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