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**Novel NIR-to-NIR up-conversion phosphor
for enhancing solar cell efficiency**

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Trivalent thulium Tm^{3+} ion is a wide-spread rare-earth dopant of various solid-state luminescent materials. Owing to a set of cross-relaxation processes involved in forming the luminescence of these materials they provide intense blue or near infra-red (NIR) emission which depends on site of Tm^{3+} ion and local concentration of dopant. Among various Tm^{3+} -doped materials, dielectric crystals and glass-ceramics (GCs) that emit long-lived NIR luminescence are attractive due to their applications in biosensing [1] and photovoltaics. Efficient NIR-to-NIR up-conversion in Tm^{3+} -doped systems permits to improve photoelectrical transformation efficiency in conventional Si-based solar cells. NIR-to-NIR up-conversion is useful when considering the problem of spectral mismatch between solar cells and solar spectrum. In particular, for the $Tm^{3+}-Yb^{3+}$ couple, absorption of sunlight by Yb^{3+} in the infra-red (IR) and by Tm^{3+} in the ultra-violet (UV)/visible can lead to the Tm^{3+} emission with the energy matching the band gap energy of silicon [2].

The rare-earth orthoniobates with common formula $RENbO_4$, where RE^{3+} is a rare-earth ion like Y, Er, Tm or Ho, are promising host materials for RE-doping [3]. When codoped with (Yb^{3+} , RE^{3+}) ions, they show intense visible upconversion luminescence (UCL) under near-IR excitation due to a very efficient $Yb^{3+} \rightarrow RE^{3+}$ energy transfer (ET). The particular case of (Yb^{3+} , Tm^{3+}) codoping is attractive as it depends on the Yb/Tm ratio and can provide either visible or near-IR UCL.

There are two stable crystal forms of RENbO_4 . The monoclinic form (M) is a low-temperature phase having the fergusonite-like structure described by the $C2/c$ space group terms. And the high-temperature tetragonal (T) phase is a sheelite-like disordered crystalline form described within the $I4_1/a$ space group. The reversible transition between M and T-phases at about $500\text{--}800^\circ\text{C}$ depends mostly on the nature of RE^{3+} ion. Recent studies of glass ceramics with $(\text{Er}, \text{Yb})\text{NbO}_4$, $\text{Eu}, \text{Yb}:\text{YNbO}_4$ nanocrystals have revealed the improved luminescent properties due to the formation of M and T-phases.

In present work, we report on intense near-IR UCL from GCs containing $\text{Yb}, \text{Tm}:\text{YNbO}_4$ nanocrystals in a dual role of nucleating agent providing volume nucleation of β -quartz solid solutions (ss) and luminescent crystals.

Experimental samples were prepared by the secondary treatment of glasses with the system $\text{Li}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ doped by Yb_2O_3 , Tm_2O_3 , Y_2O_3 , and Nb_2O_5 at $T=750\text{--}1350^\circ\text{C}$. The structural and phase transformations in the glass-ceramics resultant from the heat treatment were studied by XRD-analysis. At $T=800^\circ\text{C}$ the system exhibited the formation of the apparently disordered T-structure of $\text{Tm}, \text{Yb}:\text{YNbO}_4$. According to broadening of XRD-patterns, the size of nanocrystals (7–25 nm) was growing with the temperature of the secondary heat treatment. Recrystallization of the nanosized phase from T-structure to M-structure occurred at 900°C .

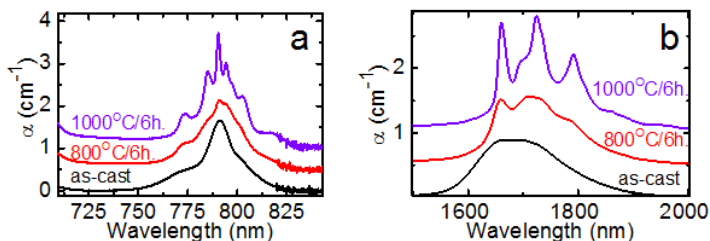


Fig. 1 - Absorption of Tm^{3+} ions related to the transitions to $^3\text{H}_4$ (a) and $^3\text{F}_4$ (b) states for initial glass and GCs heat-treated at 800°C and 1000°C .

The structural transformation is responsible for drastic changes in absorption and luminescence spectra of glass ceramics after crystallization of parent glass. All the observed absorption bands are attributed to transitions of Tm^{3+} ion from the ground state $^3\text{H}_6$ to a set of the excited states $^1\text{G}_4$, $^3\text{F}_J$, and $^3\text{H}_J$ with the energies up to 25000 cm^{-1} . The Yb^{3+} absorption band spanning from 850 to 1050 nm and related to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition was peaked at $\sim 976\text{ nm}$ and it was used for excitation of samples with an InGaAs laser diode.

The spectral shape of all transitions is changed: forming of the T-phase of Tm,Yb:YNbO_4 at 800°C results in partially resolved structure of all absorption bands. Further treatment at $T > 1000^\circ\text{C}$ leads to the marked structuring of the absorption bands referred to the transitions of Tm^{3+} and Yb^{3+} ions as a result of the fact that Tm^{3+} and Yb^{3+} ions are incorporated into high-order monoclinic crystals Tm,Yb:YNbO_4 .

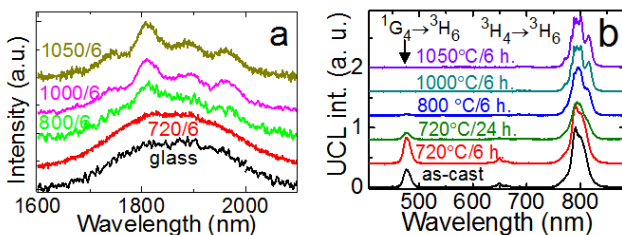


Fig. 2 - PL spectra of glass ceramics under 800 nm excitation (a) and UCL spectra (excitation at 980 nm) (b).

In a similar way the qualitative changes observed for photoluminescence (PL) spectra of the crystallized samples may be explained by reorganization of local surroundings of Tm^{3+} ions. This is clearly seen in Fig. 2 (a) showing NIR luminescence spectra of Tm^{3+} ions excited at 800 nm, which are associated with the transition $^3\text{F}_4 \rightarrow ^3\text{H}_6$. The spectral shapes undergo structuring in the process of heat treatment.

Crystallization of M' phase leads to redistribution of the PL intensity for all of the observed transitions.

Under excitation at 980 nm (absorption band of Yb³⁺ ion), the intense NIR up-conversion luminescence was observed as a sharp structured band at 800 nm, Fig. 2 (b). Meanwhile the blue UCL at 469 nm (¹G₄→³H₆) is dramatically suppressed and the lifetime of NIR luminescence at 800 nm significantly increases – up to 2 ms. Changes in the lifetimes correlate well with the above mentioned intensity redistribution in the PL and UCL spectra. ET efficiency is determined from the shortening of ²F_{5/2} lifetime of Yb³⁺ ions for singly doped Yb:YNbO₄ GCs and codoped Yb,Tm:YNbO₄ GCs to be $\eta_{ET} = 90 \pm 5\%$ for heat-treatments at 800-1000 °C.

In summary, transparent GCs containing Yb,Tm:YNbO₄ nanocrystals and β -quartz ss are synthesized for the first time. They provide intense pure near-IR Tm³⁺ UCL at ~800 nm and are promising up-conversion substrate for efficient third- and second-generation solar cells.

References:

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