Supporting information:

Persistent energy transfer in ZGO:Cr$^{3+}$,Yb$^{3+}$: A new strategy to design nano glass-ceramics featuring deep red and near infrared persistent luminescence

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Fig. S1: (from left to right) Digital images of ZnGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$ precursor glass, nano glass-ceramics elaborated via glass crystallization at $T_{\text{cryst1}} = 900 \, ^{\circ}\text{C}$ and $T_{\text{cryst2}} = 1000 \, ^{\circ}\text{C}$, respectively.

Figure S2: (a) XRPD pattern of ZnGa$_2$O$_4$ (blue), ZnGa$_2$O$_4$:Cr$^{3+}$ (red) and ZnGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$ glass-ceramics elaborated at 1000 $^{\circ}\text{C}$. (b) zoom between 25 $^{\circ}$ and 45 $^{\circ}$ of the XRPD pattern of the same samples.
Fig. S3: Comparison of the normalized photoluminescence spectra recorded at different temperatures (100, 300 and 500 K). This comparison is exposed for samples crystallized at 800, 900 and 1000 °C. ($\lambda_{\text{exc}} = 330$ nm)

Fig. S4: Photoluminescence spectra (normalized on the right side) of ZnGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$ - nGC 1000 °C recorded at temperatures ranging from 100 K to 600 K. ($\lambda_{\text{exc}} = 330$ nm)

These figures show a drastic thermal quenching of $^2E \rightarrow ^4A_2$ emission. Nevertheless, an interesting rise of the $^4T_2 \rightarrow ^4A_2$ broad contribution is observed as the sample temperature is increased. On the normalized spectra a noticeable increase of the Yb$^{3+}$ emission relatively to Cr$^{3+}$ emission is displayed with increasing temperature. This points out the rise of the Cr$^{3+}$ to Yb$^{3+}$ energy transfer with temperature.
The comparison of the normalized photoluminescence spectrum of singly and co-doped materials shows that co-doping leads to the appearance of Yb$^{3+}$ emission ($\lambda_{\text{exc}} = 975 \text{ nm}$) and the decrease of the broad band attributed to the $^4T_2 \rightarrow ^4A_2$ transition. It also shows that this decrease is less and less pronounced as $T_{\text{cryst}}$ increases.
**Fig. S6:** Comparison of persistent luminescence intensities (2 minutes after UV excitation) of Cr$^{3+}$ and Yb$^{3+}$ in samples prepared with different crystallization temperatures. The values have been taken relatively to the Cr$^{3+}$ afterglow intensity of the sample elaborated at 1000 °C. Logarithm scale is used for the vertical axis to underline weak variations.

The comparison of afterglow intensities shows that the sample elaborated at 1000 °C have much higher afterglow intensities for both Cr$^{3+}$ and Yb$^{3+}$. The difference for the Cr$^{3+}$ afterglow intensities is really impressive. On the other hand, for Yb$^{3+}$ persistent intensity, the difference is quite small especially going from 900 °C to 1000 °C. This may be due to the balance between the lower energy transfer but more efficient Cr$^{3+}$ persistent emission using materials elaborated at higher temperatures.
Fig. S7. 2D PL/PLE spectra of the singly doped sample.

On that supplementary figure, it can be observed that no distinct excitation band located at 975 nm is obtained looking at Cr$^{3+}$ emission in the singly doped material. This corroborates the effect of Yb$^{3+}$ in the up conversion properties obtained with the co-doped sample.
As described in the manuscript, excitation through the Yb\(^{3+}\) band (i.e. \(\lambda = 975\) nm) corresponds to an energy of 1.27 eV while two photon excitation (2.54 eV i.e. 487.5 nm) appears, as seen on Figure 5, in the Cr\(^{3+}\) \(4A_2 \rightarrow 4T_2\) excitation band. Therefore, as proposed in other hosts by Heer et al., the involved two photon up-conversion mechanism may be the cooperative sensitization from two Yb\(^{3+}\) to Cr\(^{3+}\).\(^1,2\) The cooperative sensitization from two Yb\(^{3+}\) to Cr\(^{3+}\) is depicted in Figure S8 (a). Moreover, on the photoluminescence spectra exciting in the Yb\(^{3+}\) \(2F_{7/2} \rightarrow 2F_{5/2}\) band (\(\lambda_{\text{exc}} = 976\) nm), it is possible to observe additional bands around 600 nm (inset of figure S8 (b)). Due to its spectral position, these bands can be attributed to Er\(^{3+}\) \(4F_{9/2} \rightarrow 4I_{15/2}\). Indeed, it is very likely to find Er\(^{3+}\) as an impurity coming from the ytterbium oxide precursor. Hence, an energy transfer up-conversion (ETU) mechanism may be considered as it is well known that Yb\(^{3+}\) efficiently acts as an efficient sensitizer of Er\(^{3+}\).\(^3–5\) Though the Er\(^{3+}\) presence is very minute, its up-conversion efficiency with Yb\(^{3+}\) is significant. Therefore, some contribution from Er\(^{3+}\) in the up-conversion process can be expected. This related up-conversion mechanism is depicted in figure 8 (b).
Fig. S9: Thermoluminescence spectrum of ZnGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$ nGC – 1000 °C recorded at different temperatures.

On the one hand, the thermoluminescence spectrum shows an increase of the Cr$^{3+}$ thermoluminescence intensity until 330 K followed by its decrease. On the other hand, the Yb$^{3+}$ thermoluminescence intensity shows an increase until 380 K followed by its decrease. This reveals the effect of temperature on the persistent energy transfer from Cr$^{3+}$ to Yb$^{3+}$.


