Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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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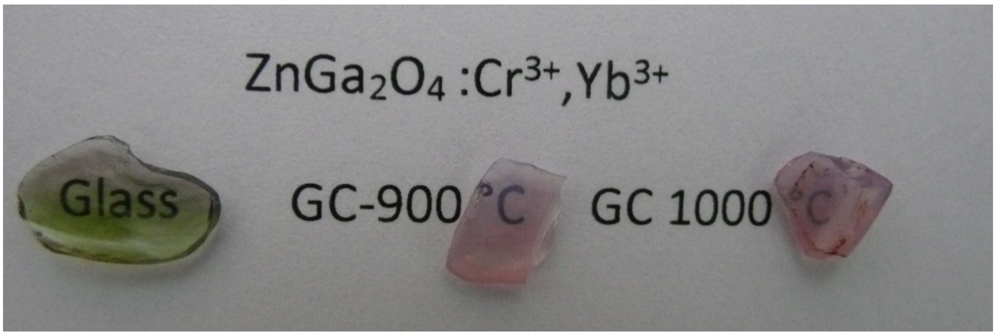

Fig. S1: (from left to right) Digital images of $ZnGa_2O_4$:Cr^{3+},Yb^{3+} precursor glass, nano glass-ceramics elaborated via glass crystallization at T_{cryst1} = 900 °C and T_{cryst2} = 1000 °C, respectively.

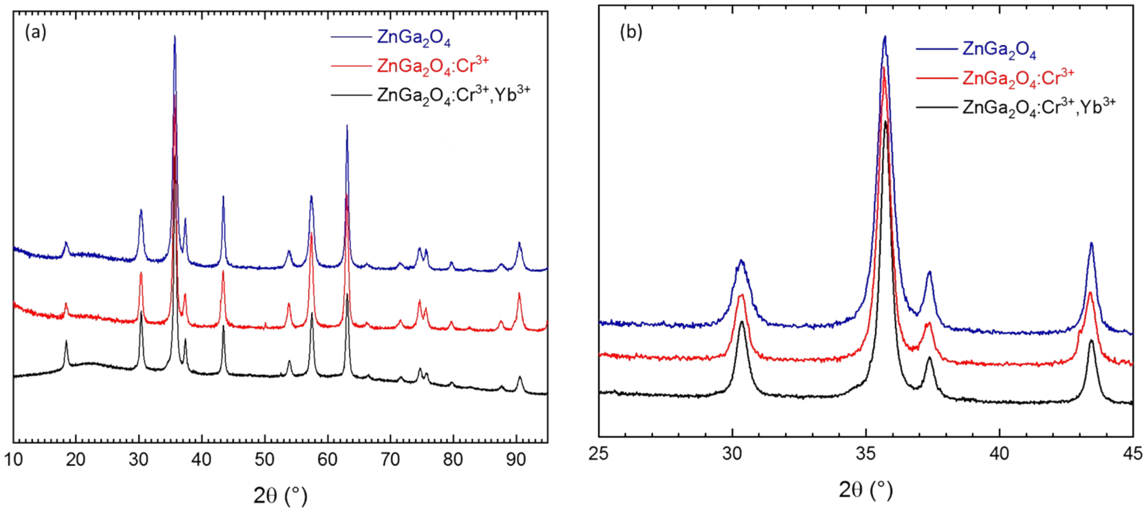

Figure S2: (a) XRPD pattern of $ZnGa_2O_4$ (blue), $ZnGa_2O_4$:Cr^{3+} (red) and $ZnGa_2O_4$:Cr^{3+},Yb^{3+} glass-ceramics elaborated at 1000 °C. (b) zoom between 25 ° and 45 ° of the XRPD pattern of the same samples.

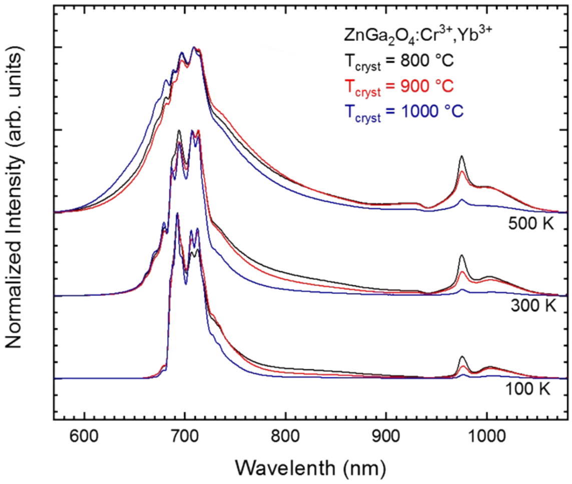

Fig. S3: Comparison of the normalized photoluminescence spectra recorded at different temperatures (100, 300 and 500 K). This comparison is exposed for samples crystallized at 800, 900 and 1000 °C. (λ_{exc} = 330 nm)

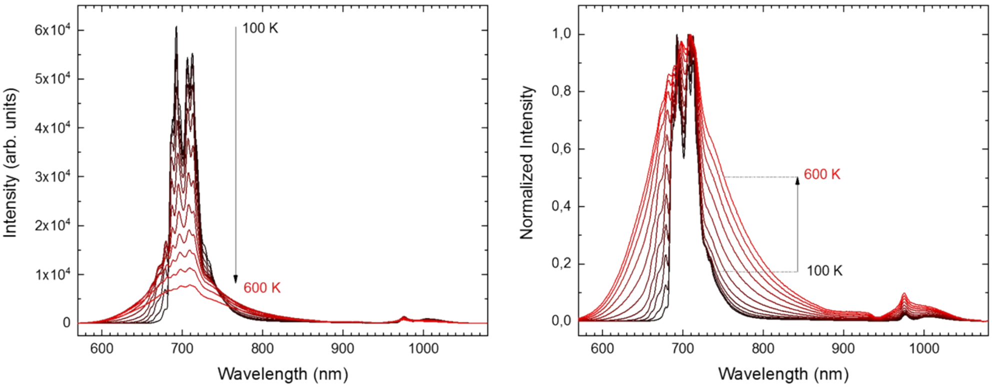

Fig. S4: Photoluminescence spectra (normalized on the right side) of $ZnGa_2O_4$:Cr^{3+},Yb^{3+} - nGC 1000 °C recorded at temperatures ranging from 100 K to 600 K. (λ_{exc} = 330 nm)

These figures show a drastic thermal quenching of $^2E \longrightarrow {}^4A_2$ emission. Nevertheless, an interesting rise of the $^4T_2 \longrightarrow {}^4A_2$ 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.

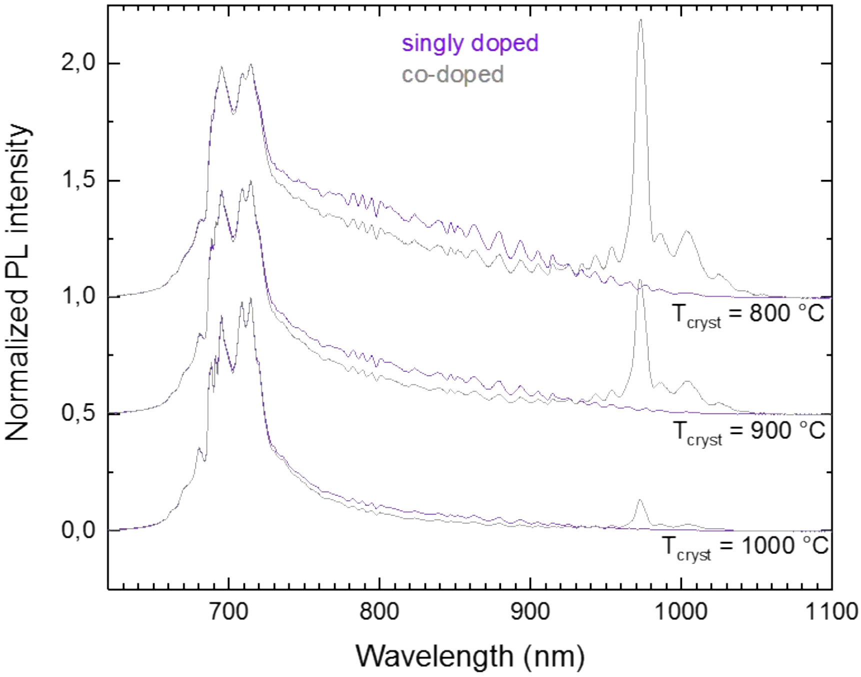

Fig. S5: Comparison of normalized photoluminescence spectra of singly and co-doped $ZnGa_2O_4$ nGC elaborated at different temperatures. (λ_{exc} = 365 nm)

The comparison of the normalized photoluminescence spectrum of singly and co-coped materials shows that co-doping leads to the appearance of Yb^{3+} emission (λ_{exc} = 975 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_{cryst} increases.

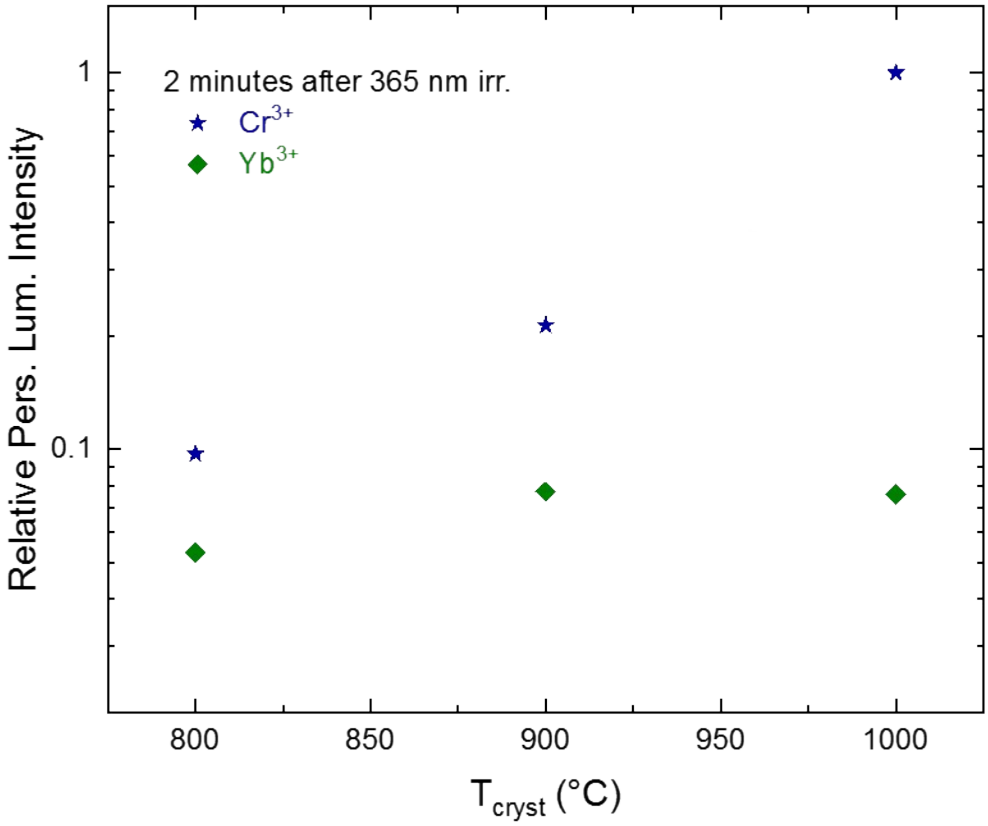

Fig. S6: Comparison of persistent luminescence intensities (2 minutes after UV excitation) of Cr^{3+} and Yb^{3+} in samples prepared with different crystallization temperatures. The values have been taken relatively to the Cr^{3+} afterglow intensity of the sample elaborated at 1000 °C. Logarithm scale 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.

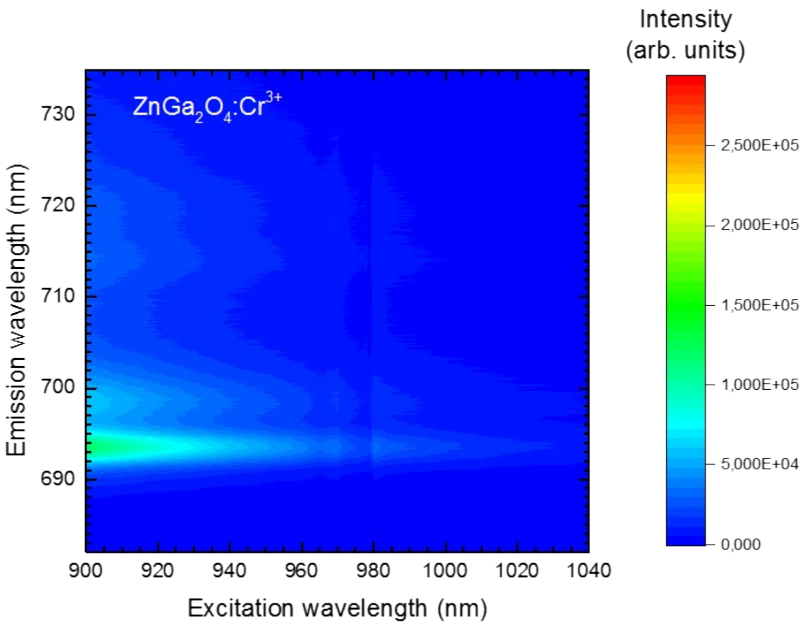

Fig. S7. 2D PL/PLE spectra of the singly doped sample.

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.

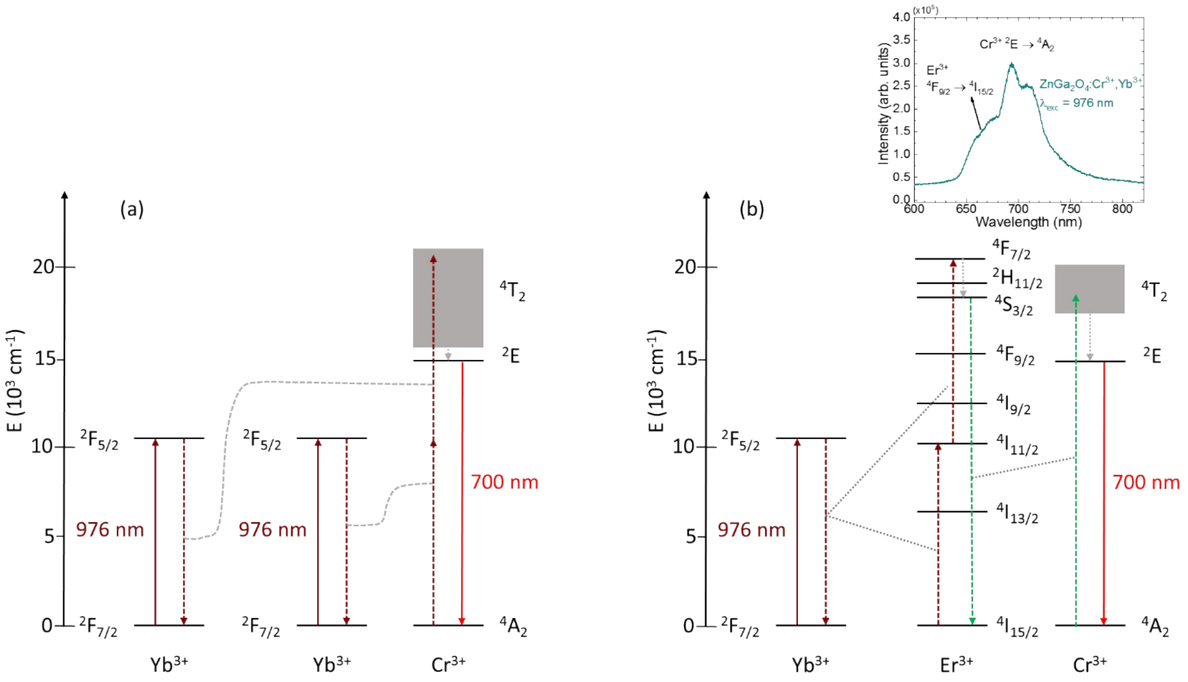

Fig. S8: (a) Cooperative sensitization up-conversion mechanism. (b) Possible ETU mechanism as erbium is a common impurity in the ytterbium doped compounds. In the inset, the PL spectrum of the sample is depicted (λ_{exc} = 976 nm).

As described in the manuscript, excitation through the Yb^{3+} band (i.e. λ = 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 (λ_{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).

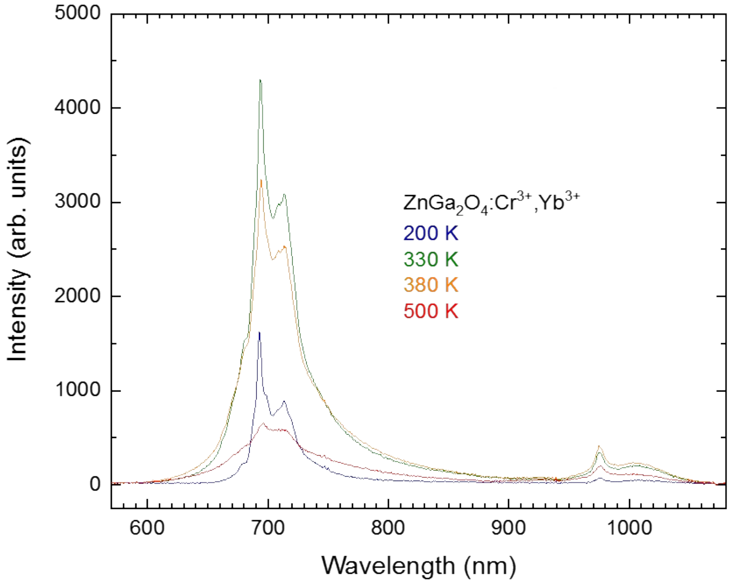

Fig. S9: Thermoluminescence spectrum of ZnGa2O4:Cr3+,Yb3+ nGC – 1000 °C recorded at different temperatures.

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+}.

1. Heer, S., Wermuth, M., Krämer, K., Ehrentraut, D. & Güdel, H. U. Up-conversion excitation of sharp Cr3+ 2E emission in YGG and YAG codoped with Cr3+ and Yb3+. *Journal of Luminescence* **94–95**, 337–341 (2001).
2. Heer, S., Wermuth, M., Krämer, K. & Güdel, H. U. Sharp 2 E upconversion luminescence of Cr 3 + in Y 3 Ga 5 O 12 codoped with Cr 3 + and Yb 3 +. *Physical Review B* **65**, (2002).
3. Auzel, F. E. Compteur quantique par transfert d'énergie entre deux ions de terres rares dans un tungstate mixte et dans un verre. 1016 (1966).
4. Bril, A. On the Efficiency of Yb3+-Er3+ Activated Up-Conversion Phosphors. *J. Electrochem. Soc.* **122**, 660 (1975).
5. Auzel, F. Upconversion and Anti-Stokes Processes with f and d Ions in Solids. *Chem. Rev.* **104**, 139–174 (2004).