**Figure S1**: Rietveld refinement of X-ray powder diffraction pattern (Rwp=2.41%, Rp=1.70% and GOF=2.60) of the ZnGa$_2$O$_4$ glass-ceramic crystallized at 1000°C for 10 min. The powder has been mixed with pure Li$_2$CO$_3$ as internal standard for amorphous phase quantification. Set of blue and green vertical lines correspond to reflection positions of ZnGa$_2$O$_4$ (ICSD 9394) and Li$_2$CO$_3$ (ICSD 16713), respectively.
Figure S2. TEM images of different SiO$_2$-Na$_2$O-ZnO-Ga$_2$O$_3$ glass compositions showing the effect of the SiO$_2$ and Na$_2$O content on the phase separation nanostructure.
Figure S3. TEM images of 55SiO$_2$-5Na$_2$O-17ZnO-23Ga$_2$O$_3$ glass-ceramics heated during 10 minutes at (a) 800°C, (b) 1100°C and (c) 1200°C.

Figure S4: DSC thermogram of the 55SiO$_2$-5Na$_2$O-17ZnO-23Ga$_2$O$_3$ glass
Figure S5. TEM images of 55SiO$_2$-5Na$_2$O-20ZnO-20Ga$_2$O$_3$ glass (a) glass-ceramics heated at 680°C (b) with the corresponding selected area electron diffraction pattern embedded.

Figure S6: In situ X-ray diffractograms collected during heating and starting from a 55SiO$_2$-5Na$_2$O-20ZnO-20Ga$_2$O$_3$ glass powder sample. The ZnGa$_2$O$_4$ and Zn$_2$SiO$_4$ spinel phases appear simultaneously at 675°C and SiO$_2$ at 1000°C.
Figure S7. (bottom) STEM-EDX cationic composition profile through the crystallizing phase in the 55SiO₂-5Na₂O-17 ZnO-23Ga₂O₃ (a) glass and (b) glass-ceramic elaborated at 900°C. (top) The localization of the analysis points is illustrated on the associated STEM-HAADF image.

Figure S8. STEM-HAADF images of 55SiO₂-5Na₂O-17ZnO-23Ga₂O₃ (a) glass and (b) glass-ceramic elaborated at 900°C with associated Ga (cyan), Zn (purple) and Si (green) STEM-EDX elemental mappings showing the localization of Zn and Ga in the crystallizing phase.
**Figure S9.** (a) Excitation spectrum (recording emission at 696nm) and (b) emission spectra recorded at different excitation wavelengths of 55SiO$_2$-5Na$_2$O-17ZnO-23Ga$_2$O$_3$ glass-ceramic elaborated at 1000°C.

**Figure S10.** UV-excited fluorescence spectra recorded on a 0.05% Cr$^{3+}$-doped 55SiO$_2$-5Na$_2$O-17ZnO-23Ga$_2$O$_3$ glass (dash line) and glass-ceramic heated during 10 min at 1000°C (solid line).