Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

ELECTRONIC SUPPLEMENTARY INFORMATION

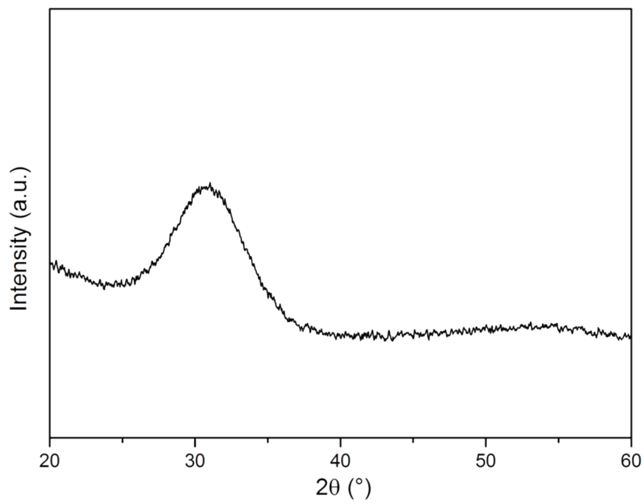

Fig. S1: X-Ray diffractogram of the $Gd_{1.6}Sr_{0.4}Ga_3O_{7.3}$ glass elaborated by aerodynamic levitation coupled to CO_2 laser heating.

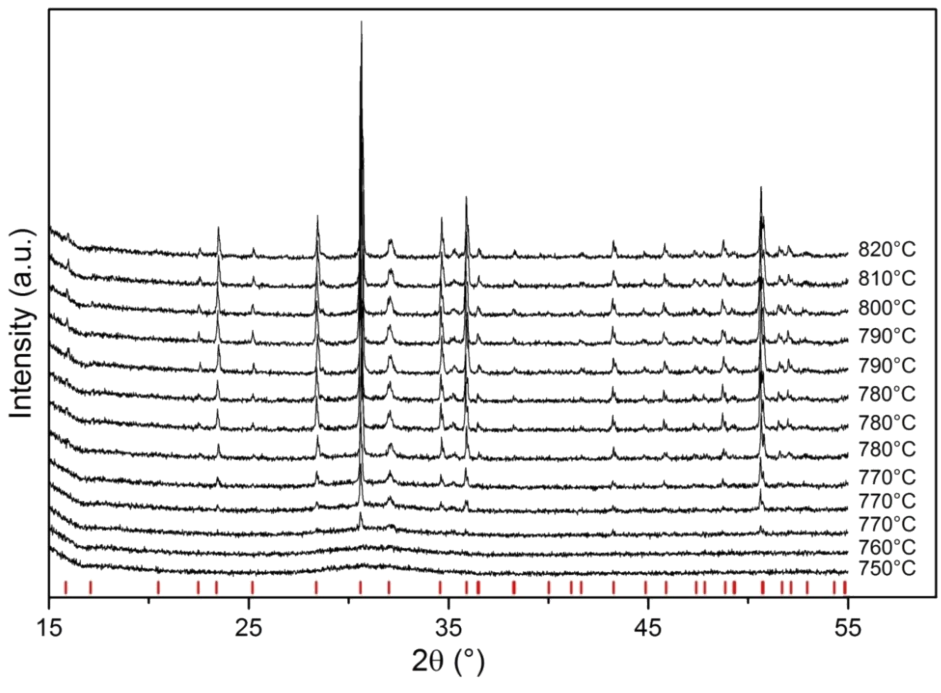

Fig. S2: *In situ* X-ray diffraction data of the $Gd_{1.6}Sr_{0.4}Ga_3O_{7+\delta}$ parent glass heated from 750°C up to 820 °C (some measurements have been repeated at a same temperature to track possible isothermal evolution). Only the melilite phase crystallizes from the glass at around 770°C, in good agreement with the DSC measurements. The red marks correspond to the indexation of the $Gd_{1.6}Sr_{0.4}Ga_3O_{7+\delta}$ melilite.

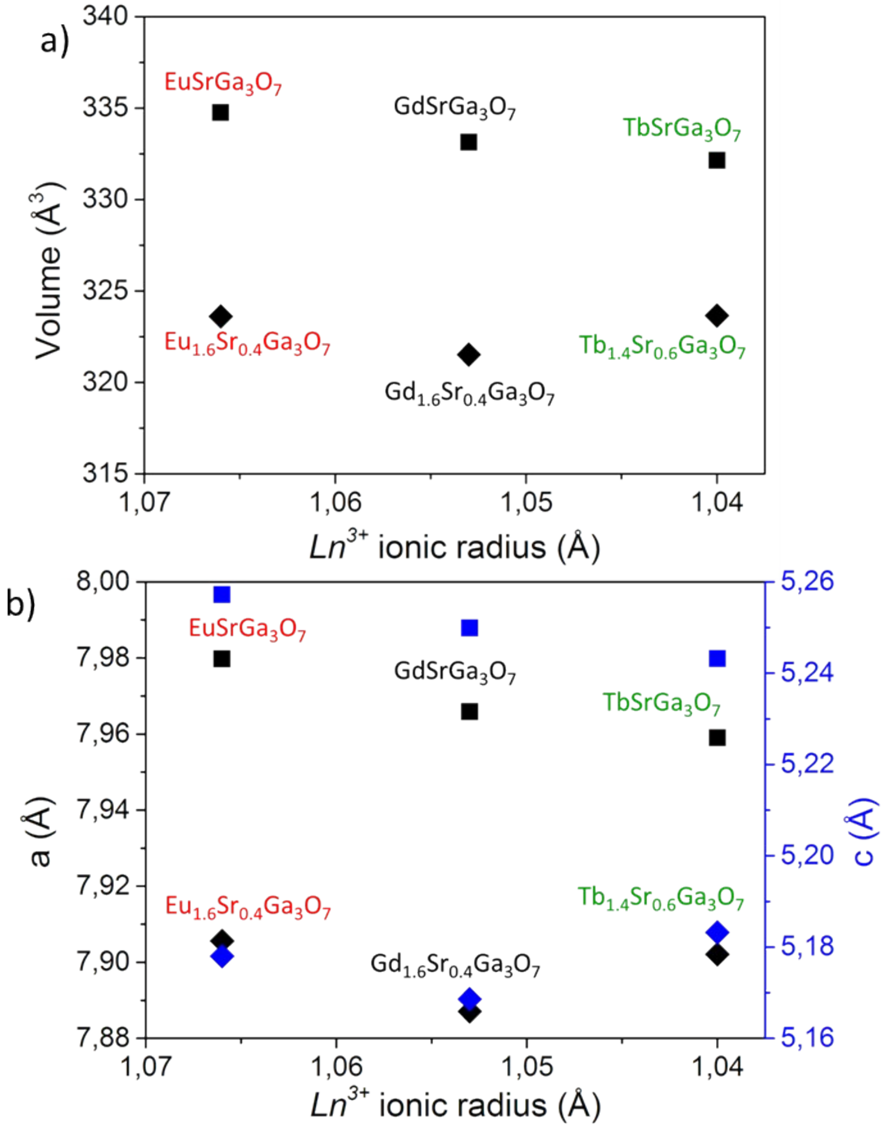

Fig. S3: a) Volume and b) cell parameters (*a* (black) and *c* (blue)) according to the lanthanide radius, of the stoichiometric (square) and non-stoichiometric (diamond) melilite ceramics. The $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ cell parameters decrease to a lesser extent than those of the gadolinium and europium based-materials, in agreement with their lower substitution level.

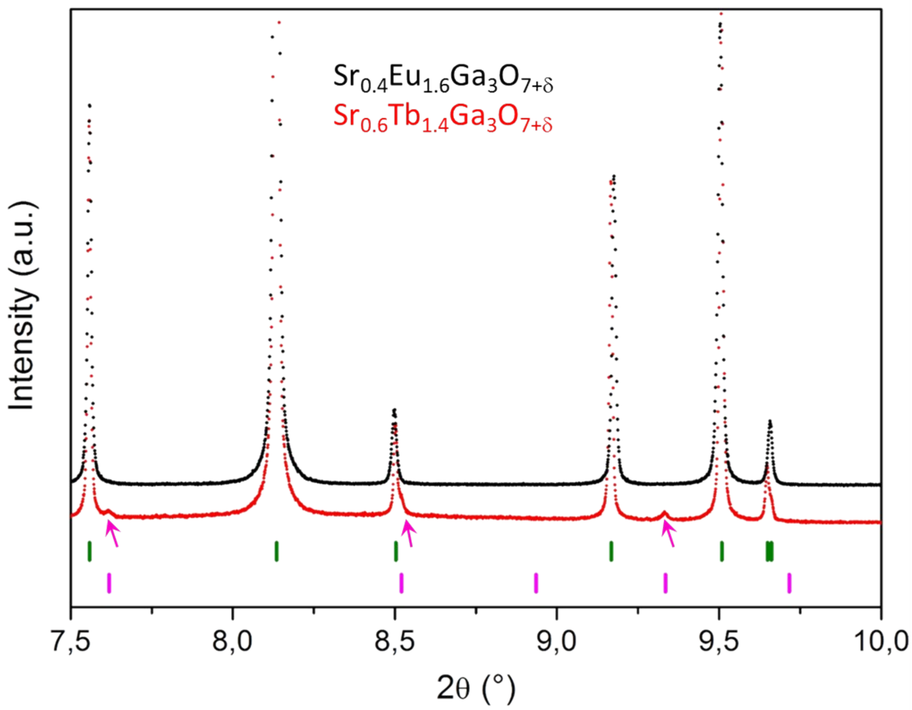

Fig. S4: Synchrotron powder diffraction data of $Eu_{1.6}Sr_{0.4}Ga_3O_{7+\delta}$ (in black) and $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ (in red) ceramics (enlargement of the 7.5 to 10° 2θ zone). The set of green and pink vertical lines corresponds to $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ (melilite) and $Tb_3Ga_5O_{12}$ (garnet) reflection positions respectively. The arrows point to the $Tb_3Ga_5O_{12}$ secondary phase.

	U11	U22	U33	U12	U13	U23
Sr1	2,18(1)	2,18(1)	1,49(2)	1,42(2)	0,13(2)	-0,13(2)
Tb1	2,18(1)	2,18(1)	1,49(2)	1,42(2)	0,13(2)	-0,13(2)
Ga1	0,85(2)	0,85(2)	1,36(4)	0	0	0
Ga2	1,33(2)	1,33(2)	0,48(3)	0,34(3)	0,01(2)	-0,01(1)
O1	3,93(5)	3,93(5)	0,08(5)	0,84(9)	0,23(4)	-0,23(4)
O2	2,3(6)	7,29(9)	2,52(6)	-2,46(6)	1,35(5)	-2,09(5)
O3	4,9(1)	4,9(1)	0,7(9)	3,8(1)	0	0

Fig. S5: Anisotropic displacement parameters (ADP) (Å² x 100) of the final $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ ceramic determined from the combined Rietveld refinement.

	Archimedes' method		Rietveld Refinement
	ρ (glass) g.cm^{-3}	ρ (ceramic) g.cm^{-3}	ρ (ceramic) g.cm^{-3}
$Eu_{1.6}Sr_{0.4}Ga_3O_{7+\delta}$	6.25 ± 0.05	6.26 ± 0.05	6.20 ± 0.01
$Gd_{1.6}Sr_{0.4}Ga_3O_{7+\delta}$	6.28 ± 0.05	6.32 ± 0.05	6.33 ± 0.01
$Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$	6.16 ± 0.05	6.13 ± 0.05	6.17 ± 0.01

Fig. S6: Density of the glasses and corresponding ceramics determined from Archimedes' method and calculated from Rietveld refinement.

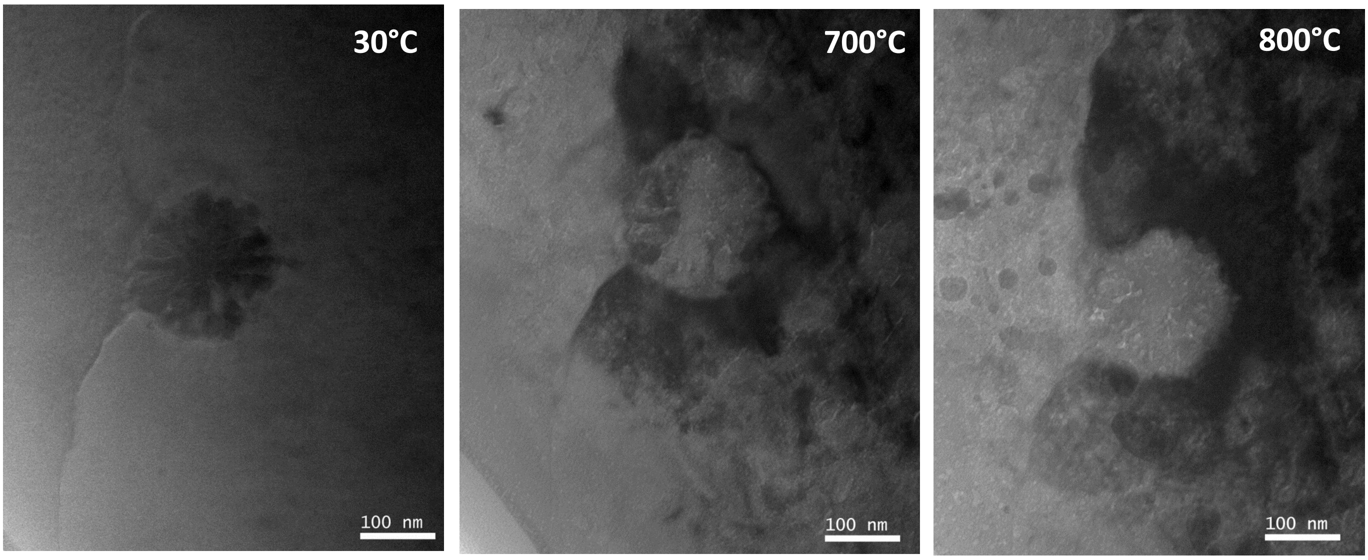

Fig S7: *In situ* observations of the $Tb_{1.4}Sr_{0.6}Ga_3O_{7.2}$ ceramic heated from room temperature up to 800 °C. Bright field TEM images showing two melilite grains separated by a grain boundary and one $Tb_3Ga_5O_{12}$ nanoparticle aggregate. No microstructural evolution can be observed. Black marks appearing at 800°C are related to carbon contamination during STEM experiment.

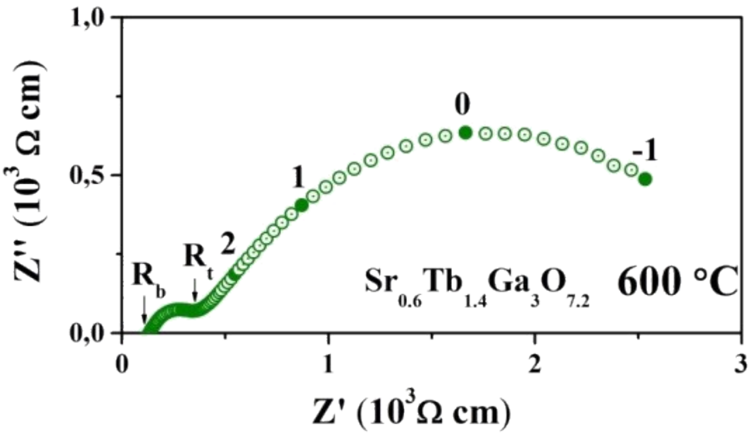

Fig S8: Complex impedance plots at 600 °C for the $Tb_{1.4}Sr_{0.6}Ga_3O_{7.2}$ ceramic. R_b and R_t denote the bulk and total resistivities, respectively. The numbers denote the logarithms of selected frequencies marked by filled circles.

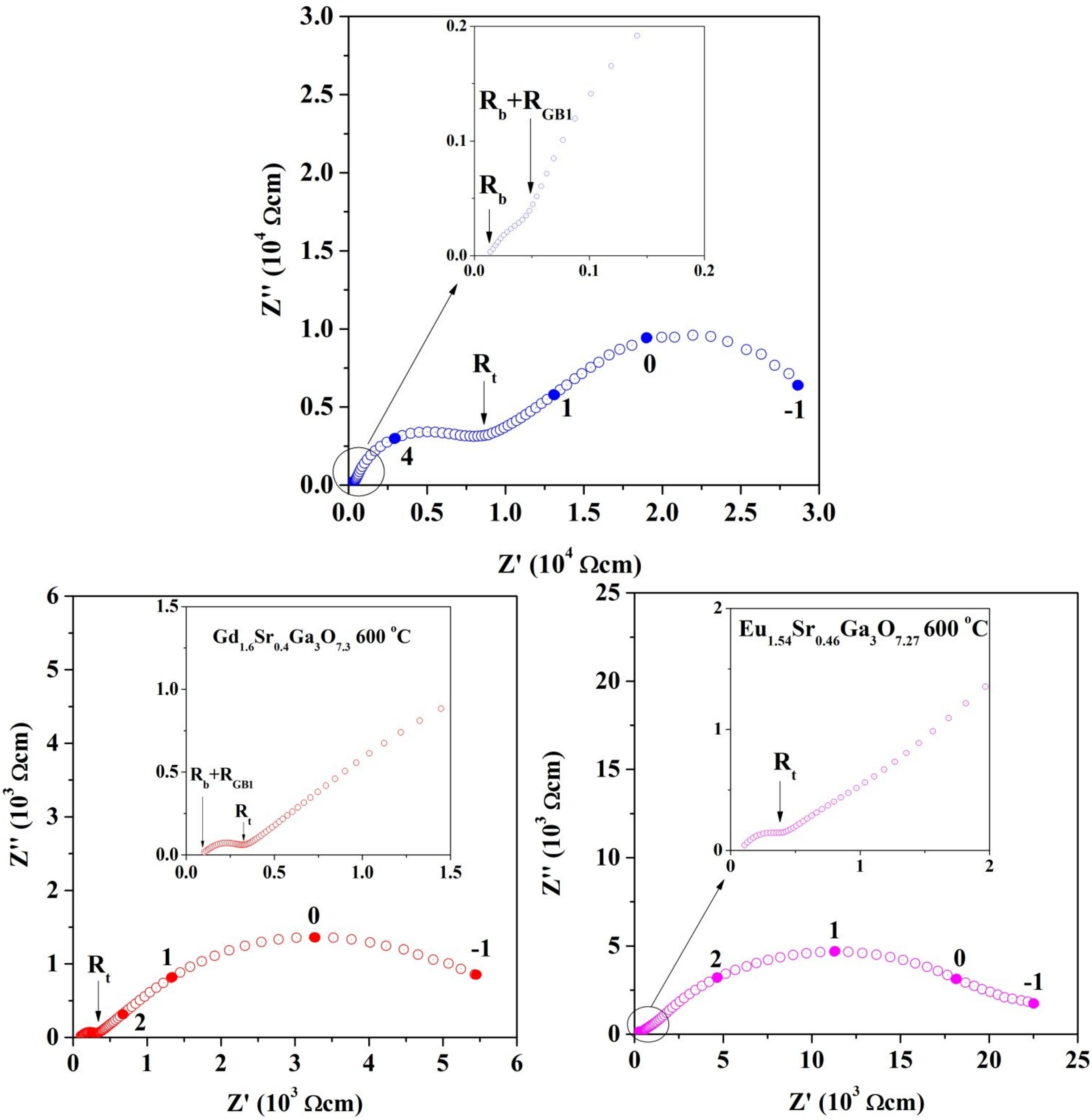

Fig. S9: Complex impedance plot at 500 °C (top) for $Gd_{1.6}Sr_{0.4}Ga_3O_{7.3}$ ceramic and 600 °C (down) for $Gd_{1.6}Sr_{0.4}Ga_3O_{7.3}$ and $Eu_{1.54}Sr_{0.46}Ga_3O_{7.27}$ ceramics. The numbers denote the logarithms of selected frequencies marked by filled circles. The insets enlarges the plots in the high frequency range.

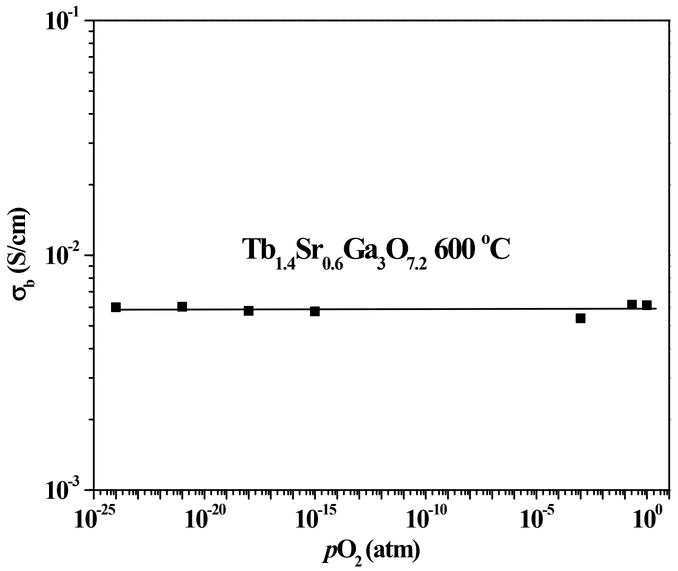

Fig. S10: Bulk conductivity as a function of pO_2 for $Tb_{1.4}Sr_{0.6}Ga_3O_{7.2}$ No evolution is observed, proving the pure ionic conductivity of these ceramics.

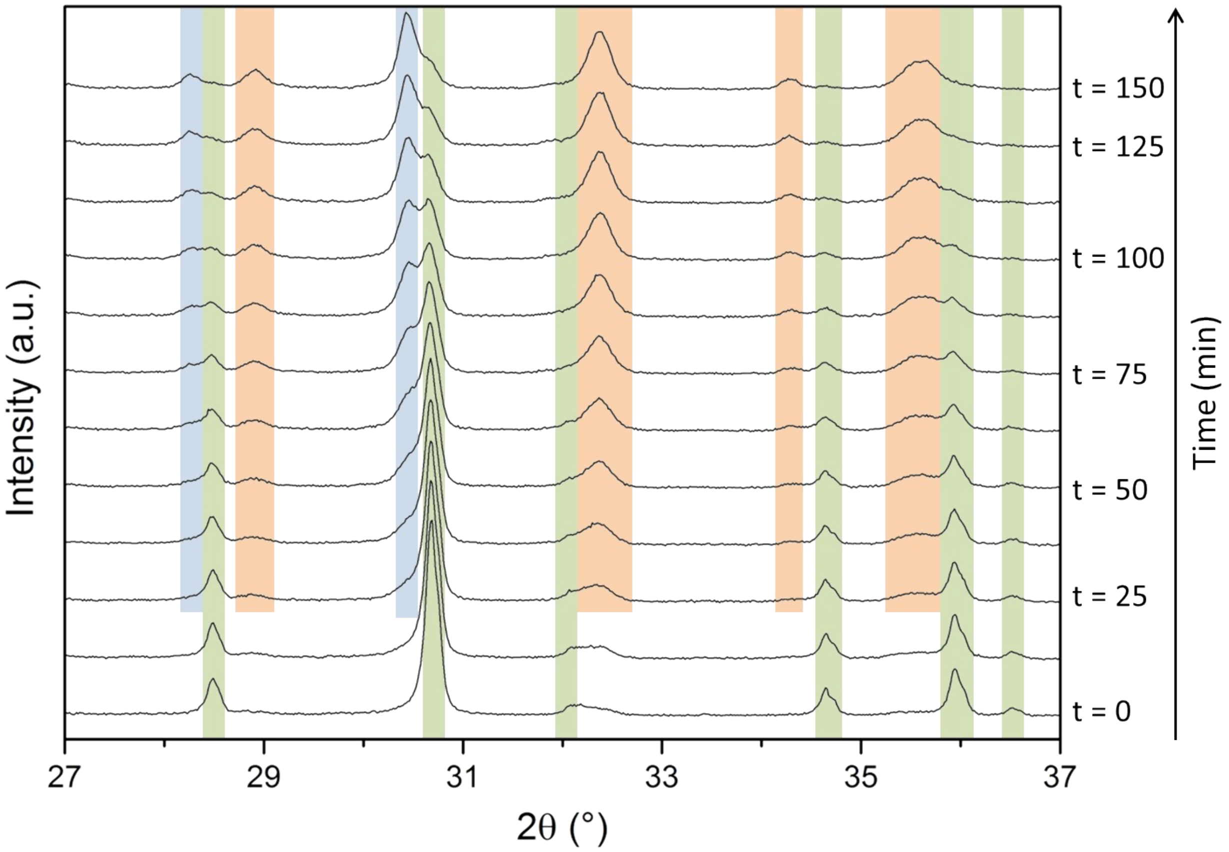

Fig. S11: *in situ* XRD measurement of the $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ ceramic at 900°C for 2h30min. The diffractograms were acquired each 12.5 min. Green bands correspond to the $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ reflections whereas the blue and orange ones are related to the degradation into $TbSrGa_3O_7$ (stoichiometric melilite) and $Tb_3Ga_5O_{12}$ (garnet) phases respectively.

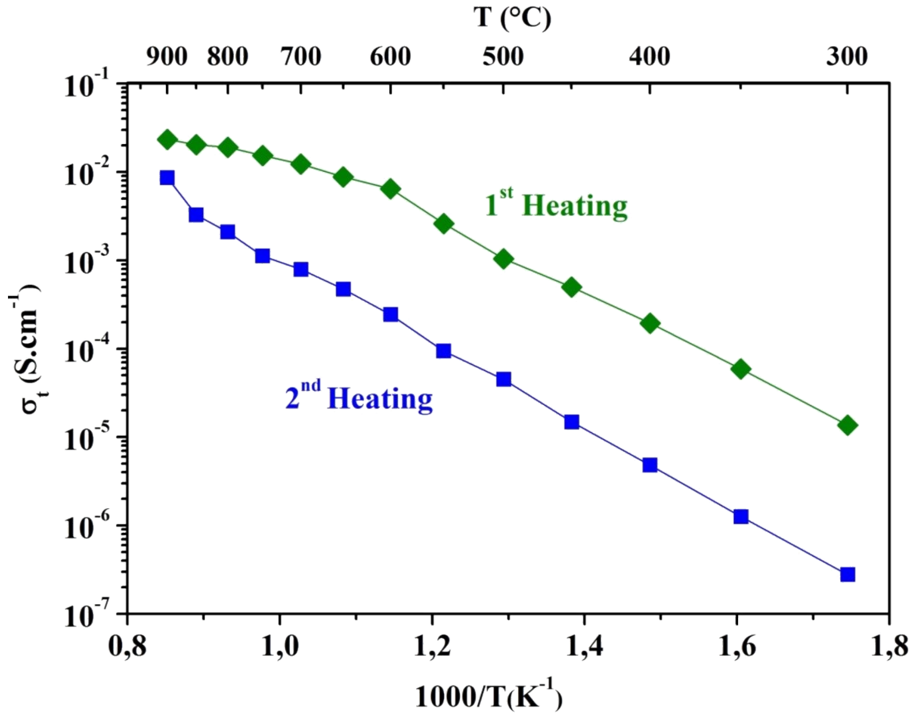

Fig. S12: Total conductivity of a $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ ceramic bead, after a first (green) and a second heating cycle (blue).

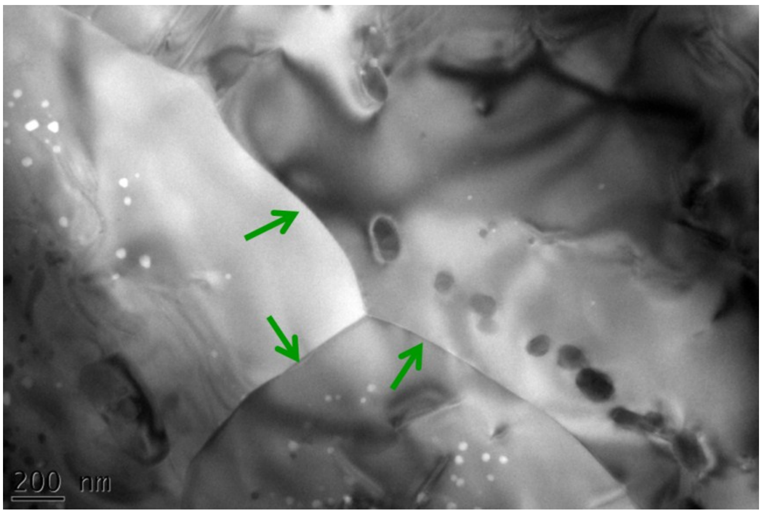

Fig. S13: Bright field TEM micrograph of intact thin grain boundaries (green arrows) in the $Tb_{1.4}Sr_{0.6}Ga_3O_{7+\delta}$ ceramic after ionic conductivity measurements at high temperature.