Towards economic processing of high performance garnets – Case study on zero Li excess Ga-substituted LLZO

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Supplementary information

Extended ICP-OES results

Table SI1. Comparison of the ICP-OES results for different dwell times and excess lithium. Stoichiometry in reference to La. Errors on Hf and Al content on the overall stoichiometry are insignificant and therefore not shown.

| Lithium excess	Sample	Li (mol)	La (mol)	Zr (mol)	Al (mol)	Hf (mol)	Ga (mol)
0%	theoretical value	6.4	3	1.98	0	0.02	0.2
20%	1. calcination	7.75(21)	3.00	1.86(6)	< 0.005	0.02	0.23(1)
	2. calcination	7.67(36)	3.00	1.88(7)	< 0.005	0.02	0.23(2)
	1 h	7.10(41)	3.00	1.87(12)	< 0.005	0.02	0.21(1)
	5 h	7.44(52)	3.00	1.88(13)	0.01	0.02	0.22(2)
	10 h	7.05(22)	3.00	1.89(8)	0.01	0.02	0.19(1)
	20 h	6.73(28)	3.00	1.90(7)	0.01	0.02	0.14(2)
10%	1. calcination	7.09(27)	3.00	1.88(8)	< 0.005	0.02	0.23(1)
	2. calcination	7.08(19)	3.00	1.88(5)	< 0.005	0.02	0.24(1)
	1 h	7.07(51)	3.00	1.83(13)	0.05	0.02	0.23(2)
	5 h	6.80(28)	3.00	1.85(7)	0.01	0.02	0.22(1)
	10 h	6.67(60)	3.00	1.80(16)	0.03	0.02	0.19(2)
	20 h	6.54(20)	3.00	1.88(6)	0.02	0.02	0.19(1)
5%	1. calcination	6.72(48)	3.00	1.87(10)	< 0.005	0.02	0.22(1)
	2. calcination	6.72(49)	3.00	1.87(11)	< 0.005	0.02	0.22(1)
	1 h	6.72(33)	3.00	1.88(10)	< 0.005	0.03	0.26(2)
	5 h	6.67(32)	3.00	1.86(9)	< 0.005	0.02	0.23(1)
	10 h	6.64(33)	3.00	1.85(8)	0.04	0.02	0.24(3)
	20 h	6.56(36)	3.00	1.85(9)	0.04	0.02	0.23(2)
0%	1. calcination	6.51(23)	3.00	1.82(5)	< 0.005	0.02	0.22(1)
	2. calcination	6.42(17)	3.00	1.86(3)	< 0.005	0.02	0.22(1)
	1 h	6.62(40)	3.00	1.87(12)	< 0.005	0.02	0.23(2)
	5 h	6.56(31)	3.00	1.86(9)	< 0.005	0.02	0.23(2)
	10 h	6.66(58)	3.00	1.89(17)	0.03	0.03	0.25(2)
	20 h	6.56(62)	3.00	1.87(18)	0.03	0.02	0.23(3)

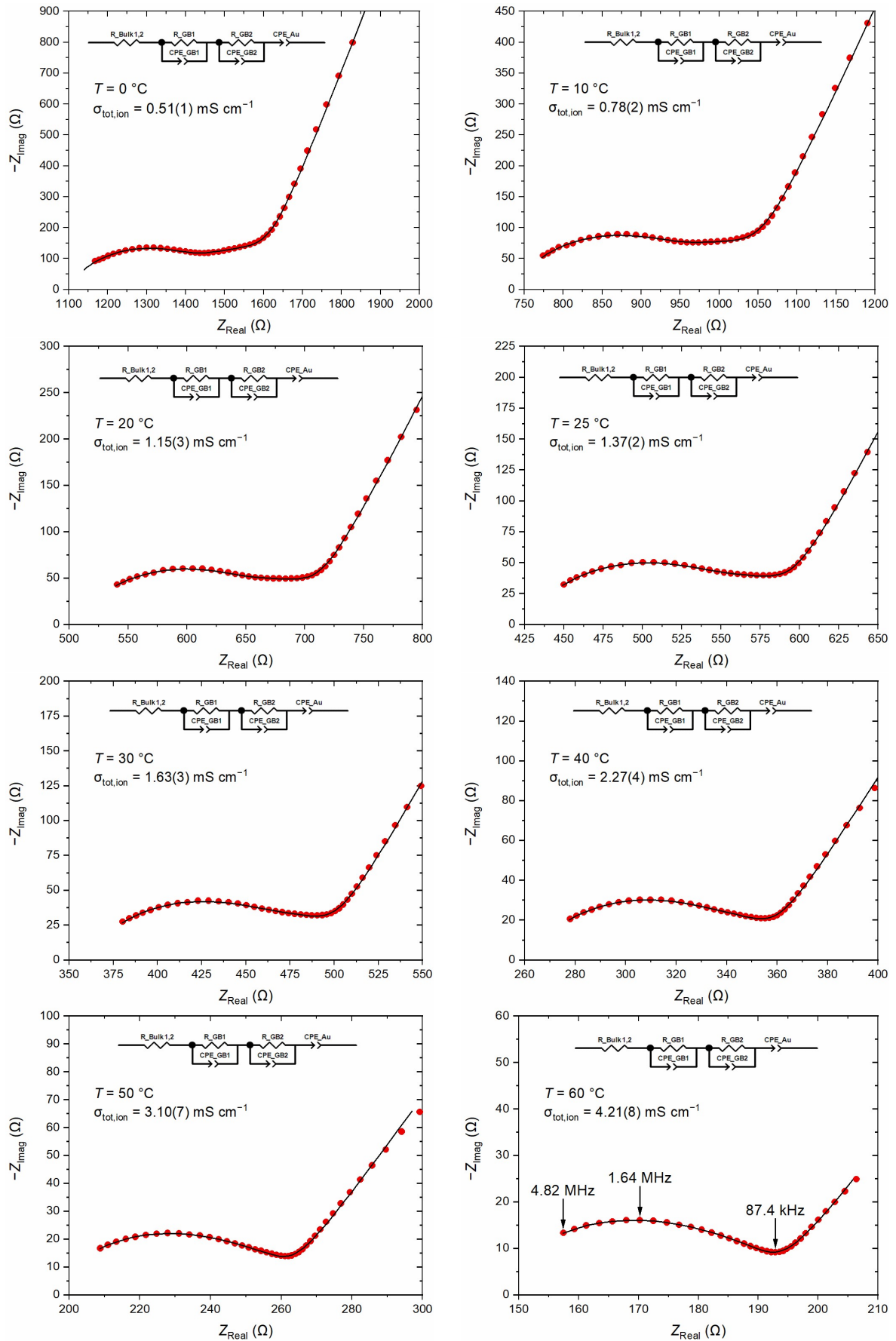# X-ray diffraction patterns of sintered pellets
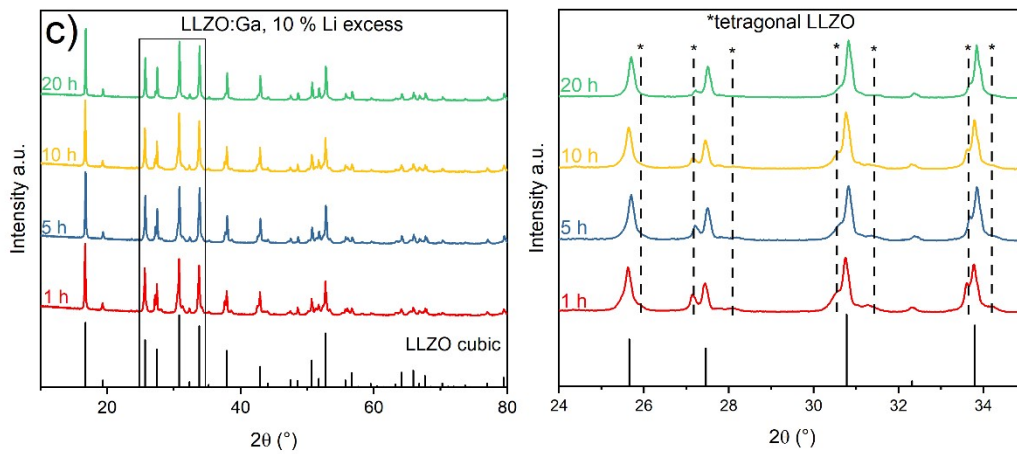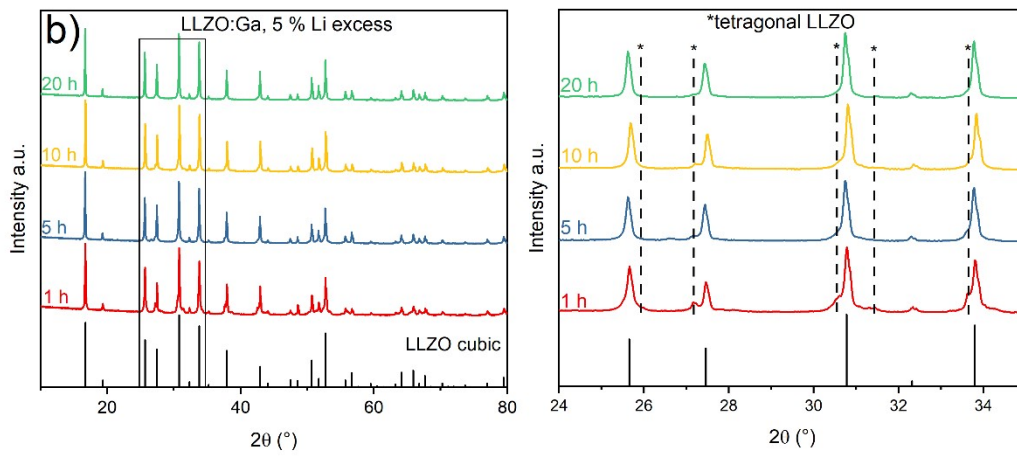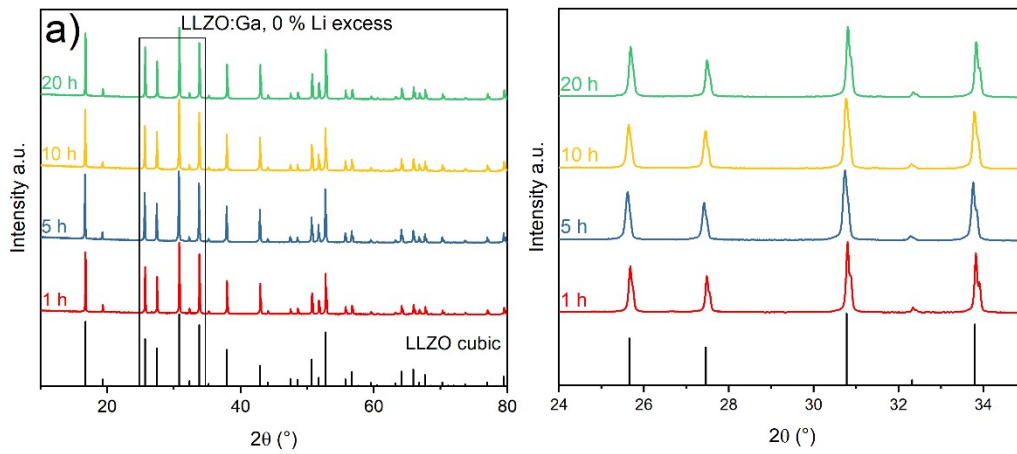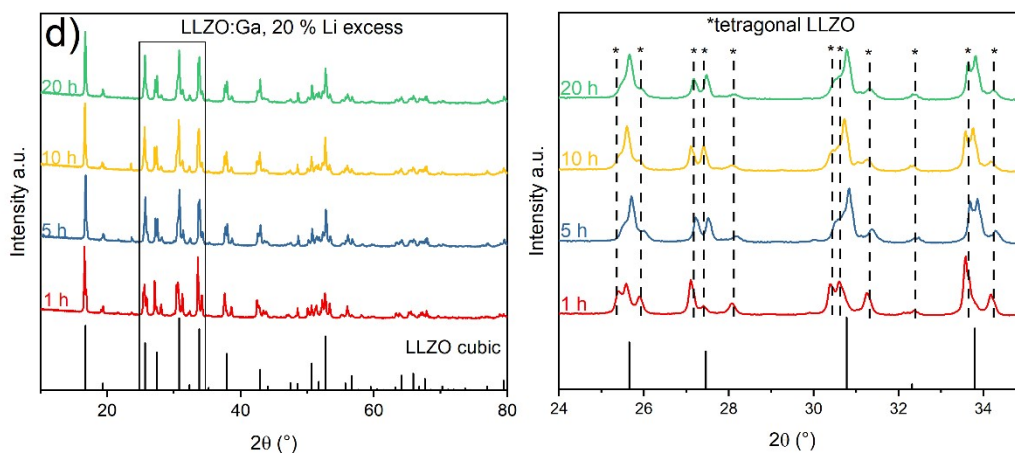
Figure SI1. XRD patterns of LLZO:Ga with (a) 0 % (b) 5% (c) 10% and (d) 20 % Lithium excess after different dwell times at 1175 °C.

EIS results and respective fits of 0% Li excess LLZO:Ga sintered at 1175 °C for 5 h in a temperature range of −40 °C to +60 °C.
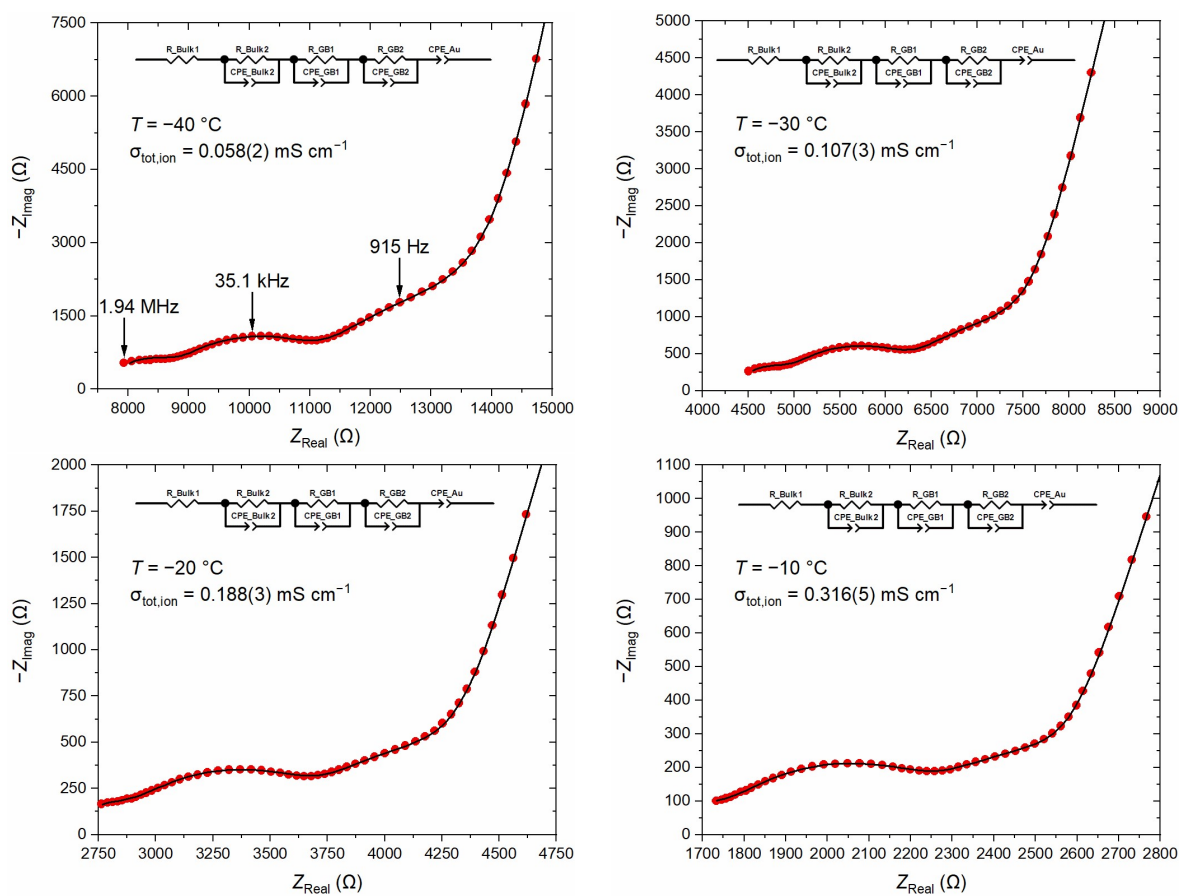
Figure SI2. EIS fits of 0% Li excess LLZO:Ga sintered at 1175 °C for 5 h in a temperature range from −40 °C to +60 °C.

Table SI2. EIS fit results of 0% Li excess LLZO:Ga sintered at 1175 °C for 5 h in a temperature range from −40 °C to +60 °C.

Parameter	−40 °C	−30 °C	−20 °C	−10 °C
R_{Bulk1} (Ω)	7635(15)	4316(8)	2617(3)	1621(4)
R_{Bulk2} (Ω)	1109(21)	543(12)	247(3)	124(3)
C_{Bulk2} (F)	$1.21(5) \cdot 10^{-10}$	$1.48(5) \cdot 10^{-10}$	$1.94(5) \cdot 10^{-10}$	$1.3(7) \cdot 10^{-10}$
R_{GB1} (Ω)	2475(86)	1447(43)	890(11)	556(7)
C_{GB} (F)	$1.8(8) \cdot 10^{-9}$	$1.8(7) \cdot 10^{-9}$	$1.7(3) \cdot 10^{-9}$	$1.6(3) \cdot 10^{-9}$
R_{GB2} (Ω)	2728(167)	1168(54)	513(12)	248(7)
C_{GB2} (F)	$7.6(35) \cdot 10^{-8}$	$8.0(31) \cdot 10^{-8}$	$8.9(17) \cdot 10^{-8}$	$9.4(21) \cdot 10^{-8}$
$\sigma_{\text{tot,ion}}$ (mS cm^{-1})	0.058(2)	0.107(3)	0.188(3)	0.316(5)

Parameter	0 °C	10 °C	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C
$R_{\text{Bulk1,2}}$	1098(3)	735(3)	506.8(17)	426.5(7)	360.2(7)	262.0(5)	195.1(5)	146.0(3)
R_{GB1} (Ω)	360(8)	236(7)	158(5)	135(3)	113(3)	81(2)	55(2)	38.8(12)
C_{GB} (F)	$1.4(6) \cdot 10^{-9}$	$1.4(9) \cdot 10^{-9}$	$1.5(9) \cdot 10^{-9}$	$1.5(5) \cdot 10^{-9}$	$1.5(6) \cdot 10^{-9}$	$1.6(6) \cdot 10^{-9}$	$1.7(9) \cdot 10^{-9}$	$1.8(7) \cdot 10^{-9}$
R_{GB2} (Ω)	131(5)	66(5)	37(3)	27.5(16)	21.3(17)	12.1(14)	9.2(16)	6.6(8)
C_{GB2} (F)	$8.1(7) \cdot 10^{-8}$	$8.3(10) \cdot 10^{-8}$	$8.4(12) \cdot 10^{-8}$	$9.4(11) \cdot 10^{-8}$	$8.7(17) \cdot 10^{-8}$	$8.7(17) \cdot 10^{-8}$	$6.1(16) \cdot 10^{-8}$	$5.8(11) \cdot 10^{-8}$
$\sigma_{\text{tot,ion}}$ (mS cm^{-1})	0.51(1)	0.78(2)	1.15(3)	1.37(2)	1.63(3)	2.27(4)	3.10(7)	4.21(8)