Supplementary Information:

The effect of extra framework species on the intrinsic negative thermal expansion property of zeolites with the LTA topology

Thomas Carey, Avelino Corma, Fernando Rey, Chiu C. Tang,
Joseph A. Hriljac and Paul A. Anderson.

ITQ–29

Table 1: Refined atomic parameters at 300K obtained from Rietveld analysis of ITQ-29[a]

Atom	Wyckoff position	x	y	z	Occupancy	B
Si(1)	24k	0	0.370(3)	0.184(3)	1	1.4(1)
O(1)	12h	0	0.5	0.223(7)	1	1.7(1)
O(2)	12i	0	0.291(4)	0.291(4)	1	1.7(1)
O(3)	24m	0.109(3)	0.109(3)	0.348(4)	1	1.7(1)

[a] Lattice Parameter: a = 11.8531(1) Å, space group: *Pm–3m*, χ^2 = 1.59, R_{wp} = 7.29 %, R_p = 5.56 %.

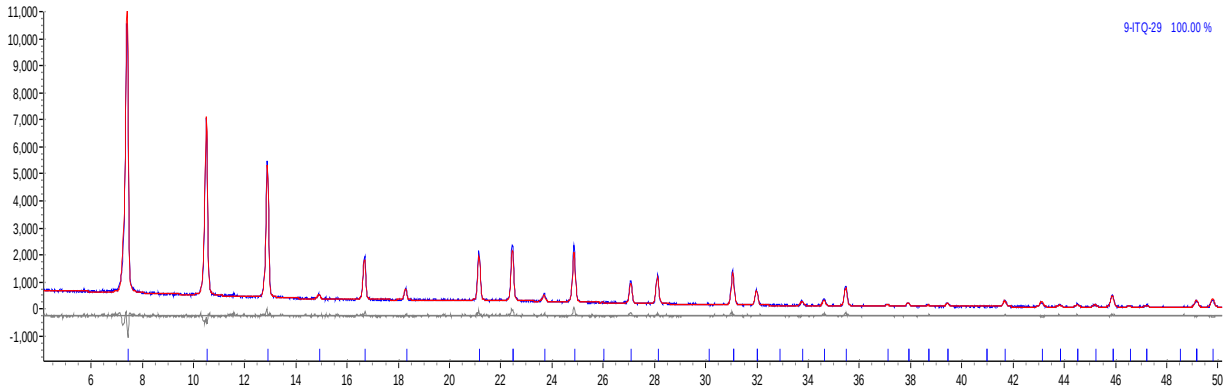

Figure 1: Powder XRD (λ = 1.5406 Å) Rietveld fit for ITQ–29 at 300 K (refinement done using the computer program TOPAS[1]).

References

1. A. Coelho, Topas Academic Version 4.1. Computer Software, Topas Academic, Coelho Software, Brisbane, 2007.

Table 2: Bond Distances (Å) and Angles (deg) in ITQ-29 between 300–100 K (errors at 3σ level).

Bond Length/Angle	**Temperature**										
	300 K	**280 K**	**260 K**	**240 K**	**220 K**	**200 K**	**180 K**	**160 K**	**140 K**	**120 K**	**100 K**
Si – O1	1.62(2)	1.62(1)	1.62(1)	1.62(1)	1.61(1)	1.61(1)	1.61(1)	1.61(1)	1.61(2)	1.59(1)	1.59(2)
Si – O2	1.58(1)	1.58(1)	1.58(1)	1.58(1)	1.58(1)	1.58(1)	1.58(1)	1.58(1)	1.58(2)	1.59(1)	1.58(2)
Si – O3	1.58(9)	1.59(9)	1.59(9)	1.59(9)	1.59(9)	1.59(9)	1.59(1)	1.59(1)	1.60(1)	1.61(2)	1.61(2)
Si – O1 – Si	143(2)	144(2)	144(2)	145(2)	146(2)	146(2)	146(2)	150(2)	152(2)	153(5)	156(3)
Si – O2 – Si	165(2)	164(2)	164(2)	163(2)	162(2)	161(2)	162(2)	158(2)	157(2)	156(4)	158(3)
Si – O3 – Si	153(1)	153(1)	153(1)	153(1)	153(1)	152(2)	152(2)	151(1)	151(2)	149(3)	147(3)
O1 – Si – O2	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	110(1)	109(3)	112(3)
O1 – Si – O3	108.7(8)	109.0(8)	109.0(8)	108.8(8)	108.8(8)	108.7(8)	108.7(8)	108.1(9)	108(1)	105(2)	106(2)
O2 – Si – O3	110.9(7)	110.8(8)	110.9(8)	111.0(8)	111.1(8)	111.2(8)	111.2(8)	111.8(8)	111(1)	111(2)	109(2)
O3 – Si – O3	108(1)	108(1)	108(1)	108(1)	108(1)	108(1)	108(1)	108(1)	108(2)	114(4)	114(3)
Lattice Parameter (Å)	11.853(2)	11.855(2)	11.856(2)	11.858(2)	11.859(2)	11.862(2)	11.864(2)	11.864(2)	11.866(2)	11.872(2)	11.872(6)
Unit Cell Volume (Å)	1665.3(7)	1666.1(6)	1666.5(7)	1667.4(7)	1667.8(7)	1669.1(7)	1669.9(7)	1669.9(7)	1670.7(7)	1673.3(8)	1673.3(8)

Dehydrated AgA

Table 3: Refined atomic parameters obtained from Rietveld analysis of dehydrated silver zeolite A[b]

Atom	Wyckoff position	x	y	z	Occupancy	B
Si(1)	96i	0	0.0939(3)	0.1841(3)	1	0.70(4)
Al(1)	96i	0	0.1853(3)	0.0914(3)	1	0.70(4)
O(1)	96i	0	0.1109(2)	0.2479(7)	1	1.38(9)
O(2)	96i	0	0.1476(6)	0.1515(6)	1	1.38(9)
O(3)	192j	0.0526(3)	0.0568(3)	0.1714(2)	1	1.38(9)
Ag(1)	64g	0.0964(3)	0.0964(3)	0.0964(3)	0.97(3)	2.90(4)
Ag(2)	96i	0	0.2227(2)	0.2089(3)	0.19(1)	2.90(4)
Ag(3)	48e	0	0	0.0806(3)	0.17(2)	2.90(4)

[b] Lattice Parameter: a = 24.66358(7) Å, space group: *Fm–3c*, χ^2 = 1.30, R_{wp} = 8.89 %, R_p = 6.99 %.

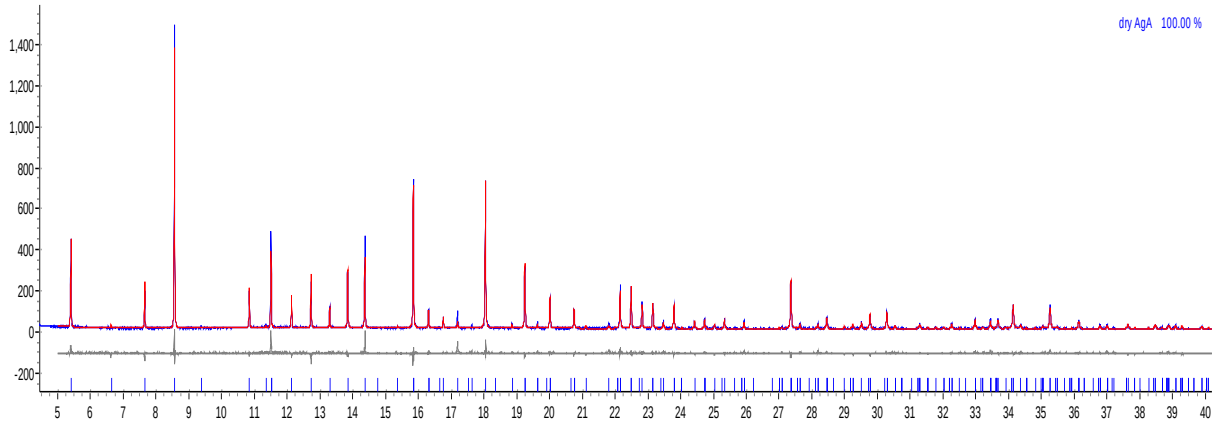

Figure 2: Synchrotron powder XRD (λ = 0.825035 Å) -Rietveld fit of dehydrated silver zeolite A at 300 K.

Table 4: Selected Bond Distances (Å) and Angles (deg) in Dehydrated AgA between 300–100 K (errors at 3σ level).

Bond Length/Angle	**Temperature**										
	300 K	**280 K**	**260 K**	**240 K**	**220 K**	**200 K**	**180 K**	**160 K**	**140 K**	**120 K**	**100 K**
Si – O1	1.63(6)	1.63(5)	1.62(5)	1.62(5)	1.62(5)	1.62(5)	1.62(5)	1.62(5)	1.62(5)	1.64(5)	1.61(5)
Si – O2	1.55(5)	1.53(5)	1.53(5)	1.53(4)	1.53(4)	1.52(4)	1.52(4)	1.52(4)	1.52(4)	1.52(4)	1.50(5)
Si – O3	1.62(3)	1.61(2)	1.62(2)	1.63(3)	1.62(2)	1.63(2)	1.63(2)	1.63(2)	1.63(2)	1.63(2)	1.64(2)
Al – O1	1.72(6)	1.72(5)	1.70(5)	1.71(5)	1.70(3)	1.70(5)	1.70(5)	1.70(6)	1.69(5)	1.66(5)	1.70(5)
Al – O2	1.75(5)	1.77(4)	1.75(4)	1.76(2)	1.75(4)	1.77(5)	1.77(5)	1.77(5)	1.77(4)	1.77(5)	1.73(2)
Al – O3	1.73(3)	1.74(2)	1.75(2)	1.74(2)	1.75(2)	1.74(2)	1.74(2)	1.74(2)	1.74(2)	1.73(2)	1.78(4)
Si – O1 – Al	149(2)	149(2)	150(2)	151(2)	152(2)	152(2)	152(2)	153(2)	153(2)	153(2)	154(2)
Si – O2 – Al	153(3)	153(3)	153(3)	153(3)	153(3)	153(3)	153(3)	153(3)	154(3)	154(3)	154(3)
Si – O3 – Al	150(2)	149(2)	150(2)	149(1)	149(1)	149(1)	149(2)	149(2)	149(2)	149(2)	149(2)
O1 – Si – O2	106(2)	106(2)	107(2)	107(2)	107(2)	108(2)	108(2)	108(2)	108(2)	109(2)	109(1)
O1 – Si – O3	110(1)	110(1)	109(1)	109.3(9)	109(1)	109(1)	109(1)	109(1)	108(1)	108(1)	108(1)
O2 – Si – O3	112(1)	112(1)	112(1)	112(1)	112(1)	112(1)	112(1)	112(1)	112(1)	112(1)	113(1)
O3 – Si – O3	107(2)	107(2)	107(2)	106(2)	107(2)	107(2)	107(2)	106(2)	107(2)	107(2)	106(2)
O1 – Al – O2	106(2)	106(2)	108(2)	107(2)	108(2)	108(2)	108(2)	108(2)	109(2)	109(2)	109(2)
O1 – Al – O3	110(1)	110(1)	110(1)	110.0(9)	109.5(9)	110(1)	110(1)	110(1)	110(1)	110(1)	109(1)
O2 – Al – O3	111(1)	111(1)	111(1)	111(1)	111(1)	111(1)	111(1)	111(1)	111(1)	110(1)	110(1)
O3 – Al – O3	108(2)	107(2)	107(2)	107(2)	107(2)	107(2)	107(2)	107(2)	108(2)	108(2)	107(2)
Lattice Parameter (Å)	24.6636(2)	24.6704(2)	24.6739(2)	24.6752(2)	24.6762(8)	24.6769(2)	24.6778(2)	24.6789(2)	24.6796(2)	24.6799(2)	24.6801(2)
Unit Cell Volume (Å)	15002.7(3)	15015.2(3)	15021.5(3)	15023.9(3)	15025.7(3)	15026.9(3)	15028.6(3)	15030.6(3)	15031.9(3)	15032.5(3)	15032.8(3)

Hydrated AgA

Table 5: Refined atomic parameters obtained from Rietveld analysis of hydrated silver zeolite A[c]

Atom	Wyckoff position	x	y	z	Occupancy	B
Si(1)	96i	0	0.090(2)	0.184(2)	1	1.03(4)
Al(1)	96i	0	0.184(2)	0.089(2)	1	1.03(4)
O(1)	96i	0	0.109(2)	0.245(5)	1	2.26(8)
O(2)	96i	0	0.150(4)	0.151(5)	1	2.26(8)
O(3)	192j	0.051(3)	0.056(3)	0.171(2)	1	2.26(8)
Ag(1)	64g	0.069(2)	0.069(2)	0.069(2)	0.20(4)	2.06(5)
Ag(2)	64g	0.086(4)	0.086(4)	0.086(4)	0.14(4)	2.06(5)
Ag(3)	64g	0.107(3)	0.107(3)	0.107(3)	0.26(7)	2.06(5)
Ag(4)	64g	0.120(2)	0.120(2)	0.120(2)	0.33(8)	2.06(5)
Ag(5)	96i	0	0.234(3)	0.205(2)	0.13(1)	2.06(5)
O4	8a	0.25	0.25	0.25	0.23(2)	10(1)
O5	192j	0.941(5)	0.027(3)	0.025(3)	0.291(5)	10(1)
O6	64g	0.156(8)	0.156(8)	0.156(8)	0.39(2)	10(1)

[c]Lattice Parameter: a = 24.5970(4) Å, space group: *Fm–3c*, χ^2 = 1.11, R_{wp} = 8.59 %, R_p = 6.66 %.

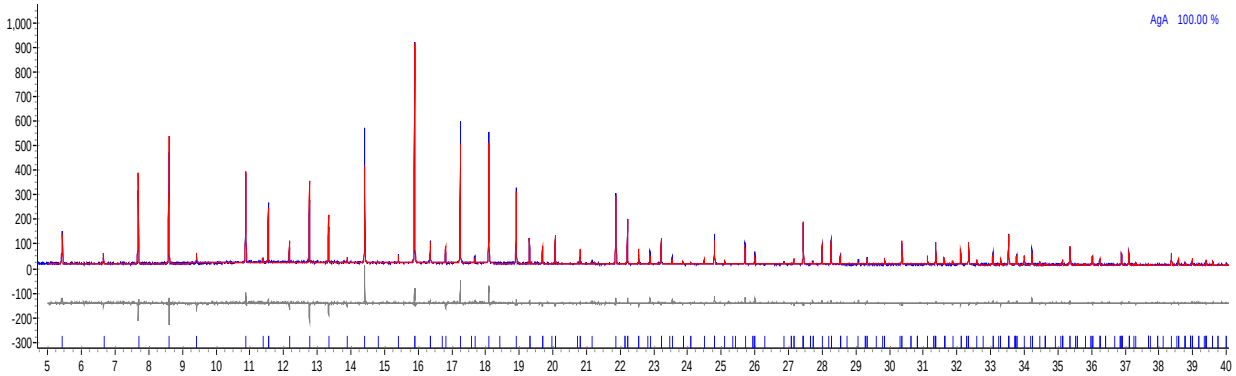

Figure 3: Synchrotron powder XRD (λ = 0.825035 Å) Rietveld fit of hydrated silver zeolite A at 300 K.

Table 6: Selected Bond Distances (Å) and Angles (deg) in Hydrated AgA between 300–100 K (errors at 3σ level).

Bond Length/Angle	**Temperature**										
	300 K	**280 K**	**260 K**	**240 K**	**220 K**	**200 K**	**180 K**	**160 K**	**140 K**	**120 K**	**100 K**
Si – O1	1.57(3)	1.56(3)	1.56(3)	1.56(3)	1.56(3)	1.56(3)	1.56(4)	1.56(4)	1.56(4)	1.56(4)	1.56(4)
Si – O2	1.68(4)	1.68(4)	1.68(4)	1.68(4)	1.68(4)	1.68(4)	1.68(4)	1.67(5)	1.67(5)	1.67(5)	1.67(5)
Si – O3	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)	1.53(2)
Al – O1	1.83(4)	1.82(3)	1.82(3)	1.82(3)	1.82(3)	1.82(4)	1.82(4)	1.82(4)	1.82(4)	1.82(4)	1.82(4)
Al – O2	1.73(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(4)	1.74(5)
Al – O3	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)	1.70(2)
Si – O1 – Al	148(1)	148(1)	148(1)	148(1)	148(1)	148(2)	149(1)	148(2)	148(1)	148(1)	148(2)
Si – O2 – Al	147(2)	146(2)	146(2)	146(2)	146(2)	146(2)	146(2)	146(2)	146(2)	146(2)	146(2)
Si – O3 – Al	150(1)	150(1)	150(1)	150(1)	150(1)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
O1 – Si – O2	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)	101(2)
O1 – Si – O3	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)	110(1)
O2 – Si – O3	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)	113(1)
O3 – Si – O3	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)	109(2)
O1 – Al – O2	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)	104(2)
O1 – Al – O3	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)	109(1)
O2 – Al – O3	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)	114(1)
O3 – Al – O3	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)	108(2)
Lattice Parameter (Å)	24.5970(2)	24.5916(2)	24.5902(2)	24.5934(2)	24.5995(2)	24.5962(2)	24.5855(2)	24.5770(2)	24.5704(2)	24.5646(2)	24.5592(2)
Unit Cell Volume (Å)	14881.5(3)	14871.7(3)	14869.1(3)	14875.0(3)	14886.0(3)	14880.0(3)	14860.6(3)	14845.2(3)	14833.3(3)	14822.8(3)	14813.0(3)