Table (S1). Cell parameters of $Ga_{1-x}Fe_xPO_4$ and $GaPO_4$, $FePO_4$.

	a(Å)	c(Å)	V(Å^3)	R_p(%)	R_{wp}(%)	χ^2
$GaPO_4$[41]	4.9029(1)	11.0523(1)	230.090(4)	13.2	17.2	1.35
$Ga_{0.81}Fe_{0.19}PO_4$	4.9234(1)	11.0839(1)	232.673 (5)	16.1	18.3	1.26
$Ga_{0.76}Fe_{0.24}PO_4$	4.9326(1)	11.0941(1)	233.760(4)	14.4	16.6	1.0
$Ga_{0.72}Fe_{0.28}PO_4$	4.9364(1)	11.0983(1)	234.213(5)	21.6	12.5	1.72
$FePO_4$[14]	5.0332(1)	11.2450(1)	246.701(5)	21.5	29.6	1.36

Table (S2). Experimental Data- $Ga_{1-x}Fe_xPO_4$ Single Crystal X-Ray Diffraction.

	$Ga_{0.96}Fe_{0.04}PO_4$	$Ga_{0.94}Fe_{0.06}PO_4$	$Ga_{0.93}Fe_{0.07}PO_4$
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Trigonal	Trigonal	Trigonal
Space groupe	$P3_221$	$P3_221$	$P3_221$
a=b (Å)	4.9020(1)	4.9043(1)	4.9068(1)
c (Å)	11.0500(6)	11.0530(6)	11.0550(6)
V (Å^3)	229.932(13)	230.231(13)	230.505(13)
h, k, l	$-7 \le h \le 7$ $-7 \le k \le 7$ $-16 \le l \le 16$	$-8 \le h \le 8$ $-8 \le k \le 8$ $-18 \le l \le 18$	$-7 \le h \le 7$ $-7 \le k \le 7$ $-17 \le l \le 17$
Density (g /cm^3)	3.529	3.524	3.520
Diffractometer	Agilent Xcalibur	Agilent Xcalibur	Agilent Xcalibur
Radiation type	Mo Kα	Mo Kα	Mo Kα
Wavelength	0.7107	0.7107	0.7107
Absorption correction	Numerical	Numerical	Numerical
μ (mm^{-1})	8.788	8.777	8.766
$R_{equivalents}$	0.035	0.033	0.032
R_{sigma}	0.012	0.015	0.023
No. of measured reflections	11122	13597	10963
No. of unique reflections	659	815	664
No. of observed reflection (I >2σ)	640	765	648
	Refinement		
R	0.024	0.019	0.027
R_W	0.057	0.045	0.065
χ^2	1.32	1.12	1.69
No. of parameters	29	29	29
Weighting scheme	$w=(\sigma^2F_o^2+(0.017P)^2+0.0319P)^{-1}$ where $P=(F_o^2+2F_C)/3$	$w=(\sigma^2F_o^2+(0.02P)^2+0.032P)^{-1}$ where $P=(F_o^2+2F_C)/3$	$w=(\sigma^2F_o^2+(0.0169P)^2+0.0319P)^{-1}$ where $P=(F_o^2+2F_C)/3$

Table (S3). Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Ga_{1-x}Fe_xPO_4$.

		$Ga_{0.93}Fe_{0.07}PO_4$		
Atom	*x*	*y*	*z*	100**U*$_{eq}$ (Å^2)
Ga/Fe	0.4564(1)	0	-0.3333	0.78(1)
P	0.4565(1)	0	-0.8333	0.78(1)
O1	0.4097(3)	0.2726(3)	-0.8723(1)	1.35(2)
O2	0.5913(3)	-0.0908(3)	-0.9408(2)	1.38(2)
		$Ga_{0.94}Fe_{0.06}PO_4$		
Ga	0.4565(1)	0	-0.3333	1.07(1)
P	0.4565 (1)	0	-0.8333	1.03(1)
O1	0.4097(3)	0.2722(3)	-0.8722(1)	1.60(2)
O2	0.5907(3)	-0.0915(3)	-0.9404(1)	1.63(3)
		$Ga_{0.96}Fe_{0.04}PO_4$		
Ga/Fe	0.4566(1)	0	-0.3333	0.76(1)
P	0.4567(1)	0	-0.8333	0.75(1)
O1	0.4093(3)	0.2728(3)	-0.8722(1)	1.35(2)
O2	0.5913(3)	-0.0911(3)	-0.9407(1)	1.39(2)

Table (S4).Anisotropic atomic displacement parameters (Å^2) for α-quartz-type $Ga_{1-x}Fe_xPO_4$.

			$Ga_{0.93}Fe_{0.07}PO_4$			
Atom	100*U_{11}	100*U_{22}	100*U_{33}	100*U_{12}	100*U_{13}	100*U_{23}
Ga/Fe	0.88(1)	0.74(1)	0.69(1)	0.36(1)	0.02(1)	0.04(1)
P	0.94(2)	0.75(2)	0.75(2)	0.37(1)	0.02(1)	0.03(2)
O1	1.94(6)	1.33(5)	1.34(5)	1.11(5)	0.39(4)	0.45(4)
O2	1.92(5)	1.19(5)	1.26(4)	0.84(4)	0.38(4)	-0.05(4)
			$Ga_{0.94}Fe_{0.06}PO_4$			
Ga/Fe	1.23(1)	1.08(1)	0.85(1)	0.06(1)	0.03(1)	0.54 (1)
P	1.20 (1)	0.99(3)	0.82(3)	0.05(2)	0.03(1)	0.49(1)
O1	2.18(6)	1.55(6)	1.42(6)	0.43(5)	0.43(5)	1.20(5)
O2	2.19(6)	1.47(6)	1.37(6)	-0.04(5)	0.41(5)	1.03(5)
			$Ga_{0.96}Fe_{0.04}PO_4$			
Ga	0.83(1)	0.71(1)	0.68(1)	0.35(1)	0.006(6)	0.01(1)

P	0.74(3)	0.90(2)	0.77(3)	0.37(1)	0.01(3)	0.01(1)
O1	2.64(8)	1.96(6)	2.12(7)	1.44(6)	0.47(6)	0.50(5)
O2	2.75(8)	1.89(6)	1.97(7)	1.24(6)	0.43(6)	-0.02(5)

Table (S5). Tetrahedral bond angles (deg) in α -quartz-type $Ga_{1-x}Fe_xPO_4$.

X	O2 –M–O2	O1 –M–O1	O1–M–O2	O1–M–O2	O1 –P–O1	O1 –P–O2	O1 –P–O2	O2 –P–O2
0[41]	111.9	111.8	105.4	110.3	109.6	108.0	111.8	107.7
0.04	111.8(11)	113.95(11)	105.21(7)	110.38(8)	107.67(15)	108.23(8)	111.56(9)	109.60(13)
0.06	111.93(8)	113.95(8)	105.26(5)	110.29(6)	108.0(1)	108.16(6)	111.54(7)	109.46(10)
0.07	112.09(11)	113.87(11)	105.21(7)	110.31(8)	107.70(14)	108.28(8)	111.51(9)	109.58(13)
0.23[19]	112.1(2)	113.3(2)	105.35(14)	110.43(17)	107.6(3)	108.36(17)	111.8(2)	109.0(3)
1.0[14]	111.6	114.3	106.3	109.3	108.5	112.0	107.7	109.0

Table (S6). Intertetrahedral bridging and tilt angles (deg.) in α-quartz-type $Ga_{1-x}Fe_xPO_4$.

	M-O-P	δ
$GaPO_4$[41]	134.6	23.4
$Ga_{0.96}Fe_{0.04}PO_4$	134.64(11)	23.19(9)
$Ga_{0.94}Fe_{0.06}PO_4$	134.76(8)	23.33(8)
$Ga_{0.93}Fe_{0.07}PO_4$	134.82(11)	23.24(8)
$Ga_{0.77}Fe_{0.23}PO_4$[19]	135.2(1)	22.98(2)
$FePO_4$[14]	137.8	21.5

Table (S7). Selected bond distances (Å) in α-quartz-type $Ga_{1-x}Fe_xPO_4$.

	M–O1	M–O2	P-O1	P-O2
$GaPO_4$[41]	1.814	1.820	1.528	1.527
$Ga_{0.96}Fe_{0.04}PO_4$	1.811(1)	1.820(1)	1.530(2)	1.528(2)
$Ga_{0.94}Fe_{0.06}PO_4$	1.810(1)	1.820(1)	1.528(1)	1.530(1)
$Ga_{0.93}Fe_{0.07}PO_4$	1.813(2)	1.824(2)	1.527(2)	1.526(2)
$Ga_{0.77}Fe_{0.23}PO_4$[19]	1.832(3)	1.821(3)	1.527(4)	1.530(3)
$FePO_4$[14]	1.858	1.858	1.531	1.521