Supplementary information for

Tunable Negative and Low Thermal Expansion in Magnetic Calcite-Type $Fe_{1-x}Cr_xBO_3$ (x = 0.0, 0.14, 1.0) Borates: A Comprehensive *In Situ* Study

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SI1. Scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS)

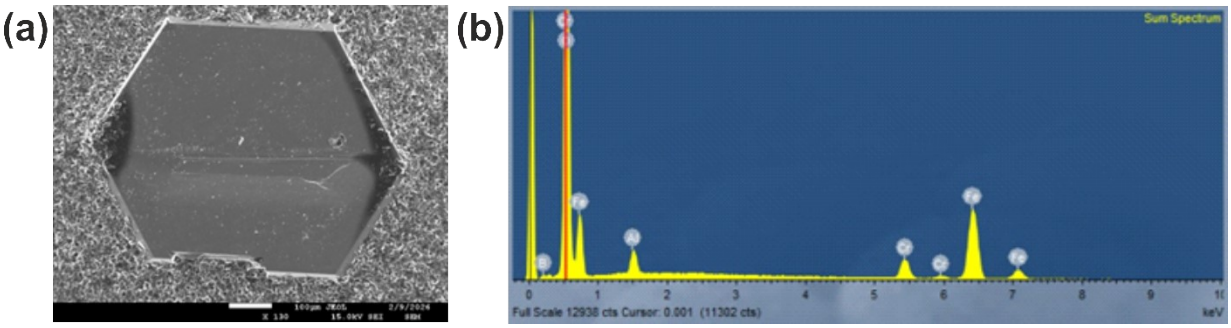

Fig. S1. The (a) SEM image and (b) EDS spectrum of $Fe_{0.86}Cr_{0.14}BO_3$ single crystal.

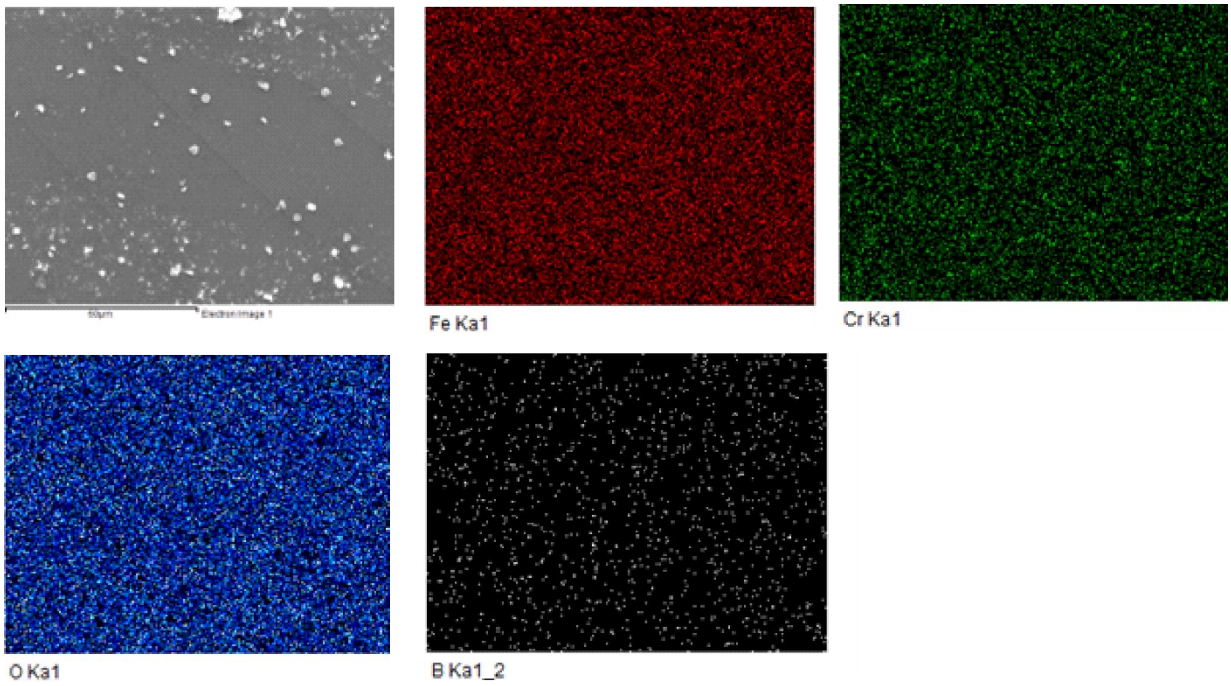

Fig. S2. The EDS elemental mapping in $Fe_{0.86}Cr_{0.14}BO_3$ sample.

SI2. *In situ* high-temperature single-crystal X-ray diffraction

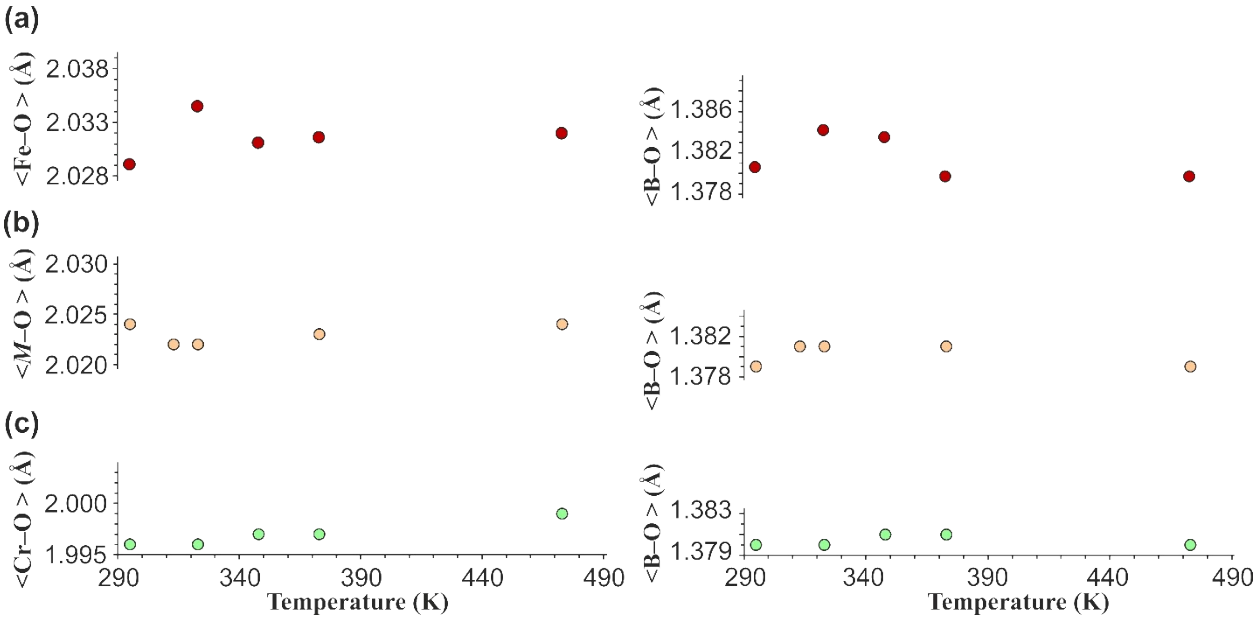

Fig. S3. Temperature dependencies of the <*M*–O> and <B–O> bond lengths in $Fe_{1-x}Cr_xBO_3$: (a) x = 0.0, (b) 0.14 and (c) 1.0.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $FeBO_3$.

	x	*y*	*z*	U_{iso}*/U_{eq}
295 K				
Fe1	0.666667	0.333333	0.333333	0.0039 (3)
B1	0.333333	0.666667	0.416667	0.0053 (11)
O1	0.6315 (3)	0.666667	0.416667	0.0049 (5)
323 K				
Fe1	0.666667	0.333333	0.333333	0.0042 (3)
B1	0.333333	0.666667	0.416667	0.0055 (11)
O1	0.6314 (3)	0.666667	0.416667	0.0051 (5)
348 K				
Fe1	0.666667	0.333333	0.333333	0.0049 (2)
B1	0.333333	0.666667	0.416667	0.0056 (9)
O1	0.6317 (3)	0.666667	0.416667	0.0058 (4)
373 K				
Fe1	0.666667	0.333333	0.333333	0.0048 (2)
B1	0.333333	0.666667	0.416667	0.0058 (10)
O1	0.6314 (3)	0.666667	0.416667	0.0059 (4)
473 K				
Fe1	0.666667	0.333333	0.333333	0.0059 (2)
B1	0.333333	0.666667	0.416667	0.0068 (9)
O1	0.6311 (3)	0.666667	0.416667	0.0071 (4)

Table S2. Atomic displacement parameters (Å^2) for $FeBO_3$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
295 K						
Fe1	0.0041 (4)	0.0041 (4)	0.0035 (4)	0.00206 (18)	0	0
B1	0.0064 (14)	0.0064 (14)	0.003 (2)	0.0032 (7)	0	0
O1	0.0048 (6)	0.0053 (7)	0.0048 (6)	0.0026 (4)	−0.0005 (2)	−0.0011 (4)
323 K						
Fe1	0.0048 (4)	0.0048 (4)	0.0031 (4)	0.00239 (18)	0	0
B1	0.0068 (14)	0.0068 (14)	0.003 (2)	0.0034 (7)	0	0
O1	0.0052 (6)	0.0060 (7)	0.0044 (7)	0.0030 (4)	−0.0006 (2)	−0.0012 (5)
348 K						
Fe1	0.0057 (3)	0.0057 (3)	0.0032 (3)	0.00284 (14)	0	0
B1	0.0064 (10)	0.0064 (10)	0.0041 (15)	0.0032 (5)	0	0
O1	0.0058 (4)	0.0067 (5)	0.0053 (5)	0.0033 (3)	−0.00077 (18)	−0.0015 (4)
373 K						
Fe1	0.0049 (3)	0.0049 (3)	0.0046 (3)	0.00246 (15)	0	0
B1	0.0063 (12)	0.0063 (12)	0.0050 (18)	0.0031 (6)	0	0
O1	0.0053 (5)	0.0062 (6)	0.0064 (6)	0.0031 (3)	−0.0007 (2)	−0.0013 (4)
473 K						
Fe1	0.0062 (3)	0.0062 (3)	0.0053 (3)	0.00310 (15)	0	0
B1	0.0076 (11)	0.0076 (11)	0.0052 (16)	0.0038 (6)	0	0
O1	0.0066 (5)	0.0074 (6)	0.0076 (6)	0.0037 (3)	−0.0008 (2)	−0.0017 (4)

Table S3. Geometric parameters (Å, º) for $FeBO_3$.

Bond	Distance, Å	Bond	Distance, Å
295 K		323 K	
Fe1—O1	2.0291 (7)	Fe1—O1	2.0345 (7)
Fe1—O1^{i}	2.0291 (7)	Fe1—O1^{i}	2.0345 (7)
Fe1—O1	2.0291 (13)	Fe1—O1	2.0345 (14)
Fe1—O1	2.0291 (7)	Fe1—O1	2.0345 (7)
Fe1—O1	2.0291 (7)	Fe1—O1	2.0345 (7)
Fe1—O1	2.0291 (13)	Fe1—O1	2.0345 (14)
<Fe1—O>$_6$		<Fe1—O>$_6$	
B1—O1	1.3806 (15)	B1—O1	1.3842 (16)
B1—O1	1.3806 (15)	B1—O1	1.3842 (16)
B1—O1	1.3806 (11)	B1—O1	1.3842 (11)
<B1—O>$_3$		<B1—O>$_3$	
348 K		373 K	
Fe1—O1	2.0311 (5)	Fe1—O1	2.0316 (6)
Fe1—O1^{i}	2.0311 (5)	Fe1—O1^{i}	2.0316 (6)
Fe1—O1	2.0311 (10)	Fe1—O1	2.0316 (12)
Fe1—O1	2.0310 (5)	Fe1—O1	2.0316 (6)
Fe1—O1	2.0310 (5)	Fe1—O1	2.0316 (6)
Fe1—O1	2.0311 (10)	Fe1—O1	2.0316 (12)
<Fe1—O>$_6$		<Fe1—O>$_6$	
B1—O1	1.3835 (12)	B1—O1	1.3797 (14)
B1—O1	1.3835 (12)	B1—O1	1.3797 (14)
B1—O1	1.3835 (8)	B1—O1	1.3797 (10)
<B1—O>$_3$		<B1—O>$_3$	
473 K			
Fe1—O1	2.0320 (6)		
Fe1—O1^{i}	2.0320 (6)		
Fe1—O1	2.0320 (12)		
Fe1—O1	2.0320 (6)		
Fe1—O1	2.0320 (6)		
Fe1—O1	2.0320 (12)		
<Fe1—O>$_6$			
B1—O1	1.3797 (14)		
B1—O1	1.3797 (14)		
B1—O1	1.3797 (10)		
<B1—O>$_3$			

Table S4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $Fe_{0.86}Cr_{0.14}BO_3$.

295 K					
	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Fe1	1	1	0.5	0.0159 (3)	0.86
Cr1	1	1	0.5	0.0159 (3)	0.14
B1	0.666667	0.333333	0.583333	0.0172 (13)	
O1	0.9652 (4)	0.333333	0.583333	0.0169 (6)	
313 K					
Fe1	0	0	0.5	0.0041 (2)	0.86
Cr1	0	0	0.5	0.0041 (2)	0.14
B1	0.666667	0.333333	0.583333	0.0044 (9)	
O1	0.3677 (3)	0.333333	0.583333	0.0052 (4)	
323 K					
Fe1	0	0	0.5	0.0041 (2)	0.86
Cr1	0	0	0.5	0.0041 (2)	0.14
B1	0.666667	0.333333	0.583333	0.0045 (9)	
O1	0.3677 (3)	0.333333	0.583333	0.0052 (4)	
373 K					
Fe1	0	0	0.5	0.0047 (2)	0.86
Cr1	0	0	0.5	0.0047 (2)	0.14
B1	0.666667	0.333333	0.583333	0.0052 (9)	
O1	0.3677 (3)	0.333333	0.583333	0.0057 (4)	
473 K					
Fe1	0	0	0.5	0.0057 (2)	0.86
Cr1	0	0	0.5	0.0057 (2)	0.14
B1	0.666667	0.333333	0.583333	0.0056 (9)	
O1	0.3681 (3)	0.333333	0.583333	0.0069 (4)	

Table S5. Atomic displacement parameters (Å^2) for $Fe_{0.86}Cr_{0.14}BO_3$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
295 K						
Fe1	0.0158 (3)	0.0158 (3)	0.0161 (4)	0.00792 (17)	0	0
Cr1	0.0158 (3)	0.0158 (3)	0.0161 (4)	0.00792 (17)	0	0
B1	0.0171 (16)	0.0171 (16)	0.017 (2)	0.0086 (8)	0	0
O1	0.0163 (6)	0.0163 (6)	0.0178(8)	0.0078 (7)	−0.0006 (3)	0.0006 (3)
313 K						
Fe1	0.0041 (3)	0.0041 (3)	0.0039 (3)	0.00207 (14)	0	0
Cr1	0.0041 (3)	0.0041 (3)	0.0039 (3)	0.00207 (14)	0	0
B1	0.0046 (11)	0.0046 (11)	0.0041 (16)	0.0023 (5)	0	0
O1	0.0044 (5)	0.0059 (6)	0.0057 (6)	0.0030 (3)	−0.0008 (2)	−0.0015 (4)
323 K						
Fe1	0.0040 (3)	0.0040 (3)	0.0043 (3)	0.00201 (13)	0	0
Cr1	0.0040 (3)	0.0040 (3)	0.0043 (3)	0.00201 (13)	0	0
B1	0.0041 (11)	0.0041 (11)	0.0054 (16)	0.0021 (5)	0	0
O1	0.0044 (5)	0.0050 (6)	0.0062 (6)	0.0025 (3)	−0.0006 (2)	−0.0012 (4)
373 K						
Fe1	0.0040 (3)	0.0040 (3)	0.0059 (3)	0.00202 (13)	0	0
Cr1	0.0040 (3)	0.0040 (3)	0.0059 (3)	0.00202 (13)	0	0
B1	0.0049 (10)	0.0049 (10)	0.0058 (16)	0.0024 (5)	0	0
O1	0.0042 (5)	0.0054 (6)	0.0079 (6)	0.0027 (3)	−0.0006 (2)	−0.0013 (4)
473 K						
Fe1	0.0052 (3)	0.0052 (3)	0.0066 (3)	0.00259 (13)	0	0
Cr1	0.0052 (3)	0.0052 (3)	0.0066 (3)	0.00259 (13)	0	0
B1	0.0054 (10)	0.0054 (10)	0.0058 (16)	0.0027 (5)	0	0
O1	0.0054 (5)	0.0066 (6)	0.0090 (6)	0.0033 (3)	−0.0008 (2)	−0.0016 (4)

Table S6. Geometric parameters (Å, º) for $Fe_{0.86}Cr_{0.14}BO_3$.

Bond	Distance, Å	Bond	Distance, Å
295 K		313 K	
M1—O1	2.0237 (9)	M1—O1	2.0220 (7)
M1—O1	2.0237 (9)	M1—O1	2.0220 (7)
M1—O1	2.0237 (9)	M1—O1	2.0220 (13)
M1—O1	2.0237 (9)	M1—O1	2.0220 (7)
M1—O1	2.0237 (9)	M1—O1	2.0220 (7)
M1—O1	2.0237 (9)	M1—O1	2.0220 (13)
$<M1—O>_6$	2.024	$<M1—O>_6$	2.022
B1—O1	1.379 (2)	B1—O1	1.3805 (14)
B1—O1	1.379 (2)	B1—O1	1.3805 (14)
B1—O1	1.379 (2)	B1—O1	1.3806 (10)
$<B1—O>_3$	1.379	$<B1—O>_3$	1.381
323 K		373 K	
M1—O1	2.0224 (7)	M1—O1	2.0230 (7)
M1—O1	2.0224 (7)	M1—O1	2.0230 (7)
M1—O1	2.0224 (12)	M1—O1	2.0230 (12)
M1—O1	2.0224 (7)	M1—O1	2.0230 (7)
M1—O1	2.0224 (7)	M1—O1	2.0230 (7)
M1—O1	2.0224 (12)	M1—O1	2.0230 (12)
$<M1—O>_6$	2.022	$<M1—O>_6$	2.023
B1—O1	1.3807 (14)	B1—O1	1.3811 (14)
B1—O1	1.3807 (14)	B1—O1	1.3812 (14)
B1—O1	1.3807 (10)	B1—O1	1.3812 (10)
$<B1—O>_3$	1.381	$<B1—O>_3$	1.381
473 K			
M1—O1	2.0242 (8)		
M1—O1	2.0242 (9)		
M1—O1	2.0242 (13)		
M1—O1	2.0242 (8)		
M1—O1	2.0242 (9)		
M1—O1	2.0242 (13)		
$<M1—O>_6$	2.024		
B1—O1	1.3787 (15)		
B1—O1	1.3787 (15)		
B1—O1	1.3787 (12)		
$<B1—O>_3$	1.379		

Table S7. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for $CrBO_3$.

	x	y	z	U_{iso}*/U_{eq}
295 K				
Cr1	0.666667	0.333333	0.333333	0.0038 (2)
B1	0.333333	0.666667	0.416667	0.0051 (9)
O1	0.6347 (3)	0.666667	0.416667	0.0057 (4)
323 K				
Cr1	0.666667	0.333333	0.333333	0.0034 (2)
B1	0.333333	0.666667	0.416667	0.0052 (10)
O1	0.6349 (3)	0.666667	0.416667	0.0053 (4)
348 K				
Cr1	0.666667	0.333333	0.333333	0.0041 (2)
B1	0.333333	0.666667	0.416667	0.0055 (8)
O1	0.6348 (3)	0.666667	0.416667	0.0061 (4)
373 K				
Cr1	0.666667	0.333333	0.333333	0.0039 (2)
B1	0.333333	0.666667	0.416667	0.0050 (9)
O1	0.6349 (3)	0.666667	0.416667	0.0060 (4)
473 K				
Cr1	0.666667	0.333333	0.333333	0.00467 (19)
B1	0.333333	0.666667	0.416667	0.0063 (8)
O1	0.6346 (3)	0.666667	0.416667	0.0069 (4)

Table S8. Atomic displacement parameters (Å^2) for $CrBO_3$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
295 K						
Cr1	0.0036 (3)	0.0036 (3)	0.0042 (3)	0.00182 (14)	0	0
B1	0.0049 (10)	0.0049 (10)	0.0055 (15)	0.0024 (5)	0	0
O1	0.0050 (5)	0.0058 (6)	0.0065 (6)	0.0029 (3)	−0.0006 (2)	−0.0013 (4)
323 K						
Cr1	0.0033 (3)	0.0033 (3)	0.0035 (3)	0.00167 (13)	0	0
B1	0.0057 (12)	0.0057 (12)	0.0043 (17)	0.0028 (6)	0	0
O1	0.0049 (5)	0.0056 (7)	0.0056 (6)	0.0028 (3)	−0.0006 (2)	−0.0012 (5)
348 K						
Cr1	0.0040 (3)	0.0040 (3)	0.0043 (3)	0.00199 (13)	0	0
B1	0.0059 (10)	0.0059 (10)	0.0046 (15)	0.0030 (5)	0	0
O1	0.0058 (5)	0.0063 (6)	0.0065 (6)	0.0032 (3)	−0.0008 (2)	−0.0016 (4)
373 K						
Cr1	0.0030 (3)	0.0030 (3)	0.0057 (3)	0.00151 (14)	0	0
B1	0.0046 (11)	0.0046 (11)	0.0060 (16)	0.0023 (5)	0	0
O1	0.0049 (5)	0.0055 (6)	0.0079 (6)	0.0027 (3)	−0.0007 (2)	−0.0014 (5)
473 K						
Cr1	0.0041 (2)	0.0041 (2)	0.0059 (3)	0.00203 (12)	0	0
B1	0.0061 (9)	0.0061 (9)	0.0068 (14)	0.0031 (5)	0	0
O1	0.0058 (4)	0.0064 (5)	0.0088 (6)	0.0032 (3)	−0.0009 (2)	−0.0017 (4)

Table S9. Geometric parameters (Å, º) for $CrBO_3$.

Bond	Distance, Å	Bond	Distance, Å
295 K		323 K	
Cr1—O1	1.9964 (6)	Cr1—O1	1.9961 (7)
Cr1—O1	1.9964 (6)	Cr1—O1	1.9961 (7)
Cr1—O1	1.9964 (12)	Cr1—O1	1.9961 (13)
Cr1—O1	1.9964 (6)	Cr1—O1	1.9961 (7)
Cr1—O1	1.9964 (6)	Cr1—O1	1.9961 (7)
Cr1—O1	1.9964 (12)	Cr1—O1	1.9961 (13)
$<Cr1—O>_6$	1.996	$<Cr1—O>_6$	1.996
B1—O1	1.3800 (13)	B1—O1	1.3804 (15)
B1—O1	1.3800 (13)	B1—O1	1.3804 (15)
B1—O1	1.3800 (9)	B1—O1	1.3804 (11)
$<B1—O>_3$	1.380	$<B1—O>_3$	1.380
348 K		373 K	
Cr1—O1	1.9973 (6)	Cr1—O1	1.9970 (7)
Cr1—O1	1.9973 (6)	Cr1—O1	1.9970 (7)
Cr1—O1	1.9973 (12)	Cr1—O1	1.9970 (13)
Cr1—O1	1.9973 (6)	Cr1—O1	1.9970 (7)
Cr1—O1	1.9973 (6)	Cr1—O1	1.9970 (7)
Cr1—O1	1.9973 (12)	Cr1—O1	1.9970 (13)
$<Cr1—O>_6$	1.997	$<Cr1—O>_6$	1.997
B1—O1	1.3807 (14)	B1—O1	1.3806 (15)
B1—O1	1.3807 (14)	B1—O1	1.3806 (15)
B1—O1	1.3807 (10)	B1—O1	1.3806 (10)
$<B1—O>_3$	1.381	$<B1—O>_3$	1.381
473 K			
Cr1—O1	1.9987 (6)		
Cr1—O1	1.9987 (6)		
Cr1—O1	1.9987 (11)		
Cr1—O1	1.9987 (6)		
Cr1—O1	1.9987 (6)		
Cr1—O1	1.9987 (11)		
$<Cr1—O>_6$	1.999		
B1—O1	1.3800 (12)		
B1—O1	1.3800 (12)		
B1—O1	1.3800 (9)		
$<B1—O>_3$	1.380		

SI3. *In situ* high-temperature powder X-ray diffraction

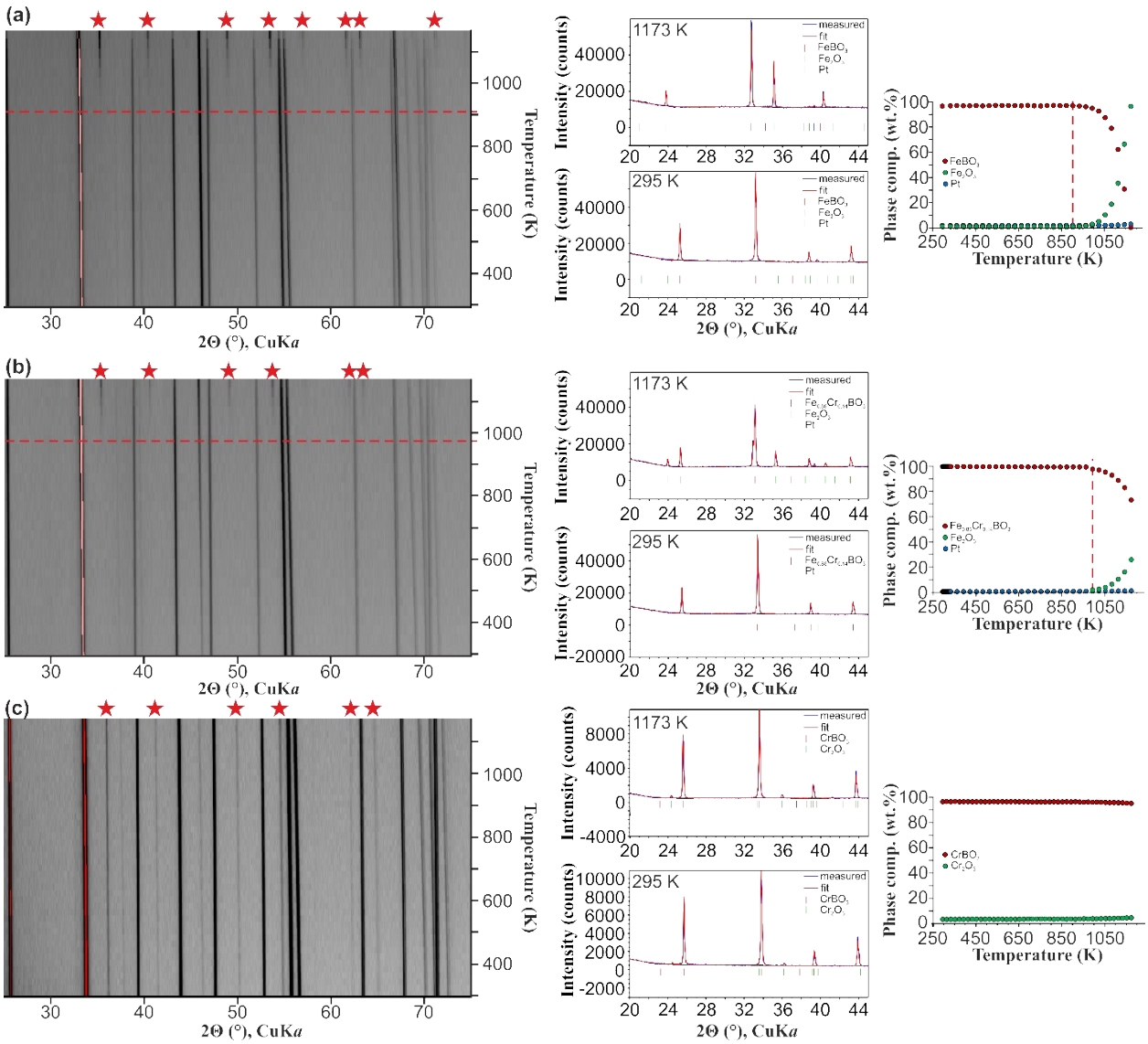

Fig. S4 2D-images of X-ray diffraction patterns (Cu$K\alpha_{1+2}$) of $Fe_{1-x}Cr_xBO_3$: (a) x = 0.0, (b) 0.14 and (c) 1.0.

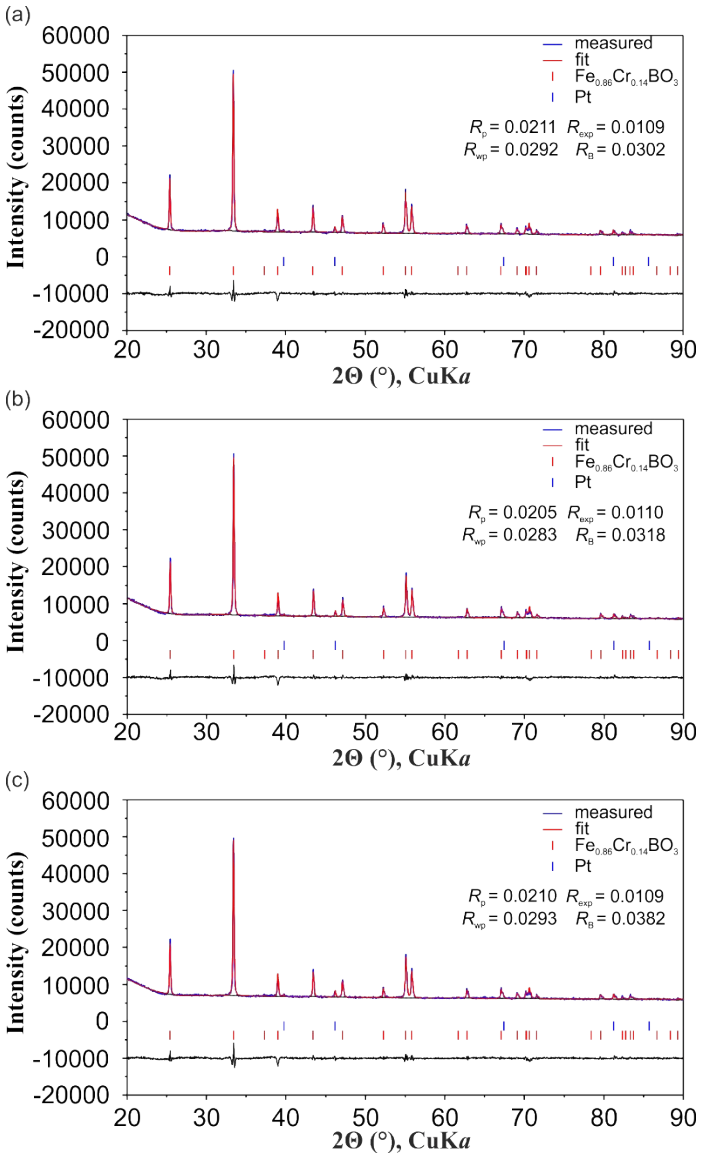

Fig. S5 X-ray diffraction patterns of $Fe_{0.86}Cr_{0.14}BO_3$ collected at (a) 295, (b) 300 and (c) 305 K. The measured data is represented by a blue line, the refinement fit by a red line and the difference between the data and refinement fit by a black line. Peak positions of $Fe_{0.86}Cr_{0.14}BO_3$ and Pt are shown by red and blue colour, respectively.

Table S10. Equations of approximation of temperature dependencies of unit cell parameters of $Fe_{1-x}Cr_xBO_3$ (x = 0.0–1.0).

	$FeBO_3$		
***T* (K)**	**Equation $l(t) = l_0 + l_1t + l_2t^2$**		
	***a*(*t*) (Å)**	***c*(*t*) (Å)**	***V*(*t*) (Å^3)**
295–353	4.6289(4) – 0.000077(25)×t + 0.000000160(38)×t^2	14.525(20) – 0.00051(12)×t + 0.00000110(19)×t^2	269.53(55) – 0.0183(34)×t + 0.0000390(52)
353–903	4.61473(25) + 0.00001846(89)×t + 0.00000000579(74)×t^2	14.4205(17) + 0.0001693(60)×t + 0.0000000288(50)×t^2	265.955(35) + 0.00523(13)×t + 0.00000126(11)
	$Fe_{0.86}Cr_{0.14}BO_3$		
295–305	4.6255(53) – 0.000037(18)×t	14.473(15) – 0.000132(52)×t	268.16(70) – 0.0067(24)×t
305–963	4.61042(11) + 0.00001158(44)×t + 0.00000000744(38)×t^2	14.38293(52) + 0.0001635(21)×t + 0.0000000233(18)×t^2	264.767(18) + 0.004321(75)×t + 0.000001330(64)
	$CrBO_3$		
295–1173	4.57006(17) + 0.00000336(60)×t + 0.00000001051(50)×t^2	14.20693(65) + 0.0001066(23)×t + 0.0000000396(20)×t^2	256.969(25) + 0.002287(91)×t + 0.000001931(77)