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Supplementary Information

Pyrochlore-type oxide solid solutions $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$

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Table S1 Compositions of the starting mixtures, heating times, compounds prepared at 1100 ºC, and cubic cell parameters, *a*, for the pyroclore phases.

Table S2 Results of EPMA of a ($Bi_{1.62}Ga_{0.14}Ti_2O_{6.64}$) single crystal prepared by slow cooling from 1250 ºC.

Table S3 Aanisotropic displacement parameters ($Å^2$) for $Bi_{1.62}Ga_{0.14}Ti_2O_{6.64}$.

Fig. S1 TG-DTA curves generated by $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ (x = 0.09, d = 0.08, sample 35) on heating (red) and on cooling (blue).

Fig. S2 Temperature dependence of the dielectric constant ε_r, and loss tanδ values determined for $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ (sample 29 (x = 0.06, d = 0.15)) at 1 MHz.

Table S1 Composition of the starting mixture, heating time, compounds prepared at 1100 ºC, and a cubic cell parameter *a* of a pyroclore phase.

Sample	Composition (mol%)			Heating time (h)	Compounds	pyroclore-phase *a* (Å)
	$BiO_{1.5}$	$GaO_{1.5}$	TiO_2			
1	15.0	5.0	80.0	48 + 48	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $BiGaTi_4O_{11}$	
2	5.0	15.0	80.0	48 + 48	Ga_2O_3, TiO_2, $BiGaTi_4O_{11}$	
3	17.2	10.3	72.4	48 + 48	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $BiGaTi_4O_{11}$	
4	33.3	0.0	66.7	12 + 12	$Bi_2Ti_4O_{11}$	
5	30.0	3.3	66.7	12 + 12	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_2Ti_4O_{11}$	
6	16.7	16.7	66.7	48 + 48	$BiGaTi_4O_{11}$, TiO_2	
7	31.7	3.3	65.0	12 + 12	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_2Ti_4O_{11}$	
8	32.7	5.8	61.5	48 + 48	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $BiGaTi_4O_{11}$	
9	5.8	32.7	61.5	48 + 48	Ga_2O_3, TiO_2, $BiGaTi_4O_{11}$	
10	25.0	25.0	50.0	48 + 48	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, Ga_2O_3, $BiGaTi_4O_{11}$	
11	35.0	20.0	45.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$,$Ga_2O_3$, $BiGaTi_4O_{11}$	
12	45.0	15.0	40.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$,$Bi_4Ti_3O_{12}$, Ga_2O_3	
13	33.3	33.3	33.3	48 + 48	(melt)	
14	14.3	52.4	33.3	48 + 48	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, Ga_2O_3, $BiGaTi_4O_{11}$	
15	50.0	25.0	25.0	48 + 48	(melt)	
16	40.0	40.0	20.0	48 + 48	(melt)	
17	25.0	50.0	25.0	48 + 48	(melt)	
18	66.7	16.7	16.7	48 + 48	(melt)	
19	85.2	11.1	3.7	48 + 48	(melt)	
20	26.4	64.2	9.4	48 + 48	(melt)	
21	50.0	0.0	50.0	12 + 12	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$	
22	45.0	1.5	53.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$,$Bi_2Ti_4O_{11}$	
23	41.5	4.5	54.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$,$Bi_2Ti_4O_{11}$	
24	37.0	8.0	55.0	12 + 12	TiO_2, $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $BiGaTi_4O_{11}$	
25	43.5	4.0	52.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_2Ti_4O_{11}$	
26	40.0	8.7	51.3	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, TiO_2	
27	39.5	10.5	50.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$,$Ga_2O_3$,$BiGaTi_4O_{11}$	
28	45.5	2.0	52.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.04$, $d = 0.19$) >>$Bi_2Ti_4O_{11}$, $Bi_4Ti_3O_{12}$	10.3522(2)
29	45.0	3.0	52.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.06$, $d = 0.15$)	10.3508(3)
30	44.0	4.5	51.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.09$, $d = 0.12$)	10.3471(2)
31	43.0	6.0	51.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.12$, $d = 0.08$)	10.3444(2)
32	42.5	7.5	50.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.15$, $d = 0.00$)	10.3451(2)
33	41.3	8.8	50.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x \sim 0.18$, $d \sim 0.00$) >>$BiGaTi_4O_{11}$, TiO_2	10.3416(2)
34	46.0	2.5	51.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x \sim 0.05$, $d \sim 0.12$) >>$Bi_4Ti_3O_{12}$	10.3550(2)
35	44.5	4.5	51.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.09$, $d = 0.08$)	10.3541(6)
36	44.5	5.0	50.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ ($x = 0.10$, $d = 0.04$)	10.3508(2)
37	43.0	8.0	49.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_{1.96}Ga_{0.04}O_{7-3d/2}$ ($x = 0.16$, $d = 0.01$)	10.3459(2)

38	45.0	5.0	50.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
39	43.5	8.5	48.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
40	47.5	2.5	50.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
41	50.0	2.5	47.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
42	50.0	5.0	45.0	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
43	48.8	2.5	48.8	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$
44	47.5	5.0	47.5	12 + 12	$(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$, $Bi_4Ti_3O_{12}$

Table S2 The results of EPMA for the single crystal ($Bi_{1.62}Ga_{0.14}Ti_2O_{6.64}$) prepared by slow cooling from 1250 ºC

Point	Bi_2O_3 (mass%)	Ga_2O_3 (mass%)	TiO_2 (mass%)	Total (mass%)
1	69.2	2.2	29.2	100.5
2	69.3	2.6	29.7	101.5
3	68.6	2.6	29.2	100.4
4	69.4	2.6	28.6	100.6
5	68.9	2.8	28.6	100.3
6	67.0	2.0	28.9	98.0
7	68.0	2.4	28.3	98.7
8	68.0	2.3	29.5	99.7
9	68.7	1.9	28.9	99.6
10	69.6	2.0	29.0	100.6
avg.(dev.)	68.7(8)	2.3(3)	29.0(4)	100(1)

Table S3 Aanisotropic displacement parameters (Å^2) for $Bi_{1.62}Ga_{0.14}Ti_2O_{6.64}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	0.0096(13)	0.0103(9)	0.040(3)	−0.0023(9)	−0.0032(8)	−0.0013(8)
Ti1a	0.0039(4)	0.0039(4)	0.0039(4)	−0.0008(4)	−0.0008(4)	−0.0008(4)
O1a	0.015(2)	0.008(2)	0.022(3)	0.0076(15)	0	0

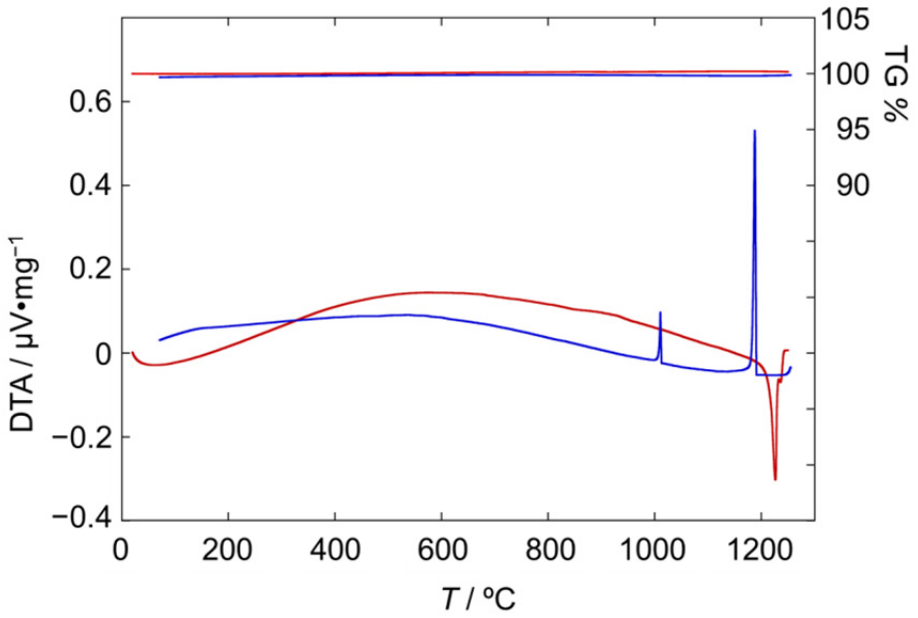

Fig. S1 TG-DTA curves generated by $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ (x = 0.09, d = 0.08, sample 35) on heating (red) and on cooling (blue).

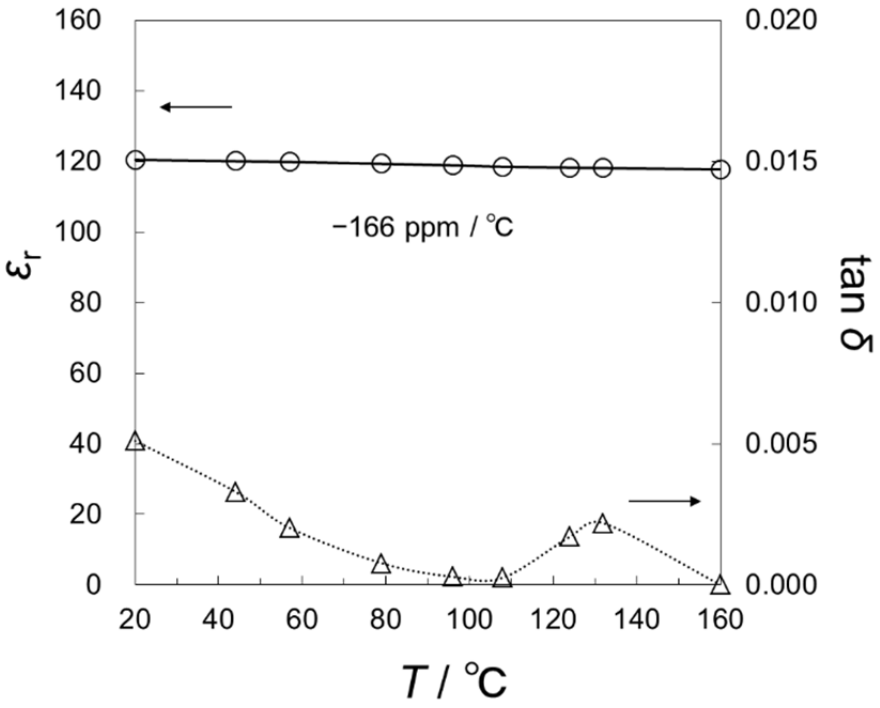

Fig. S2 Temperature dependence of the dielectric constant ε_r, and loss tanδ values determined for $(Bi_{1-x}Ga_x)_{2-d}Ti_2O_{7-3d/2}$ (sample 29 (x = 0.06, d = 0.15)) at 1 MHz.