Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information

Cationic pair substitution in $LaAlO_3:Mn^{4+}$ for octahedral-tilting dependent zero-phonon line

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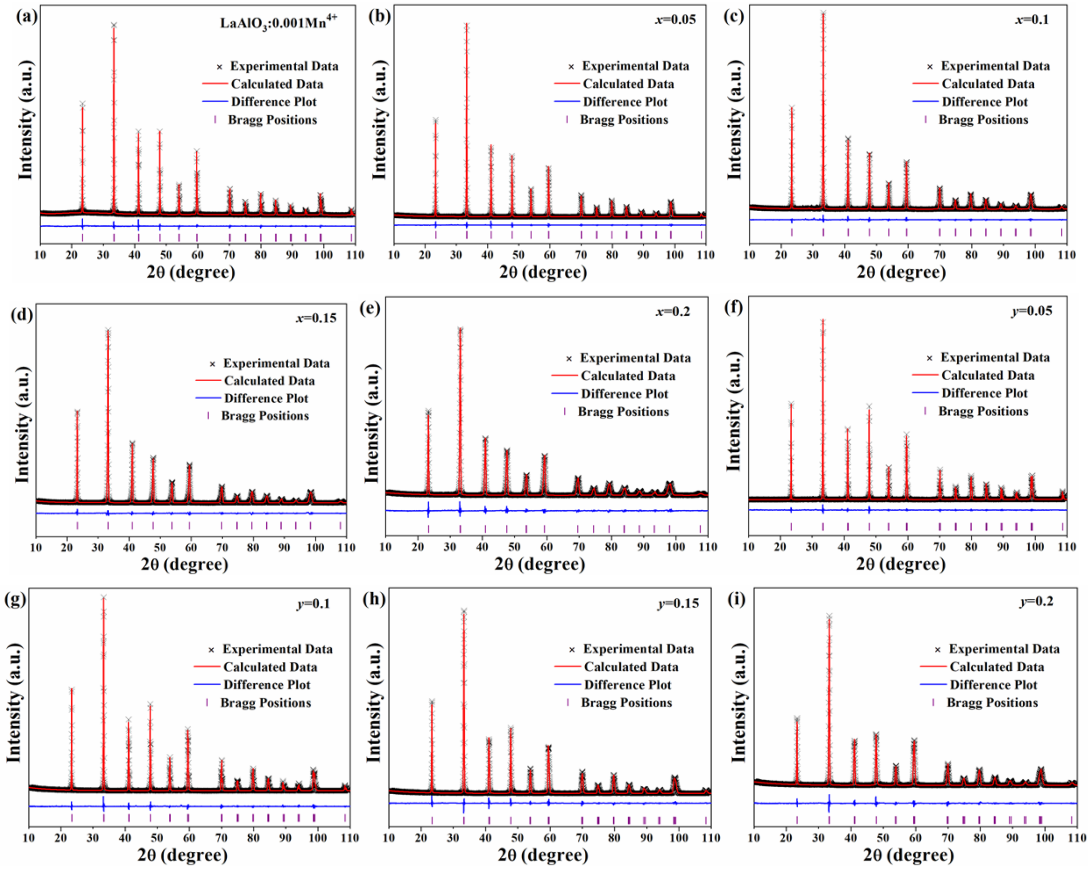


Fig. S1 Rietveld refinement of LBAT:0.001Mn^{4+} (x=0-0.2) and LYAG:0.001Mn^{4+} (y=0-0.2).

Table S1 The refined crystallographic data of LBAT:0.001Mn^{4+} (x=0-0.2) and LYAG:0.001Mn^{4+} (y=0-0.2)

Formula	a (Å)	β (°)	V (Å^3)	R_{exp} (%)	R_{wp} (%)	R_p (%)	χ^2
$LaAlO_3$:0.001Mn^{4+}	3.7908(1)	90.0853(3)	54.4728(8)	5.13	6.83	4.86	1.33
x=0.05	3.7961(2)	90.0691(30)	54.703(10)	5.31	8.05	4.90	1.52
x=0.1	3.8018(1)	90.0610(38)	54.9507(40)	5.39	9.29	5.05	1.72
x=0.15	3.8092(2)	90.041(13)	55.2716(93)	5.14	9.27	5.61	1.80
x=0.2	3.8186(2)	90.012(20)	55.6830(67)	5.59	9.46	6.27	1.69
y=0.05	3.7949(1)	90.1253(27)	54.6514(56)	7.30	13.89	5.89	1.90
y=0.1	3.7975(1)	90.1593(6)	54.7654(18)	6.53	11.21	6.32	1.72
y=0.15	3.8015(2)	90.1842(12)	54.9352(64)	5.87	9.12	6.05	1.55
y=0.2	3.8023(2)	90.2135(28)	54.970(12)	6.38	9.73	6.66	1.53

Table S2 Wyckoff lattice position (Wyck), atomic coordinates (*x*, *y*, *z*), isotropic displacement parameter (B_{iso}) and atom occupancy (Occ.) for LBAT:0.001Mn^{4+} (*x*=0-0.2) and LYAG:0.001Mn^{4+} (*y*=0-0.2)

Atom	Wyck.	*x*	*y*	*z*	B_{iso} (Å^2)	Occ.
$LaAlO_3$:0.001Mn^{4+}						
La	1a	0	0	0	0.94(15)	1
Al	1a	0.5	0.5	0.5	0.69(16)	0.999
O	3b	0.5	0.5	0	1.48(16)	1
Mn	1a	0.5	0.5	0.5	0.69(16)	0.001
x=0.05						
La	1a	0	0	0	1.45(30)	0.95
Al	1a	0.5	0.5	0.5	2.06(27)	0.949
O	3b	0.5	0.5	0	2.77(38)	1
Ba	1a	0	0	0	1.45(30)	0.05
Ti	1a	0.5	0.5	0.5	2.06(27)	0.05
Mn	1a	0.5	0.5	0.5	2.06(27)	0.001
x=0.1						
La	1a	0	0	0	0.559(64)	0.90
Al	1a	0.5	0.5	0.5	0.397(72)	0.899
O	3b	0.5	0.5	0	0.712(81)	1
Ba	1a	0	0	0	0.559(64)	0.1
Ti	1a	0.5	0.5	0.5	0.397(72)	0.1
Mn	1a	0.5	0.5	0.5	0.397(72)	0.001
x=0.15						
La	1a	0	0	0	0.749(61)	0.85
Al	1a	0.5	0.5	0.5	0.645(80)	0.849
O	3b	0.5	0.5	0	1.49(13)	1
Ba	1a	0	0	0	0.749(61)	0.15
Ti	1a	0.5	0.5	0.5	0.645(80)	0.15
Mn	1a	0.5	0.5	0.5	0.645(80)	0.001
x=0.2						
La	1a	0	0	0	0.388(43)	0.8
Al	1a	0.5	0.5	0.5	0.188(24)	0.799
O	3b	0.5	0.5	0	0.583(68)	1
Ba	1a	0	0	0	0.388(43)	0.2
Ti	1a	0.5	0.5	0.5	0.188(24)	0.2
Mn	1a	0.5	0.5	0.5	0.188(24)	0.001
y=0.05						
La	1a	0	0	0	1.19(60)	0.95
Al	1a	0.5	0.5	0.5	3.00(12)	0.949
O	3b	0.5	0.5	0	2.64(17)	1
Y	1a	0	0	0	1.19(60)	0.05
Ga	1a	0.5	0.5	0.5	3.00(82)	0.05
Mn	1a	0.5	0.5	0.5	3.00(82)	0.001

y=0.1						
La	1a	0	0	0	0.67(13)	0.90
Al	1a	0.5	0.5	0.5	0.28(17)	0.899
O	3b	0.5	0.5	0	2.21(25)	1
Y	1a	0	0	0	0.67(13)	0.1
Ga	1a	0.5	0.5	0.5	0.28(17)	0.1
Mn	1a	0.5	0.5	0.5	0.28(17)	0.001
y=0.15						
La	1a	0	0	0	0.20(20)	0.85
Al	1a	0.5	0.5	0.5	0.23(19)	0.849
O	3b	0.5	0.5	0	1.95(21)	1
Y	1a	0	0	0	0.20(20)	0.15
Ga	1a	0.5	0.5	0.5	0.23(19)	0.15
Mn	1a	0.5	0.5	0.5	0.23(19)	0.001
y=0.2						
La	1a	0	0	0	0.89(20)	0.80
Al	1a	0.5	0.5	0.5	0.80(20)	0.799
O	3b	0.5	0.5	0	3.00(24)	1
Y	1a	0	0	0	0.89(20)	0.2
Ga	1a	0.5	0.5	0.5	0.80(20)	0.2
Mn	1a	0.5	0.5	0.5	0.80(20)	0.001

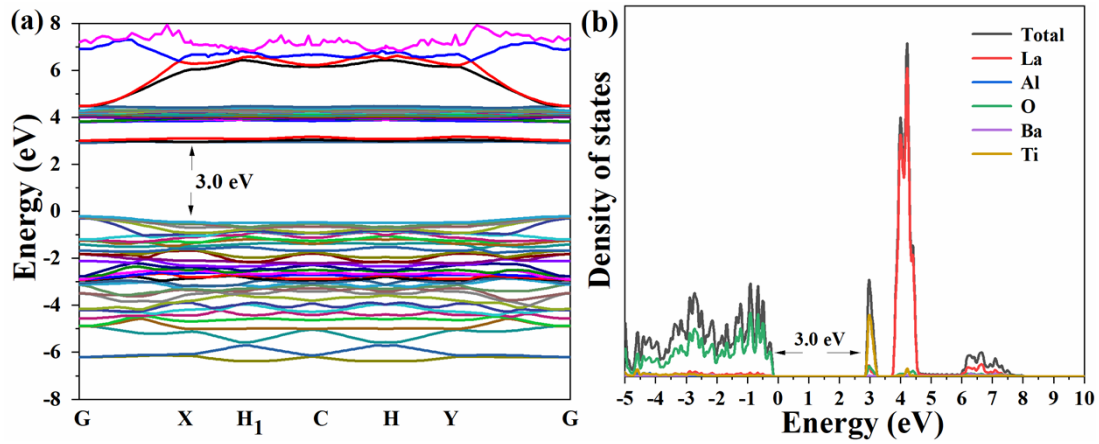


Fig. S2 Calculated band structure (a) and partial density of states (b) for the $La_{0.8}Ba_{0.2}Al_{0.8}Ti_{0.2}O_3$ host.

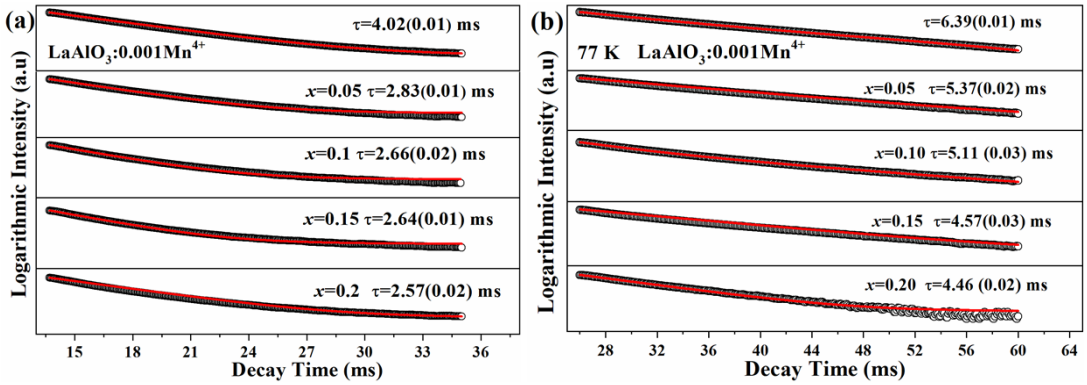


Fig. S3 Decay curves of LBAT:0.001Mn^{4+} (x=0-0.2) under excitation at 340 nm and monitoring at 726 nm at room temperature (a) and 77 K (b).

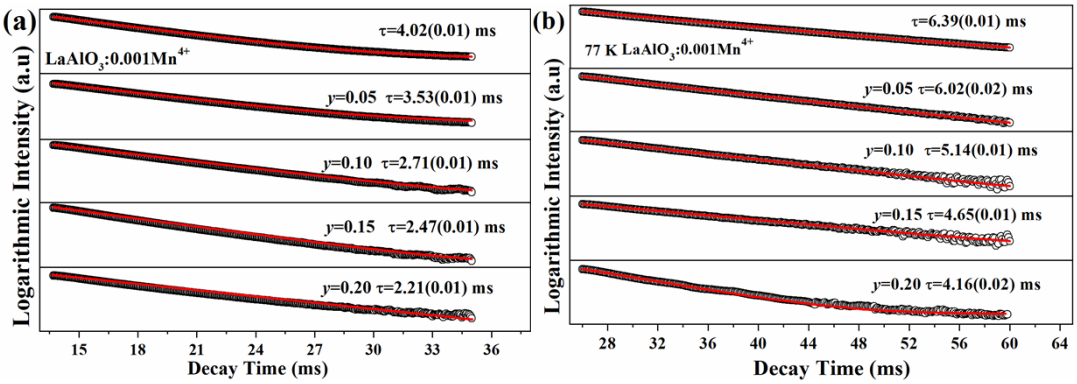
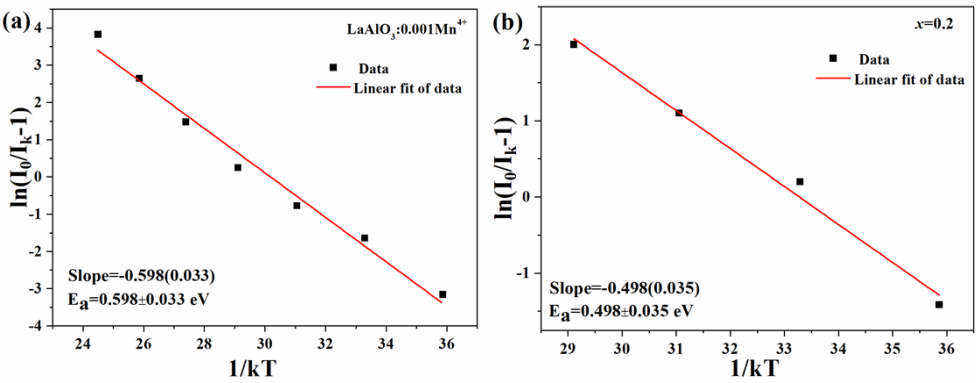


Fig. S4 Decay curves of LYAG:0.001Mn^{4+} (y=0-0.2) under excitation at 340 nm and monitoring at 726 nm at room temperature (a) and 77 K (b).



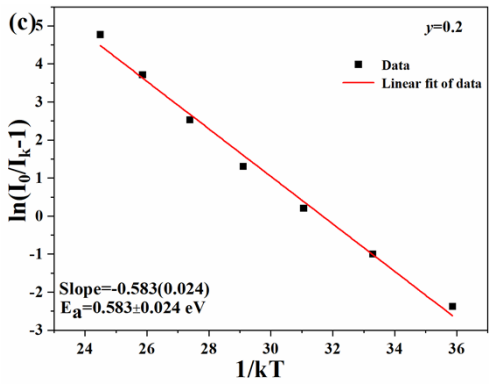


Fig. S5 The $In(I_0/I_K-1)$ *vs* 1/kT plot for determination of the activation energy of thermal quenching for (a) $LaAlO_3$:0.001Mn^{4+}, (b) x=0.2 and (c) y=0.2.