Supplementary Material

Thermal Stability Enhancement of Mn^{4+}-Activated Germanate Phosphor by Cationic Non-Equivalent Substitution Strategy

Huancheng Wu[a], Bohua Zhang[a], Xikun Zou[a], Maxim S. Molokeev[c], Xuejie Zhang[a], Ziyi Wang[a], Xiaoyu Shuang[a], and Haoran Zhang[a, b, *]

[a] *Key Laboratory for Biobased Materials and Energy of Ministry of Education, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, P. R. China*

[b] *Maoming Branch, Guangdong Laboratory for Lingnan Modern Agriculture, Maoming 525100, P. R. China*

[c] *Department of Physics and Technical Sciences, Western Caspian University, Baku, AZ 1001, Azerbaijan*

Table S1. Main parameters of processing and refinement of the $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$ samples.

x	Space Group	Cell parameters (Å), Cell Volume (Å^3)	R_{wp}, R_p, R_B, χ^2
0	Pbam	a = 14.514127(90), b = 10.223382(58), c = 5.946442(34), V = 882.3537(90)	5.8, 4.05, 1.68, 4.58
0.125	Pbam	a = 14.51892(10), b = 10.221784(68), c = 5.949599(41), V = 882.976(10)	4.84, 3.69, 1.68, 3.8
0.250	Pbam	a = 14.521963(93), b = 10.220562(64), c = 5.951228(37), V = 883.2969(96)	5.07, 3.89, 1.78, 3.91
0.375	Pbam	a = 14.52457(14), b = 10.219541(95), c = 5.952588(56), V = 883.569(14)	5.82, 4.4, 2.91, 4.51

Table S2. Fractional atomic coordinates and isotropic displacement parameters (Å^2) of $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$.

Atom	x	y	z	B_{iso}	Occ.
		x = 0			
Mg1	0	0.5	0.5	0.391(56)	1

Mg2	0	0	0.5	0.391(56)	1
Mg3	0.17553(22)	0.18025(30)	0	0.391(56)	1
Mg4	0.32708(23)	0.14823(29)	0.5	0.391(56)	1
Mg5	0.99456(14)	0.25125(19)	0.24237(35)	0.391(56)	1
Mg6	0.33076(15)	0.41936(21)	0.24736(41)	0.391(56)	1
Ge1	0	0	0	0.347(57)	1
Ge2	0.126126(81)	0.50227(14)	0	0.347(57)	1
Ge3	0.186640(84)	0.32551(10)	0.5	0.347(57)	1
O1	0.08404(39)	0.33818(58)	0	0.055(59)	1
O2	0.41846(34)	0.34567(56)	0	0.055(59)	1
O3	0.25195(38)	0.00262(50)	0	0.055(59)	1
O4	0.06889(36)	0.32668(55)	0.5	0.055(59)	1
O5	0.41566(38)	0.32883(61)	0.5	0.055(59)	1
O6	0.25681(35)	0.98324(51)	0.5	0.055(59)	1
O7	0.07440(24)	0.07483(37)	0.23030(77)	0.055(59)	1
O8	0.41130(23)	0.07810(36)	0.24260(72)	0.055(59)	1
O9	0.24189(25)	0.25188(42)	0.27360(58)	0.055(59)	1
x = 0.125					
Mg1	0	0.5	0.5	0.653(34)	1
Mg2	0	0	0.5	0.653(34)	1
Mg3	0.17463(20)	0.17921(27)	0	0.653(34)	1

Mg4	0.32589(21)	0.14760(26)	0.5	0.653(34)	1
Mg5	0.99579(14)	0.25214(18)	0.24093(33)	0.653(34)	1
Mg6	0.33044(14)	0.41882(19)	0.24767(37)	0.653(34)	1
Ge1	0	0	0	0.652(34)	1
Ge2	0.126108(75)	0.50223(13)	0	0.652(34)	1
Ge3	0.186430(80)	0.325187(95)	0.5	0.652(34)	1
O1	0.08390(36)	0.33722(53)	0	0.453(37)	1
O2	0.41882(31)	0.34517(51)	0	0.453(37)	1
O3	0.25168(35)	0.99923(47)	0	0.453(37)	1
O4	0.06791(34)	0.33044(50)	0.5	0.453(37)	1
O5	0.41544(35)	0.33194(54)	0.5	0.453(37)	1
O6	0.25976(33)	0.98173(47)	0.5	0.453(37)	1
O7	0.07534(23)	0.07694(34)	0.22867(70)	0.453(37)	1
O8	0.41290(23)	0.08125(34)	0.24290(66)	0.453(37)	1
O9	0.24233(24)	0.24991(40)	0.27157(55)	0.453(37)	1
x = 0.250					
Mg1	0	0.5	0.5	0.375(51)	1
Mg2	0	0	0.5	0.375(51)	1
Mg3	0.17399(21)	0.17978(29)	0	0.375(51)	1
Mg4	0.32616(22)	0.14743(27)	0.5	0.375(51)	1
Mg5	0.99615(14)	0.25239(18)	0.24074(34)	0.375(51)	1

Mg6	0.33053(15)	0.41865(20)	0.24584(38)	0.375(51)	1
Ge1	0	0	0	0.379(52)	1
Ge2	0.126623(77)	0.50248(13)	0	0.379(52)	1
Ge3	0.186747(83)	0.325280(98)	0.5	0.379(52)	1
O1	0.08252(37)	0.33921(53)	0	0.062(54)	1
O2	0.41853(32)	0.34689(52)	0	0.062(54)	1
O3	0.25286(36)	0.99996(47)	0	0.062(54)	1
O4	0.07112(34)	0.32724(50)	0.5	0.062(54)	1
O5	0.41630(36)	0.33277(55)	0.5	0.062(54)	1
O6	0.25799(34)	0.97999(47)	0.5	0.062(54)	1
O7	0.07449(23)	0.07624(34)	0.22600(71)	0.062(54)	1
O8	0.41159(23)	0.08183(34)	0.24465(67)	0.062(54)	1
O9	0.24424(25)	0.25049(40)	0.27558(53)	0.062(54)	1
x = 0.375					
Mg1	0	0.5	0.5	0.721(50)	1
Mg2	0	0	0.5	0.721(50)	1
Mg3	0.17353(28)	0.18013(38)	0	0.721(50)	1
Mg4	0.32650(30)	0.14851(35)	0.5	0.721(50)	1
Mg5	0.99638(20)	0.25280(23)	0.24110(45)	0.721(50)	1
Mg6	0.32973(20)	0.41968(26)	0.24700(52)	0.721(50)	1
Ge1	0	0	0	0.860(50)	1

Ge2	0.12669(11)	0.50219(18)	0	0.860(50)	1
Ge3	0.18670(11)	0.32525(13)	0.5	0.860(50)	1
O1	0.08236(50)	0.33848(73)	0	0.620(53)	1
O2	0.41579(43)	0.34375(70)	0	0.620(53)	1
O3	0.25172(50)	0.99785(63)	0	0.620(53)	1
O4	0.07074(47)	0.32807(68)	0.5	0.620(53)	1
O5	0.41801(49)	0.33301(74)	0.5	0.620(53)	1
O6	0.25915(46)	0.98169(63)	0.5	0.620(53)	1
O7	0.07593(32)	0.07735(47)	0.23228(99)	0.620(53)	1
O8	0.41236(32)	0.08223(46)	0.23992(91)	0.620(53)	1
O9	0.24295(34)	0.24910(54)	0.27070(76)	0.620(53)	1

Table S3. Main bond lengths (Å) of $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$.

x = 0			
Mg1—O4^{i}	2.0345(55)	Mg1—O8^{ii}	2.1535(38)
Mg2—O5^{iii}	2.1355(60)	Mg2—O7^{iv}	2.0792(42)
Mg3—O1^{v}	2.0904(66)	Mg3—O3^{v}	2.1279(60)
Mg3—O7^{v}	2.2784(47)	Mg3—O9^{v}	2.0275(40)
Mg4—O5^{vi}	2.2498(67)	Mg4—O6^{vii}	1.9711(60)
Mg4—O8^{vi}	2.0859(44)	Mg4—O9^{vi}	2.1128(44)
Mg5—O1^{viii}	2.1339(47)	Mg5—O2^{ix}	2.0685(43)
Mg5—O4^{x}	2.0262(40)	Mg5—O5^{xi}	2.0805(44)

Mg5—O7^{xii}	2.1449(41)	Mg5—O8^{xiii}	2.1222(40)
Mg6—O2^{v}	2.0859(43)	Mg6—O3^{xiv}	2.0806(44)
Mg6—O5^{vi}	2.1521(47)	Mg6—O6^{iii}	2.0733(42)
Mg6—O7^{xv}	2.1050(42)	Mg6—O9^{xvi}	2.1493(46)
Ge1—O2^{xvii}	1.9723(54)	Ge1—O7	1.9044(41)
Ge2—O1^{xviii}	3.4591(58)	Ge2—O1^{v}	1.7853(60)
Ge2—O3^{xiv}	1.7696(56)	Ge2—O6^{xvii}	3.4299(26)
Ge2—O8^{xiv}	1.7254(41)	Ge2—O9^{v}	3.4673(41)
Ge3—O1^{v}	3.3278(26)	Ge3—O4^{vi}	1.7090(53)
Ge3—O5^{vi}	3.3241(56)	Ge3—O6^{iii}	1.8094(52)
Ge3—O7^{vi}	3.4342(40)	Ge3—O8^{ii}	3.3214(38)
Ge3—O9^{vi}	1.7384(37)		

x = 0.125

Mg1—O4^{i}	1.9940(50)	Mg1—O8^{ii}	2.1514(36)
Mg2—O5^{iii}	2.1114(53)	Mg2—O7^{iv}	2.1026(38)
Mg3—O1^{v}	2.0842(60)	Mg3—O3^{xix}	2.1531(56)
Mg3—O7^{v}	2.2409(43)	Mg3—O9^{v}	2.0246(38)
Mg4—O5^{vi}	2.2893(60)	Mg4—O6^{vii}	1.9484(55)
Mg4—O8^{vi}	2.0965(41)	Mg4—O9^{vi}	2.1006(41)
Mg5—O1^{viii}	2.1089(43)	Mg5—O2^{ix}	2.0719(39)
Mg5—O4^{x}	2.0280(37)	Mg5—O5^{xi}	2.1155(40)

Mg5—O7^{xii}	2.1322(39)	Mg5—O8^{xiii}	2.0853(39)
Mg6—O2^{v}	2.0939(39)	Mg6—O3^{xvii}	2.0660(40)
Mg6—O5^{vi}	2.1366(42)	Mg6—O6^{iii}	2.0934(39)
Mg6—O7^{xv}	2.1204(39)	Mg6—O9^{xvi}	2.1535(43)
Ge1—O2^{xvii}	1.9733(49)	Ge1—O7	1.9146(37)
Ge2—O1^{xviii}	3.4626(53)	Ge2—O1^{v}	1.7945(55)
Ge2—O3^{xvii}	1.7746(51)	Ge2—O6^{xvii}	3.4116(24)
Ge2—O8^{xiv}	1.7497(38)	Ge2—O9^{v}	3.4799(39)
Ge3—O1^{v}	3.3287(24)	Ge3—O4^{vi}	1.7216(50)
Ge3—O5^{vi}	3.3256(52)	Ge3—O6^{iii}	1.7806(49)
Ge3—O7^{vi}	3.4126(37)	Ge3—O8^{ii}	3.3571(36)
Ge3—O9^{vi}	1.7600(35)		

x = 0.25

Mg1—O4^{i}	2.0455(50)	Mg1—O8^{ii}	2.1580(36)
Mg2—O5^{iii}	2.0973(54)	Mg2—O7^{iv}	2.1062(39)
Mg3—O1^{v}	2.1022(61)	Mg3—O3^{xix}	2.1655(57)
Mg3—O7^{v}	2.2397(44)	Mg3—O9^{v}	2.0622(38)
Mg4—O6^{vii}	1.9770(56)	Mg4—O8^{vi}	2.0731(42)
Mg4—O9^{vi}	2.0756(42)	Mg5—O1^{viii}	2.1007(44)
Mg5—O2^{ix}	2.0863(41)	Mg5—O4^{x}	2.0374(38)
Mg5—O5^{xi}	2.1172(41)	Mg5—O7^{xii}	2.1314(39)

Mg5—O8^{xiii}	2.0926(39)	Mg6—O2^{v}	2.0764(40)
Mg6—O3^{xvii}	2.0730(42)	Mg6—O5^{vi}	2.1470(43)
Mg6—O6^{iii}	2.0816(40)	Mg6—O7^{xv}	2.1238(40)
Mg6—O9^{xvi}	2.1343(44)	Ge1—O2^{xvii}	1.9617(50)
Ge1—O7	1.8937(38)	Ge2—O1^{xviii}	3.4412(55)
Ge2—O1^{v}	1.7873(55)	Ge2—O3^{xvii}	1.7503(53)
Ge2—O6^{xvii}	3.4227(25)	Ge2—O8^{xiv}	1.7565(38)
Ge2—O9^{v}	3.4985(39)	Ge3—O1^{v}	3.3414(25)
Ge3—O4^{vi}	1.6792(50)	Ge3—O5^{vi}	3.3344(53)
Ge3—O6^{iii}	1.7732(49)	Ge3—O7^{vi}	3.4344(37)
Ge3—O8^{ii}	3.3502(36)	Ge3—O9^{vi}	1.7507(35)

x = 0.375

Mg1—O4^{i}	2.0354(69)	Mg1—O8^{ii}	2.1733(50)
Mg2—O5^{iii}	2.0809(74)	Mg2—O7^{iv}	2.0930(54)
Mg3—O1^{v}	2.0910(83)	Mg3—O3^{xix}	2.1817(77)
Mg3—O7^{v}	2.2415(60)	Mg3—O9^{v}	2.0273(53)
Mg4—O6^{vii}	1.9655(75)	Mg4—O8^{vi}	2.1001(58)
Mg4—O9^{vi}	2.0958(57)	Mg5—O1^{viii}	2.0942(59)
Mg5—O2^{ix}	2.0984(55)	Mg5—O4^{x}	2.0330(52)
Mg5—O5^{xi}	2.1070(56)	Mg5—O7^{xii}	2.1337(53)
Mg5—O8^{xiii}	2.0812(53)	Mg6—O2^{v}	2.0799(54)

Mg6—O3^{xvii}	2.0492(57)	Mg6—O5^{vi}	2.1671(60)
Mg6—O6^{iii}	2.0823(54)	Mg6—O7^{xv}	2.1169(54)
Mg6—O9^{xvi}	2.1558(59)	Ge1—O2^{xvii}	2.0114(68)
Ge1—O7	1.9372(53)	Ge2—O1^{xviii}	3.4454(74)
Ge2—O1^{v}	1.7926(76)	Ge2—O3^{xvii}	1.7665(74)
Ge2—O6^{xvii}	3.4134(33)	Ge2—O8^{xiv}	1.7407(52)
Ge2—O9^{v}	3.4839(54)	Ge3—O1^{v}	3.3426(33)
Ge3—O4^{vi}	1.6845(70)	Ge3—O5^{vi}	3.3606(72)
Ge3—O6^{iii}	1.7817(66)	Ge3—O7^{vi}	3.3979(51)
Ge3—O8^{ii}	3.3710(50)	Ge3—O9^{vi}	1.7709(49)

Symmetry codes: (i) -x, -y+1, -z+1; (ii) -x+1/2, y+1/2, -z+1; (iii) -x+1/2, y+1/2, -z+1; (iv) -x, -y, -z+1; (v) x, y, -z; (vi) x, y, -z+1; (vii) x, y-1, -z+1; (viii) x+1, y, -z; (ix) x+1/2, -y+1/2, -z; (x) x+1, y, -z+1; (xi) x+1/2, -y+1/2, -z+1; (xii) x+1, y, z; (xiii) x+1/2, -y+1/2, z; (xiv) -x+1/2, y+1/2, -z; (xv) -x+1/2, y+1/2, z; (xvi) x, y, z; (xvii) -x+1/2, y+1/2, -z; (xviii) -x, -y+1, -z; (xix) x, y-1, -z.

Table S4. The XPS elemental analysis of MSGO: 0.01Mn^{4+}.

Element	Mg	Sc	Ge	**O**	Mn
Theory (%)	28.05	0.51	10.18	**48.96**	0.02
XPS value (%)	25.56	0.43	11.27	**51.34**	0.03

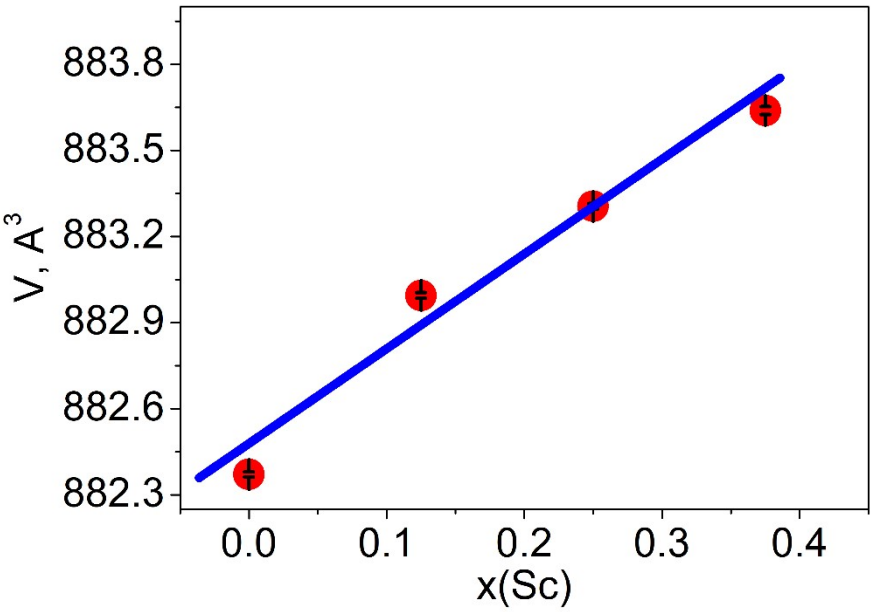

Fig. S1. Relationship between cell volume(V) and concentration (x) about $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$.

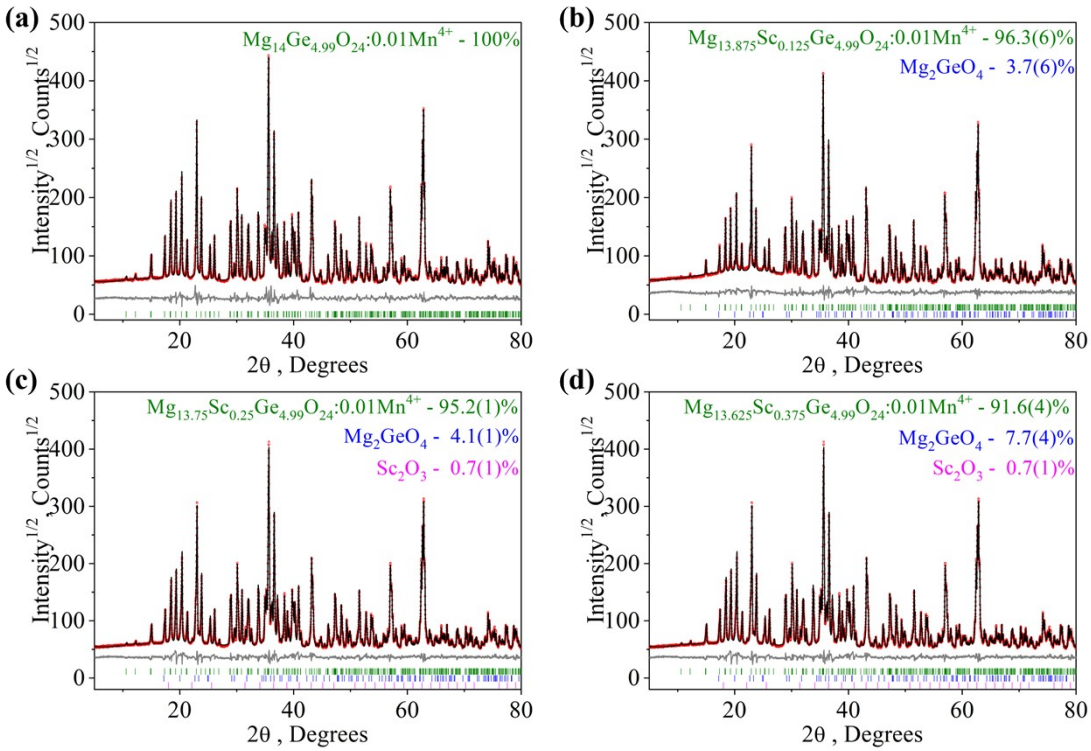

Fig. S2. Difference rietveld plot of $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$, (a) x = 0, (b) x = 0.125, (c) x = 0.25, (d) x = 0.375.

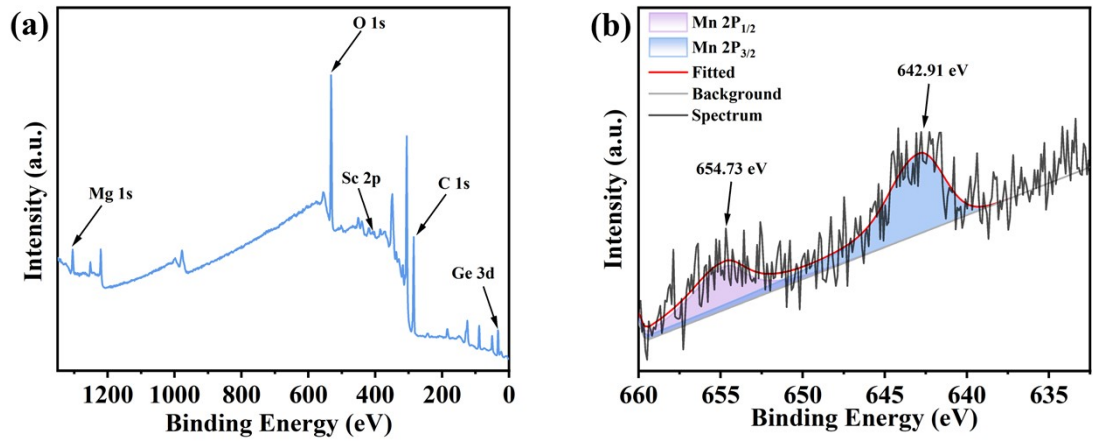

Fig. S3. (a) XPS survey spectrum of $Mg_{13.75}Sc_{0.25}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$, (b) the high resolution XPS of Mn 2p.

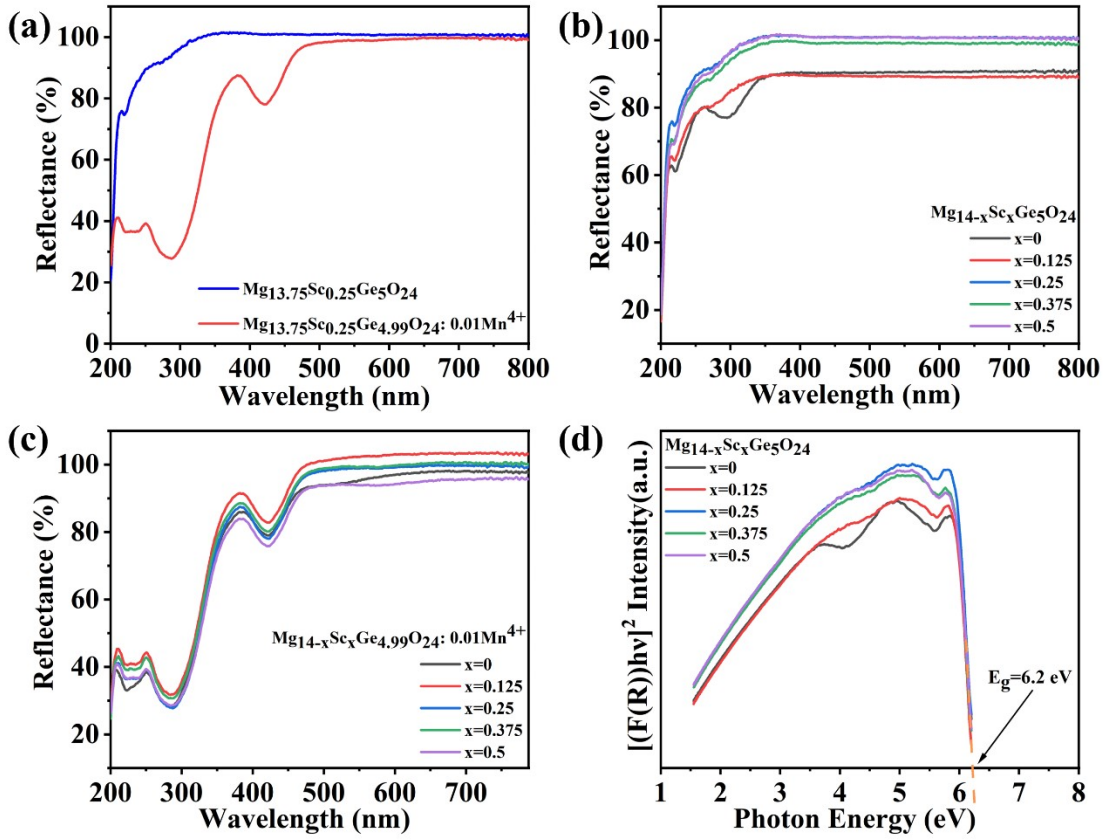

Fig. S4. Diffuse reflectance spectra of (a) $Mg_{13.75}Sc_{0.25}Ge_{5-y}O_{24}$: yMn^{4+} (y=0, 0.01), (b) $Mg_{14-x}Sc_xGe_5O_{24}$ and (c) $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$. (d) Relationship between $[F(R)hv]^2$ and photon energy of the $Mg_{14-x}Sc_xGe_{4.99}O_{24}$ samples.

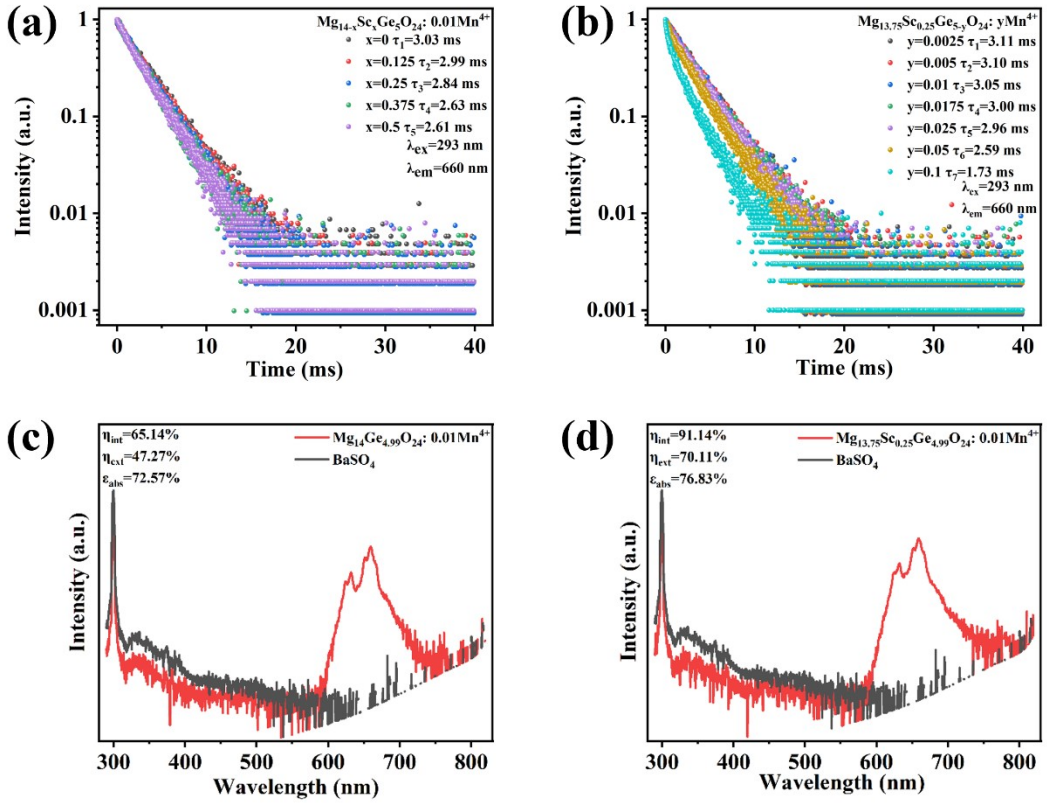

Fig. S5. Decay curves of (a) $Mg_{14-x}Sc_xGe_{4.99}O_{24}$: $0.01Mn^{4+}$ and (b) $Mg_{13.75}Sc_{0.25}Ge_{5-y}O_{24}$: yMn^{4+} phosphors at room temperature (λ_{em} = 660 nm and λ_{ex} = 293 nm); Quantum efficiency spectra of (c) $Mg_{14}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$ and (d) $Mg_{13.75}Sc_{0.25}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$ phosphor at room temperature (λ_{em} = 660 nm and λ_{ex} = 293 nm).

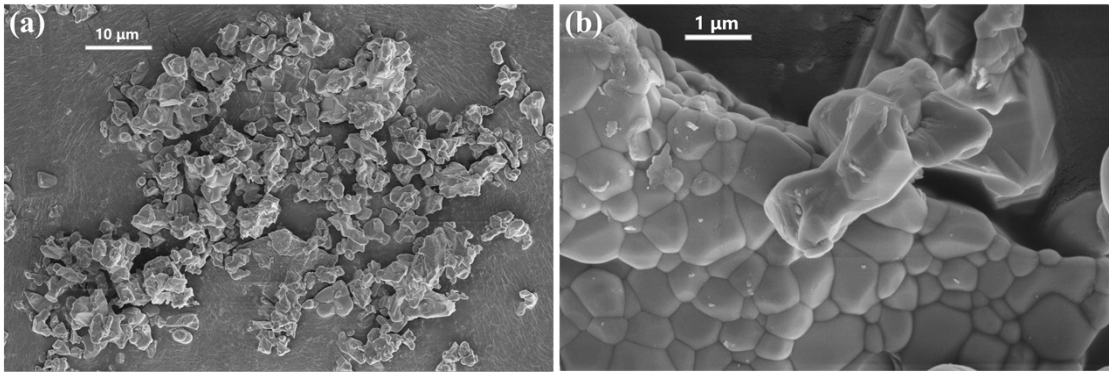

Fig. S6. (a)-(b) The SEM images of $Mg_{13.75}Sc_{0.25}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$ phosphor.

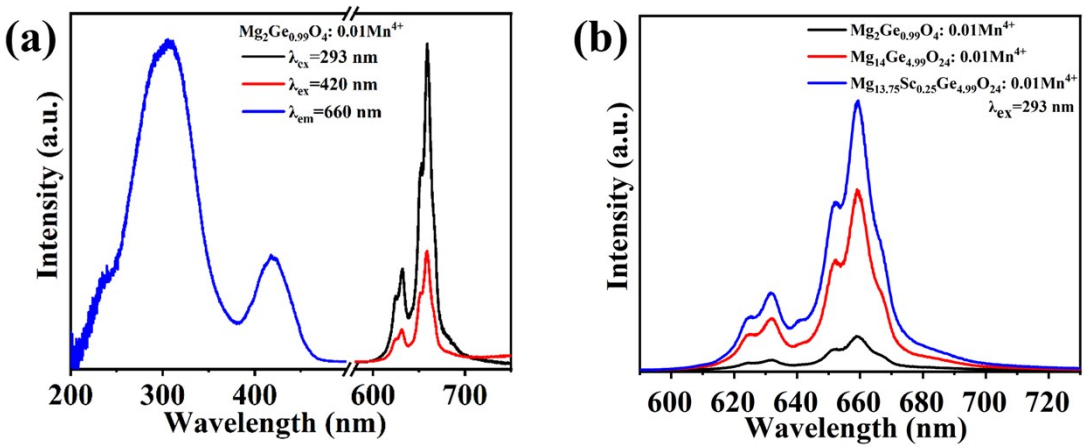

Fig. S7. (a) Excitation and emission spectra of $Mg_2Ge_{0.99}O_4$: $0.01Mn^{4+}$, (b) Emission spectra of $Mg_2Ge_{0.99}O_4$: $0.01Mn^{4+}$, $Mg_{14}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$, and $Mg_{13.75}Sc_{0.25}Ge_{4.99}O_{24}$: $0.01Mn^{4+}$ under 293 nm excitation.