Statistical and Local Structure of Dy^{3+}-doped $Bi_4Ge_3O_{12}$ Crystals: a Role of Activator Concentration in Structural Effects

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Supporting Information

Table S1. Coordinates of atoms, anisotropic displacement parameters $U_{eq} \times 10^2$ (Å^2), site occupancies *p* (SOF), main interatomic distances *d* (Å) and bond angles (ω, deg) in the structures of BGO:Dy crystals according to the XRD data

Parameter	$Bi_4Ge_3O_{12}$:1.0wt.%Dy_2O_3 (**BGO:1.0%Dy**)[a]	$Bi_4Ge_3O_{12}$:0.1wt.%Dy_2O_3 (**BGO:0.1%Dy**)[b]
Bi/Dy (16*c*)		
x	0.08739(4)	0.91253(8)
p (Bi)	0.3293(40)	0.3330(9)
p (Dy)	0.0040(4)	0.0003(9)
U_{eq}	2.05(2)	2.28(6)
Ge (12*a*)		
x	0	0
y	1/4	3/4
z	3/8	5/8
p	0.2500	0.2500
U_{eq}	1.86(5)	2.1(1)
O (48*e*)		
x	0.0721(11)	0.925(3)
y	0.1260(10)	0.874(2)
z	0.2905(9)	0.710(2)
p	1.0	1.0
U_{eq}	2.6(2)	3.1(4)
Bi– 3 × O1	2.177(10)	2.17(2)
– 3 × O2	2.587(10)	2.59(2)
$[Bi–O]_{avr}$	2.382	2.38
Ge – 4 × O	1.748(10)	1.76(2)
O2–Ge–O2	104.9(3)	104.7(6)
O2–Ge–O2	119.0(6)	119.5(9)
O1–Bi–O2	84.5(4)	84.5(3)
O1–Bi–O2	70.8(4)	70.9(8)
O1–Bi–O1	84.52(15)	83.4(9)
O2–Bi–O2	153.7(4)	152.7(9)

[a] right form, [b] left form

Table S2. Coordinates of atoms, isotropic displacement parameters U_{iso} (Å^2), site occupancies p (SOF) and main interatomic distances d (Å) in the structures of powdered BGO:Dy crystals according to the Rietveld refinement

Parameter	$Bi_4Ge_3O_{12}$:1.0wt.%Dy_2O_3 (**BGO:1.0%Dy**)	$Bi_4Ge_3O_{12}$:0.1wt.%Dy_2O_3 (**BGO:0.1%Dy**)
a, Å	10.52689(9)	10.52421(4)
Scherrer size, nm	680	1330
Bi/Dy *x x x* U_{iso} *p* (Bi) *p* (Dy)	 0.08732(4) 0.01604(12) 0.993(1) 0.007(1)	 0.08737(6) 0.0269(2) 0.998(1) 0.002(1)
Ge *x y z* U_{iso} *p*	 0 0 0 0.0184(6) 1.0	 0 0 0 0.0236(12) 1.0
O *x y z* U_{iso} *p*	 0.0714(4) 0.1261(4) 0.2897(4) 0.0221(15) 1.0	 0.0699(6) 0.1297(7) 0.2868(6) 0.030(4) 1.0
$R_p/R_{wp}/GOF$	0.75/1.35/1.19	1.36/2.44/1.89
Bi – 3 × O1 – 3 × O2 $[Bi–O]_{avr}$	2.169(4) 2.591(5) 2.380	2.148(3) 2.640(5) 2.394
Ge – 4 × O	1.748(4)	1.729(4)

Table S3. The results of two-sphere EXAFS fit for BGO:Dy crystals (Bi L_3-edge; *k*-range: 2 – 13 Å^{-1}; *R*, interatomic distance (the length for single scattering path); CN, coordination number; σ^2, the Debye–Waller factor). Coordination numbers were defined to be equal during the fit.

Sample	R_{Bi-O}, Å	CN Bi	σ^2, Å^2	R_f, %
$Bi_4Ge_3O_{12}$:1.0%Dy (**BGO:1.0%Dy**)	2.13 ± 0.012	2.9 ± 0.4	0.0038 ± 0.001	0.9
	2.57 ± 0.016	2.9 ± 0.4	0.0057 ± 0.002	
$Bi_4Ge_3O_{12}$:1.0%Dy (**BGO:0.1%Dy**)	2.13 ± 0.001	2.5 ± 0.3	0.0020 ± 0.001	1.0
	2.58 ± 0.015	2.5 ± 0.3	0.0045 ± 0.002	

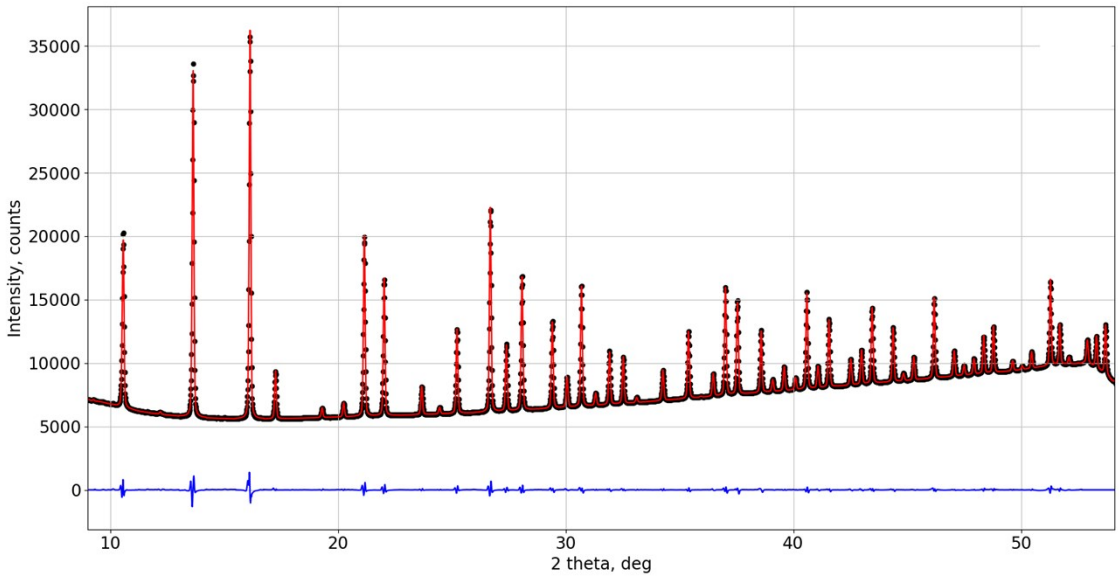

Figure S1. Observed (black dots), calculated (red line), and difference (blue line) X-ray powder patterns for BGO:1.0%Dy sample.

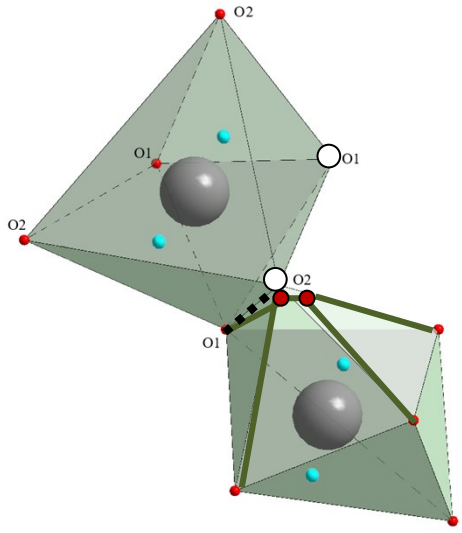

Figure S2. An idealized model of rearrangement of the BiO_6 octahedron into a vacancy octahedron (BiO_5) and DyO_6 octahedron into a DyO_7 octahedron with a split vertex.

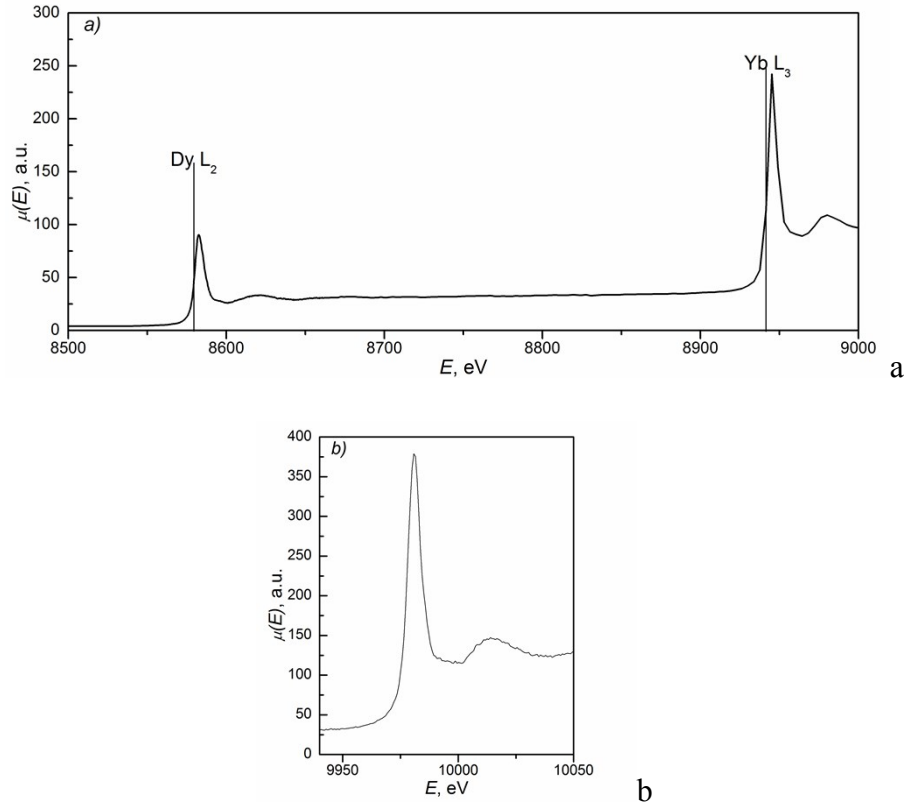

Figure S3. The Dy L_2 and Yb L_3 edge steps (*a*) and the Yb L_2 edge step (*b*) for the BGO:1.0%Dy sample. The fluorescence is normalized to the intensity of the incident beam.

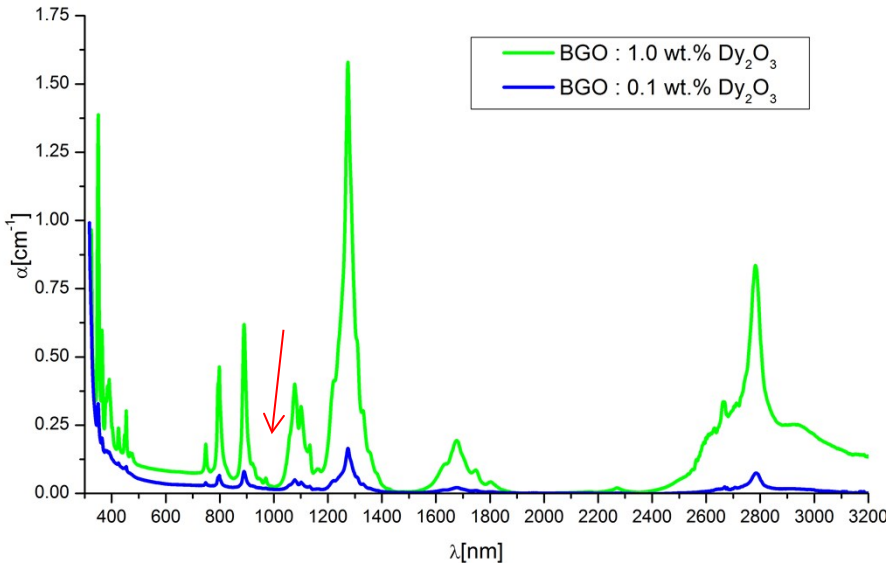

Figure S4. Absorption spectra for the BGO:1.0%Dy and BGO:0.1%Dy samples.

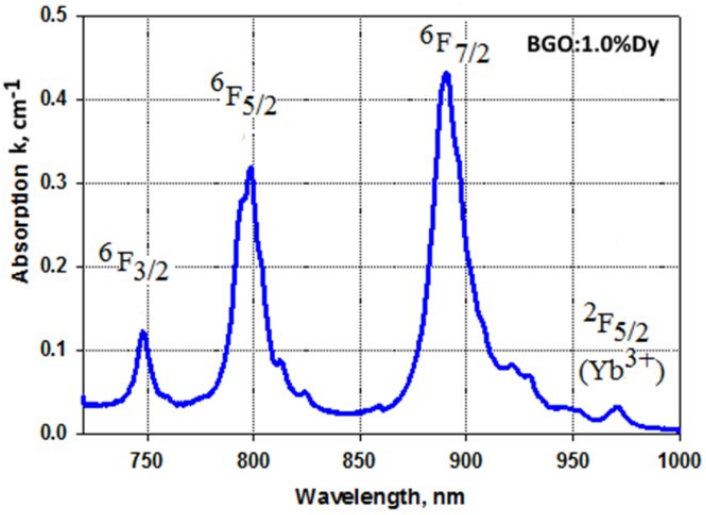

Figure S5. A part of the absorption spectra of the BGO:1.0%Dy.

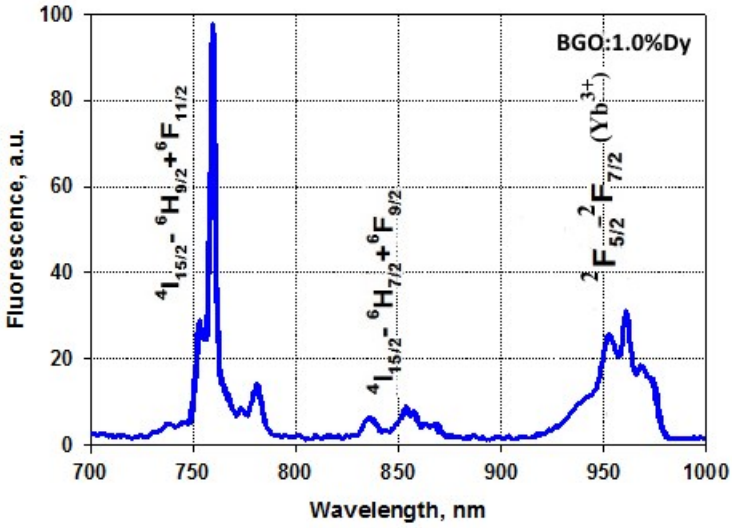

Figure S6. Luminescence spectrum for the BGO:1.0%Dy crystal under excitation by diode laser at 453 nm.