Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary for the paper titled

"Importance of inversion disorder in visible light induced persistent luminescence in Cr^{3+} doped AB_2O_4 "

1 EPR spectra

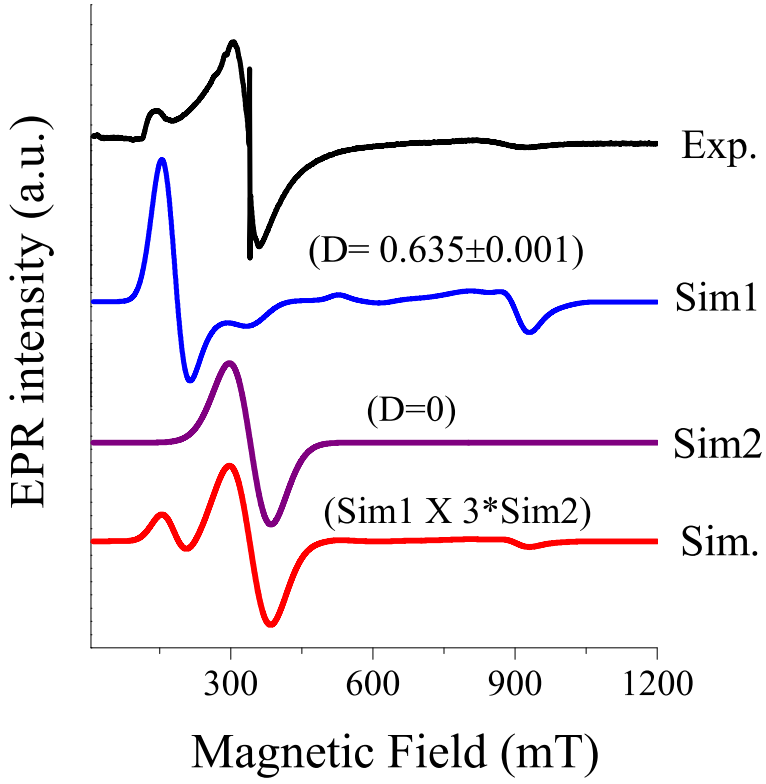

Figure 1: Details of the simulation of the X-band EPR spectrum of Cr^{3+} in MGO. The simulated spectrum (Sim) is the weighted sum of isolated Cr^{3+} ions (Sim1) and clusters of antiferromagnetically coupled Cr^{3+} ions (Sim2). Sim1 considers Cr^{3+} in octahedral sites with trigonal distortion, submitted to strong strain broadening induced by the high level of antisite disorder.

2 XRD and Rietveld refinement

The reference compound $ZnCr_2O_4$ (ZCO) compound (compared for EXAFS pattern in Figure 6 of main paper) was prepared by solid state method by mixing thoroughly the constituents, ZnO and CrO_3, in cation stoichiometric ratio and annealed at 1300°C. The sample was characterized by X-ray diffraction using Cu-Kα radiation in the angular range of 20° to 80°. The diffraction patterns of all compounds were Reietveld refined using FullProf

Table 1: Simulation parameters of powder EPR spectra of Cr-doped ZGO, ZAO and MGO samples.

Sample	$g_x = g_y$	g_z	D (cm^{-1})
d-ZGO	1.976	1.977	0.525±0.002
d-ZAO	1.98(2)	1.97(2)	0.932±0.001
d-MGO	1.99(5)	1.95(5)	0.635±0.001

suite and the data along with calculated patterns and residues are presented in Figure 2. The parameters obtained after refinement are given in Table 2.

3 EXAFS measurements

The parameters obtained from Cr K edge EXAFS fitting of the Cr^{3+} doped ZGO compounds, d-MGO, d-ZAO and ZCO in the k range 3 to 10 $Å^{-1}$ are shown in the Table 3 below.

Zn K edge and Ga K edge EXAFS patterns were fit for d-ZGO, s-ZGO and e-ZGO compounds. The experimental curves along with the fits for one of the compounds d-ZGO are shown in the Figure 3, and the parameters obtained by fitting are tabulated in Table 4.

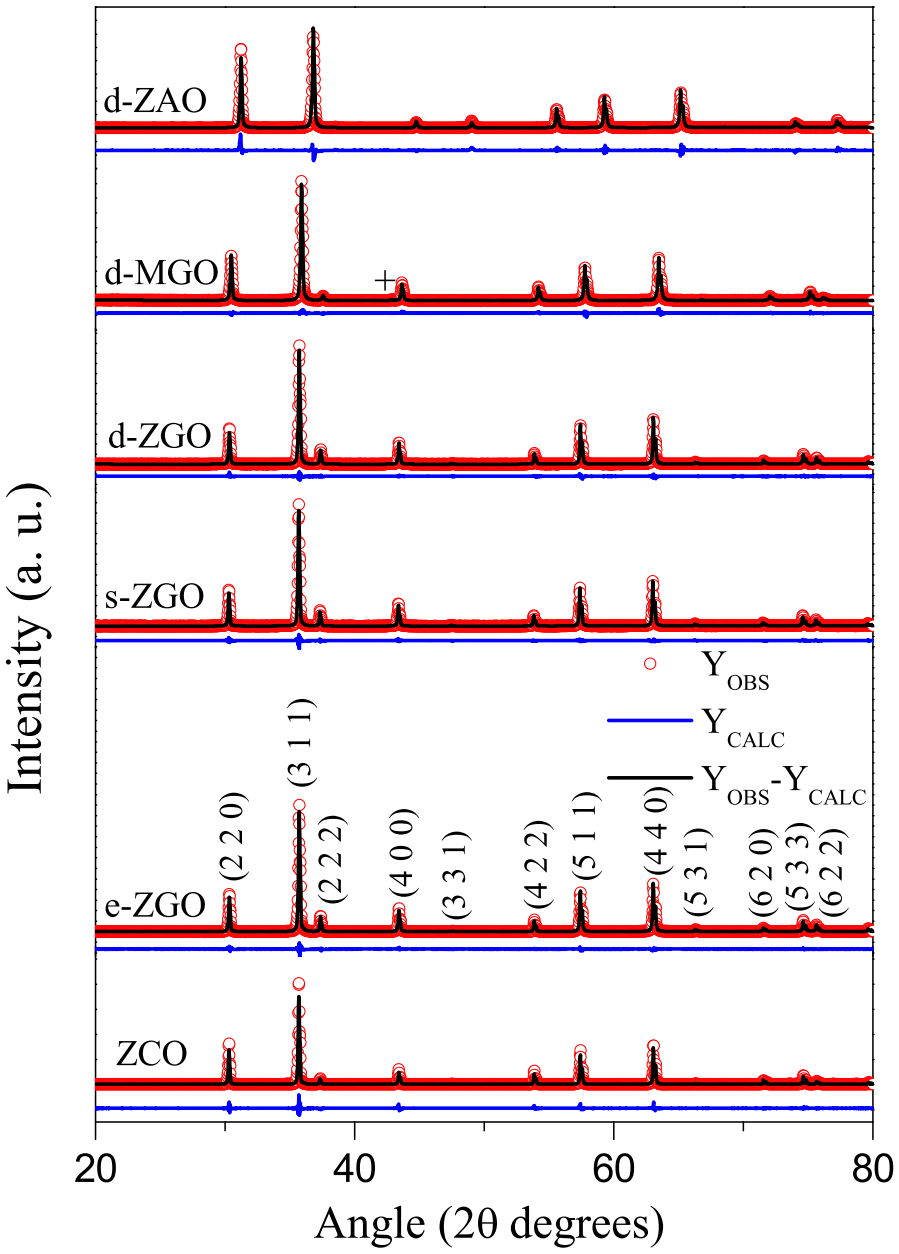

Figure 2: Rietveld refined XRD patterns along with residual patterns (blue lines) for the Cr^{3+} doped ZGO, MGO and ZAO compounds, and for ZCO compound (bottom). The peaks are indexed for e-ZGO compound (JCPDS 38-1240).

Table 2: Parameters obtained from Rietveld refinement of XRD patterns.

Parameters	e-ZGO	s-ZGO	d-ZGO	d-MGO	d-ZAO	ZCO
a (Å)	8.33631(4)	8.33592(4)	8.33291(3)	8.28012(5)	8.09372(6)	8.33075(6)
A site occupancy	0.04207# (Zn)	0.04166# (Zn)	0.04125# (Zn)	0.00423(14) (Mg) 0.03702(14) (Ga)	0.04125* (Zn)	0.04166 (Zn)
B site occupancy	0.08291# (Ga) 0.00042 (Cr)	0.08291# (Ga) 0.00042 (Cr)	0.08291# (Ga) 0.00042 (Cr)	0.04589(14) (Ga) 0.03702(14) (Mg) 0.00042 (Cr)	0.08291* (Al) 0.00042 (Cr)	0.08333 (Cr)
χ^2 (Global)	2.11	1.97	1.86	1.74	3.83	2.17
R_{Bragg}	2.25	2.01	2.74	3.06	7.11	5.78
R_p	9.24	8.83	8.76	9.82	16.5	18.8
R_{wp}	13.6	13.3	12.7	13.8	19.8	25.4
R_e	9.65	9.71	9.61	10.8	10.3	17.8

unrefined occupancies

* d-ZAO pattern was fitted with only normal spinel structure model since an attempt to fit also the inverse spinel model yielded unphysical occupancies.

Table 3: Parameters obtained from fitting Cr K edge EXAFS data in AB_2O_4:Cr^{3+} (A = Zn or Mg, B = Ga or Al) compounds.

Samples	Cr-O			Cr-Ga		Cr-Zn	
	R (Å)	σ^2 (Å^2)	C_3 (Å^3)	R (Å)	σ^2 (Å^2)	R (Å)	σ^2 (Å^2)
e-ZGO	1.94 (2)	0.0014 (6)	0.0004 (2)	2.95 (2)	0.005 (1)	3.42 (5)	0.009 (4)
s-ZGO	1.95 (1)	0.0014 (5)	0.0010 (2)	2.95 (1)	0.004 (1)	3.41 (4)	0.010 (4)
d-ZGO	1.96 (2)	0.0001 (12)	0.0011 (4)	2.95 (3)	0.004 (2)	3.42 (5)	0.004 (3)
d-MGO[1]	2.056 (2)	0.005 (5)		2.93 (1)	0.007 (3)	3.41 (2)	0.005 (4)
d-MGO[2]	1.90 (2)	0.005 (5)		2.90 (2)	0.005 (3)	3.44 (1)	0.007 (3)
d-ZAO	1.992 (4)	0.0026 (7)		2.882 (7)	0.0003 (15)	3.350 (6)	0.0029 (9)
ZCO	1.98 (1)	0.0045 (6)		2.95 (1)*	0.0054 (5)*	3.46 (1)	0.010 (2)

d-MGO[1] refers to normal spinel MGO model and d-MGO[2] refers to inverse spinel MGO model. *Cr-Cr bond length and σ^2 in case of ZCO.

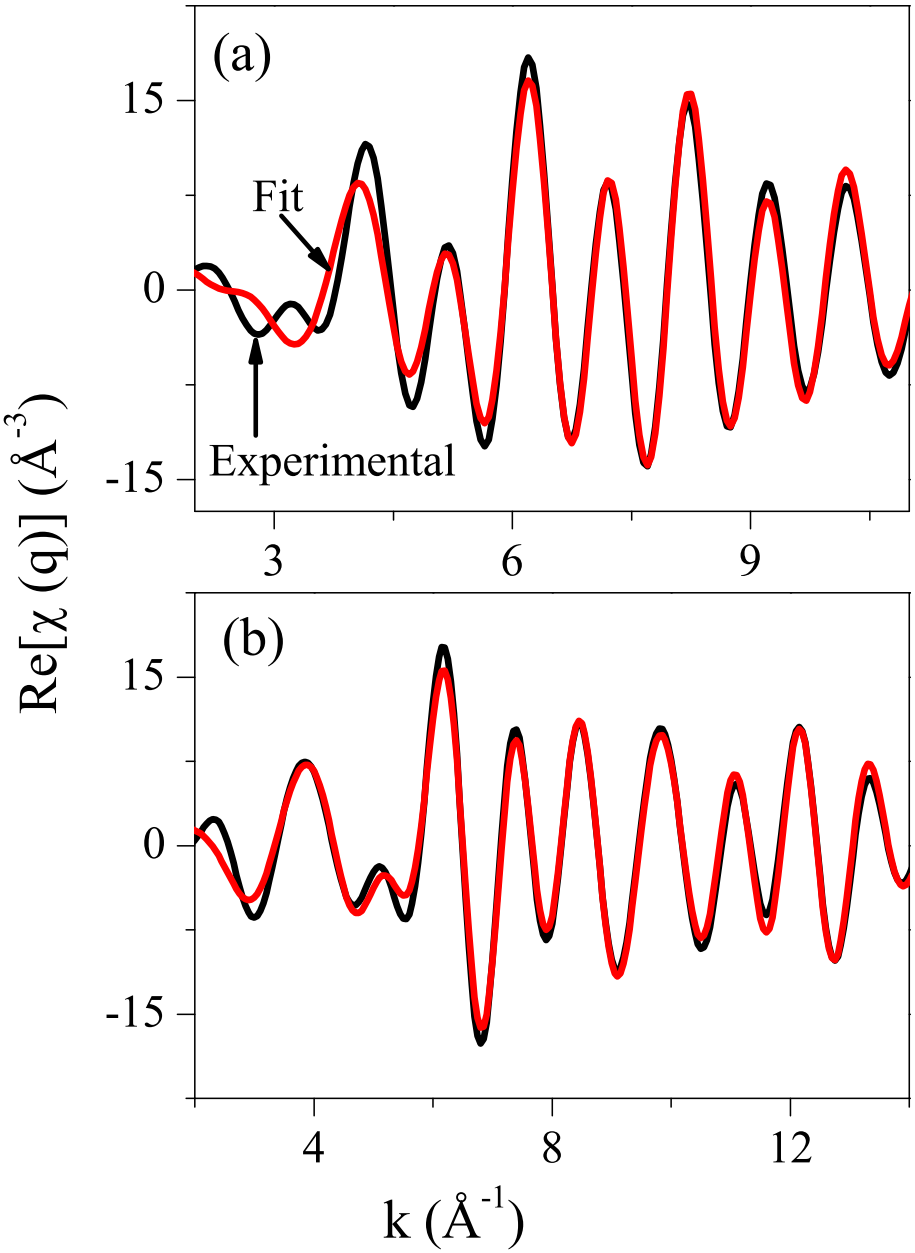

Figure 3: FT magnitude of EXAFS pattern: (a) Zn K edge experimental spectrum along with fit in back transformed k space in k range 2 to 11 Å^{-1}, (b) Ga K edge experimental spectrum along with fit in the k range 2 to 14 Å^{-1} in back transformed k space for d-ZGO compound.

Table 4: Parameters obtained by Zn K edge and Ga K edge EXAFS fitting for the Cr^{3+} doped d-MGO and d-ZAO compounds.

Zn K edge fitting						
Samples	Zn-O		Zn-Ga		Zn-Zn	
	R (Å)	σ^2 (Å^2)	R (Å)	σ^2 (Å^2)	R (Å)	σ^2 (Å^2)
d-ZGO	1.96 (2)	0.005 (5)	3.452(5)	0.0072 (5)	3.572 (6)	0.0027 (9)
s-ZGO	1.97 (2)	0.005 (3)	3.459 (4)	0.0069 (3)	3.586 (5)	0.0034 (7)
e-ZGO	1.97 (2)	0.005 (3)	3.465 (4)	0.0069 (3)	3.591 (5)	0.0038 (7)
Ga K edge fitting						
Samples	Ga-O		Ga-Ga		Ga-Zn	
	R (Å)	σ^2 (Å^2)	R (Å)	σ^2 (Å^2)	R (Å)	σ^2 (Å^2)
d-ZGO	1.981 (8)	0.005 (1)	2.964 (8)	0.0043 (2)	3.45 (2)	0.007 (1)
s-ZGO	1.97 (1)	0.0055 (7)	2.963 (9)	0.0048 (2)	3.458 (9)	0.007 (1)
e-ZGO	1.97 (1)	0.0061 (7)	2.957 (7)	0.0049 (2)	3.464 (8)	0.007 (1)