Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Observation of Dielectric Dispersion and Relaxation Behavior in Ni^{2+} Substituted Cobalt Ferrite Nanoparticles

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Supporting Information

SI.1. Experimental Details

The proposed chemical equation to obtain $Co_{1-x}Ni_xFe_2O_4$ samples can be expressed as:

$$3(1-x)Co(NO_3)_2.6H_2O+3(x)Ni(NO_3)_2.6H_2O+6Fe(NO_3)_3.9H_2O+4C_6H_{12}O_6+4CO(NH_2)_2$$
$$\rightarrow 3Co_{1-x}Ni_xFe_2O_4+16N_2+28CO_2+122H_2O$$

The stoichiometric coefficient (Φ) is referred as the equivalence ratio of oxidizer to fuel is estimated using the following equation.

$$\Phi = \frac{\sum(Coefficient\ of\ oxidizers\ in\ the formula) \times (valency)}{\sum(Coefficient\ of\ reducers\ in\ the\ formula) \times (valency)}$$

The redox mixture is said to be stoichiometric when Φ=1; this is achieved by maintaining the molar ratio of oxidizer to fuel as unity. In the proposed synthesis technique, oxygen is only the oxidizing agent whose valency is considered as -2 ; carbon, hydrogen and metal cations are participated as reducing elements with valencies +4, +1, +3/+2 respectively. The nitrogen valency is treated as zero. By using the above modified concept the valencies of oxidizers is estimated as negative and that of reducers is positive. Oxidizing valency of oxidizers (metal nitrates) is estimated as follows;

$Co(NO_3)_2.6H_2O$ = -10 ; [Co= +2, 2N= 0 , 6O= -12, 12H= +12, 6O= -12]

$Ni(NO_3)_2.6H_2O$ = -10 ; [Ni= +2, 2N= 0, 6O= -12, 12H= +12, 6O= -12]

$Fe(NO_3)_3.9H_2O$ = -15 ; [Fe= +3, 3N= 0, 9O= -12, 18H= +18, 9O= -18]

Here a mixture of urea and glucose is used as fuel for the first time. Reducing valencies of reducers (Fuel) is estimated as follows;

$CO(NH_2)_2$ = +6 ; [C= +4, 4H= 4, 2N= 0, O= -2]

$C_6H_{12}O_6$ = +24 ; [6C= +24, 12H= +12, 6O = -12]

Accordingly, equation (2) Φ is estimated as;

$$\Phi = \frac{[3(1-x)\times(-10)] + [3(x)\times(-10)] + [6\times(-15)]}{[4\times(+24)] + [4\times(+6)]} = \frac{120}{120} = 1$$

When this is the condition, energy released is maximum to complete the synthesis with no carbon residue.

The detailed synthesis procedure and the grade of chemicals used were mentioned elsewhere [23]. Stoichiometry calculations to synthesize (CNF) $Co_{1-x}Ni_xFe_2O_4$; x=0.0, 0.25, 0.5, 0.75 and 1.0 nanoparticles were presented here:

x = 0.0, $CoFe_2O_4$

Weight of fuel for $Fe(NO_3)_3$

Weight of urea =

$$\frac{weight\ of\ Fe(No3)3}{molecular\ weight\ of\ Fe(No3)3} \times \frac{valency\ of\ Fe(No3)3}{valency\ of\ urea} \times molecular\ weight\ of\ urea$$

$$= \frac{4}{404} \times \frac{15}{6} \times 60.06$$

Weight of urea = 1.48663 g

To calculate Co:

2 mol of $Fe(NO_3)_3$= $2 \times 404 = \frac{808}{100}$ = 8.08 g/mol

Molecular weight of $Co(NO_3)_2$= $\frac{291.03}{100}$ = 2.9103 g

$$\frac{8.08}{4} = \frac{2.9103}{?(Co)}$$

$$Co = \frac{4 \times 2.9103}{8.08}$$

Co = 1.44074 g

Weight of fuel for Co = $\frac{weight\ of\ Co(NO_3)_2}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Co(NO_3)_2}{valency\ of\ urea} \times$

$molecular\ weight\ of\ urea$

$$= \frac{1.44074}{291.03} \times \frac{10}{6} \times 60.06$$

Weight of urea for Co = 0.495544 g

Weight of glucose for Fe = $\frac{weight\ of\ Fe(No3)3}{molecular\ weight\ of\ Fe(No3)3} \times \frac{valency\ of\ Fe(No3)3}{valency\ of\ glucose} \times$

$molecular\ weight\ of\ glucose$

$$= \frac{4}{404} \times \frac{15}{24} \times 180.156$$

= 0.11483 g

Weight of glucose for Co = $\frac{weight\ of\ Co(NO_3)_2}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Co(NO_3)_2}{valency\ of\ glucose} \times$

$molecular\ weight\ of\ glucose$

$$= \frac{1.44074}{291.03} \times \frac{10}{24} \times 18_{0.156}$$

Weight of glucose for Co = 0.37161 g

To prepare $CoFe_2O_4$

$Fe(NO_3)_3$ = 4 g

$Co(NO_3)_2$ = 1.44074 g

Urea = (1.48663+0.49554) × 0.5 = 0.991085 g

Glucose = (1.11483+0.37161) × 0.5 = 0.74322 g

x = 0.25, $Co_{0.75}Ni_{0.25}Fe_2O_4$

Weight of fuel for $Fe(NO_3)_3$

Weight of urea = 1.48663 g

To calculate Co

$$\frac{8.08}{4} = \frac{2.9103 \times (0.75)}{?(Co)}$$

$$Co_{0.75} = \frac{4\ X\ 2.9103 \times (0.75)}{8.08}$$

$Co_{0.75}$ = 1.08056 g

Weight of fuel for $Co_{0.75}$ = $\frac{weight\ of\ Co_{0.75}}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Co(NO_3)_2}{valency\ of\ urea} \times$

$molecular\ weight\ of\ urea$

$$= \frac{1.08056}{291.03} \times \frac{10}{6} \times 60.06$$

Weight of urea for $Co_{0.75}$ = 0.6253 g

To calculate $Ni_{0.25}$

$$\frac{8.08}{4} = \frac{2.9079 \times (0.25)}{?(Ni)}$$

$$Ni_{0.25} = \frac{4\ X\ 2.9079\ X\ (0.25)}{8.08}$$

$Ni_{0.25}$ = 0.359889 g

Weight of fuel for $Ni_{0.25}$ = $\frac{weight\ of\ Ni_{0.25}}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Ni(NO_3)_2}{valency\ of\ urea} \times$

$molecular\ weight\ of\ urea$

$$= \frac{0.359889}{290.79} \times \frac{10}{6} \times 60.06$$

Weight of urea for $Ni_{0.25}$ = 0.123886 g

Weight of fuel for $Fe(NO_3)_3$ =1.11483 g

Weight of glucose for $Co_{0.75}$ = $\frac{weight\ of\ Co_{0.075}}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Co(NO_3)_2}{valency\ of\ glucose} \times$

$molecular\ weight\ of\ glucose$

$$= \frac{1.08056}{291.03} \times \frac{10}{24} \times 18_{0.156}$$

Weight of glucose for $Co_{0.75}$ = 0.278707 g

Weight of glucose for $Ni_{0.25}$ = $\frac{weight\ of\ Ni_{0.25}}{molecular\ weight\ of\ Co(NO_3)_2} \times \frac{valency\ of\ Ni(NO_3)_2}{valency\ of\ glucose} \times$

$molecular\ weight\ of\ glucose$

$$= \frac{0.359889}{290.79} \times \frac{10}{24} \times 180.156$$

Weight of glucose for $Ni_{0.25}$ = 0.092902 g

To prepare $Co_{0.75}Ni_{0.25}Fe_2O_4$

$Fe(NO_3)_3$ = 4 g

$Co_{0.75}(NO_3)_2$ = 1.08056 g

$Ni_{0.25}(NO_3)_2$ = 0.359889 g

Urea = (1.48663+0.37166+0.123886) $\times 0.5$ = 0.991085 g

Glucose = (1.11483+0.278707+0.092902) $\times 0.5$ = 0.74322 g

Similarly, the calculations were continued for rest of the compositions and the weight of the precursors to be weighed to synthesize the (CNF) $Co_{1-x}Ni_xFe_2O_4$; x = 0.0, 0.25, 0.5, 0.75 and 1.0 (CNF) nanoparticles is presented in the Table SI-1.

Table SI-1. Amount of precursors used to synthesize $Co_{1-x}Ni_xFe_2O_4$ nanoparticles.

x	$Co(NO_3)_2$ (g)	$Ni(NO_3)_2$ (g)	$Fe(NO_3)_3$ (g)	Fuel (g)
0.0	1.44074	0	4	
0.25	1.08056	0.35988	4	Urea =0.991085

0.5	0.72037	0.71978	4	and
0.75	0.360186	1.07966	4	Glucose=0.74322
1.0	0	1.43955	4	

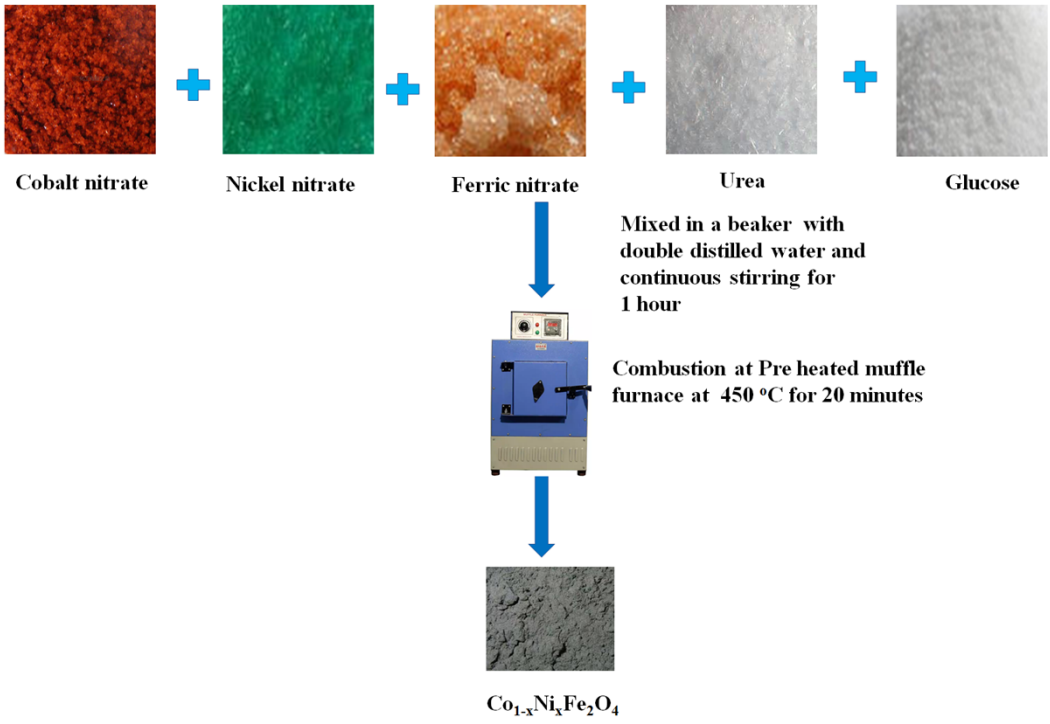


Figure SI-1. Schematic diagram of solution combustion process of $Co_{1-x}Ni_xFe_2O_4$ nanoparticles.

SI.2. Theoretical Details

Table SI-2 shows the related spin distributions together with an acronym, where "FEM" indicates ferromagnetism, "AFM" indicates antiferromagnetism, and "FiM" indicates ferrimagnetism. The primitive 14-atom unit cell was used to reduce the amount of data and simplify the representation. In this case, six atomic positions of inverse spinel structure are occupied by magnetic cations, being the tetrahedral 8a site occupied by Fe^{3+} cations, while both Fe^{3+} and Co/Ni^{2+} cations occupy the octahedral 16d site.

Table SI-2. Investigated Spin States and Their Acronyms.

Atomic positions						***Acronym***
8a			***16d***			
1	**2**	**3**	**4**	**5**	**6**	
↑	↑	↑	↑	↑	↑	FEM
↑	↓	↑	↓	↑	↓	AFM
↓	↓	↑	↑	↑	↑	FiM-1
↑	↑	↓	↓	↑	↑	FiM-2
↑	↑	↑	↑	↓	↓	FiM-3
↑	↑	↑	↓	↑	↓	FiM-4

SI.3. Structural analysis

The **Figure SI.2** presents the polyhedral structure of $Co_{1-x}Ni_xFe_2O_4$ nanoparticles obtained from Rietveld refinement, the interatomic distances, and the bond angles for possible configurations estimated from the equations presented in **Table SI-3**.

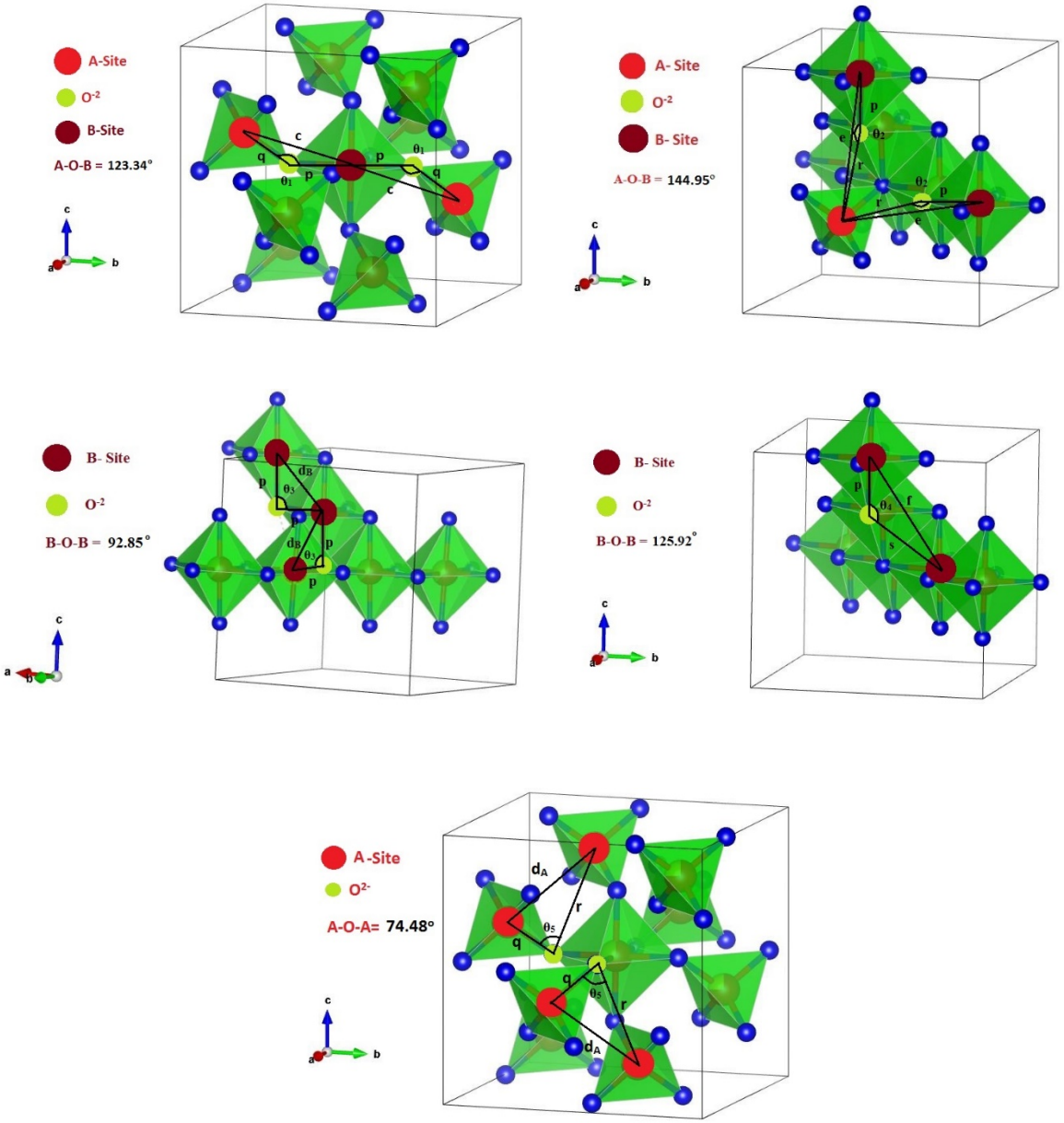


Figure SI.2 Polyhedral structures of $Co_{1-x}Ni_xFe_2O_4$ nanoparticles representing the possible configurations of inter atomic distances and the respective bond angles.

Table SI-3. Equations employed to calculate the interionic bond lengths and bond angles.

Interaction	Interionic distance	Interionic bond angles
A-A	$d = \frac{a\sqrt{3}}{4}$	$\theta_5 = cos^{-1}\left(\frac{r^2 + q^2 - d^2}{2rq}\right)$
B-B	$b = \frac{a\sqrt{2}}{4}$	$\theta_3 = cos^{-1}\left(\frac{2p^2 - b^2}{2p^2}\right)$
	$f = \frac{a\sqrt{6}}{4}$	$\theta_4 = cos^{-1}\left(\frac{p^2 + s^2 - f^2}{2ps}\right)$
A-B	$e = \frac{a3\sqrt{3}}{8}$	$\theta_2 = cos^{-1}\left(\frac{p^2 + r^2 - e^2}{2pr}\right)$
	$c = \frac{a\sqrt{11}}{8}$	$\theta_1 = cos^{-1}\left(\frac{p^2 + q^2 - c^2}{2pq}\right)$
A-O	$q = a\left(u^{43m} - \frac{1}{4}\right)$ $r = a\left(u^{43m} - \frac{1}{4}\right)\sqrt{11}$	$u^{43m} = 0.375$
B-O	$p = a\left(\frac{5}{8} - u^{43m}\right)$ $s = a\left(\frac{u_{43m}}{3} + \frac{1}{8}\right)\sqrt{3}$	

In addition, the DFT/PBE0 optimized lattice parameters and M-O bond distances were estimated as presented in **Table SI-4**.

Table SI-3. Theoretical values for lattice parameters and M-O bond distances (Å)

$Co_{1-x}Ni_xFe_2O_4$	*a*	Fe_{tetra}-O	Fe_{octa}-O	Co-O	Ni-O
x = 0.0	8.436	1.903 (2x) 1.921 (2x)	2.026 (2x) 2.031 (4x)	2.069 (4x) 2.142 (2x)	-
x = 0.25	8.425	1.894 (2x) 1.930 (2x)	2.013 (2x) 2.032 (4x)	2.078 (2x) 2.085 (2x) 2.116 (2x)	2.061 (2x) 2.070 (2x) 2.090 (2x)
x = 0.5	8.414	1.894 (2x) 1.923 (2x)	2.010 (2x) 2.028 (2x) 2.037 (2x)	2.080 (4x) 2.106 (2x)	2.071 (4x) 2.086 (2x)
x = 0.75	8.404	1.892 (2x) 1.927 (1x) 1.932 (1x)	2.008 (2x) 2.030 (2x) 2.035 (2x)	2.091 (4x) 2.094 (2x)	2.071 (4x) 2.085 (2x)
x = 1.0	8.391	1.893 (2x) 1.926 (2x)	2.010 (2x) 2.027 (4x)	-	2.066 (4x) 2.081 (2x)

SI.4. Dielectric analysis

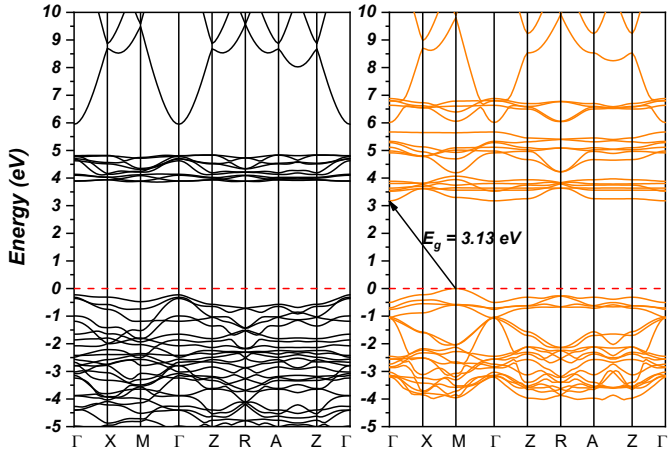
Table SI-4. Electrical parameters of $Co_{1-x}Ni_xFe_2O_4$ (x = 0.0, 0.25, 0.5, 0.75 and 1.0) nanoparticles estimated from impedance spectroscopy.

Concentration ↓ (x)	Frequency ↓ f(Hz)	ε′	tanδ	σ_{ac} (S/cm)
0.0	50	279.27	2.6699	2.07×10^{-8}
	100	209.72	1.9838	2.31×10^{-8}
	1k	102.13	0.7953	4.52×10^{-8}
	10k	49.789	0.6769	1.89×10^{-7}
	100k	16.852	0.5945	7.45×10^{-7}
	1M	9.3082	0.3627	1.88×10^{-6}
	10M	4.3496	0.2165	5.24×10^{-6}
0.25	50	18.245	2.7404	1.39×10^{-9}
	100	15.083	1.8092	1.52×10^{-9}
	1k	9.8321	0.4441	2.43×10^{-9}
	10k	8.2324	0.1185	5.48×10^{-9}
	100k	7.6116	0.0925	3.92×10^{-8}
	1M	5.9763	0.1213	4.03×10^{-7}
	10M	5.5021	0.1711	5.23×10^{-6}
0.5	50	20.458	2.9958	1.70×10^{-9}
	100	17.124	1.9417	1.85×10^{-9}
	1k	10.543	0.5411	3.17×10^{-9}
	10k	8.0427	0.1691	7.64×10^{-9}
	100k	7.2551	0.0545	2.20×10^{-8}
	1M	7.0035	0.0254	9.89×10^{-8}
	10M	6.6415	0.1102	4.07×10^{-6}
0.75	50	31.498	6.6716	5.85×10^{-9}
	100	24.611	4.4963	6.15×10^{-9}
	1k	11.208	1.2924	8.05×10^{-9}
	10k	8.3778	0.2801	1.32×10^{-8}
	100k	7.3616	0.1212	4.96×10^{-8}
	1M	6.1282	0.1721	5.87×10^{-7}
	10M	4.7582	0.2737	7.24×10^{-6}
1.0	50	33.059	5.3578	4.93×10^{-9}
	100	25.944	3.6245	5.23×10^{-9}
	1k	12.356	1.0715	7.39×10^{-9}
	10k	8.9784	0.2557	1.29×10^{-8}
	100k	8.0312	0.0671	3.00×10^{-8}
	1M	7.7243	0.0274	1.18×10^{-7}
	10M	7.3035	0.1266	5.14×10^{-6}

SI.5. Electronic Structure analysis

Figure SI-3. Band Structure profiles for $Co_{1-x}Ni_xFe_2O_4$ models, where a) x 0.0, b) x = 0.25, c) x = 0.5, d) x = 0.75 and e) x = 1.0 indicating the spin-up (black) and spin-down (orange) channels.

a)



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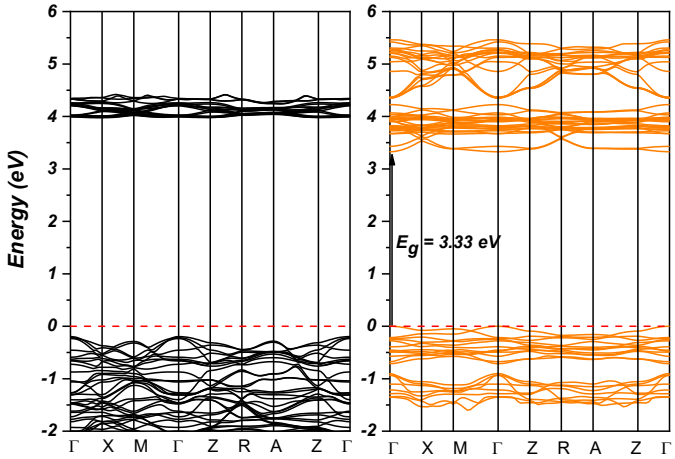

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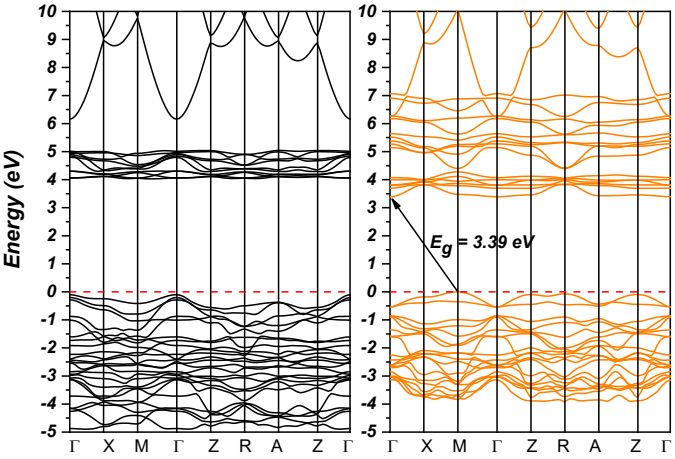

d)

e)