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

Supporting Information

d_{z^2} Orbitals Mediated Bound Magnetic Polarons in Ferromagnetic Ce Doped $BaTiO_3$ Nanoparticles and its Enriched Two Photon Absorption Cross Section

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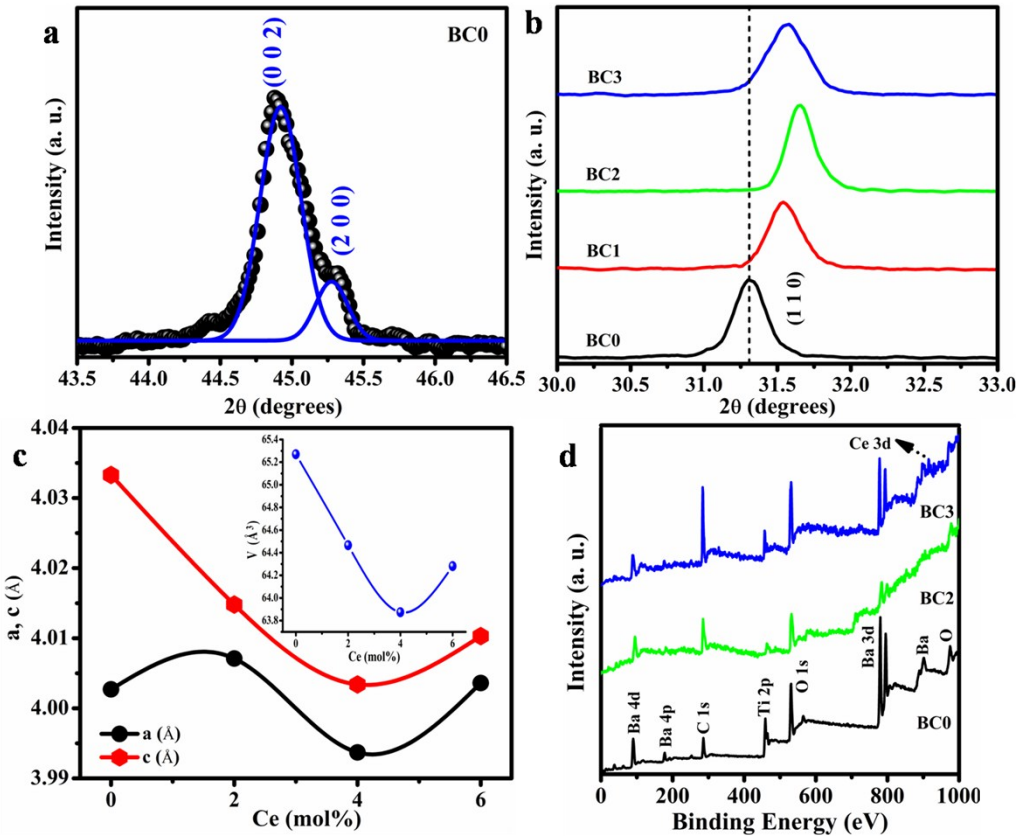

Fig. S1. (a) Appearance of tetragonal (0 0 2) plane with (2 0 0) (b) shifting of prominent (1 1 0) diffraction peak (c) the variation of lattice parameters (*a*, *c* and *V*) as a function Ce concentration (d) XPS survey spectra of pristine and Ce doped BT nanoparticles.

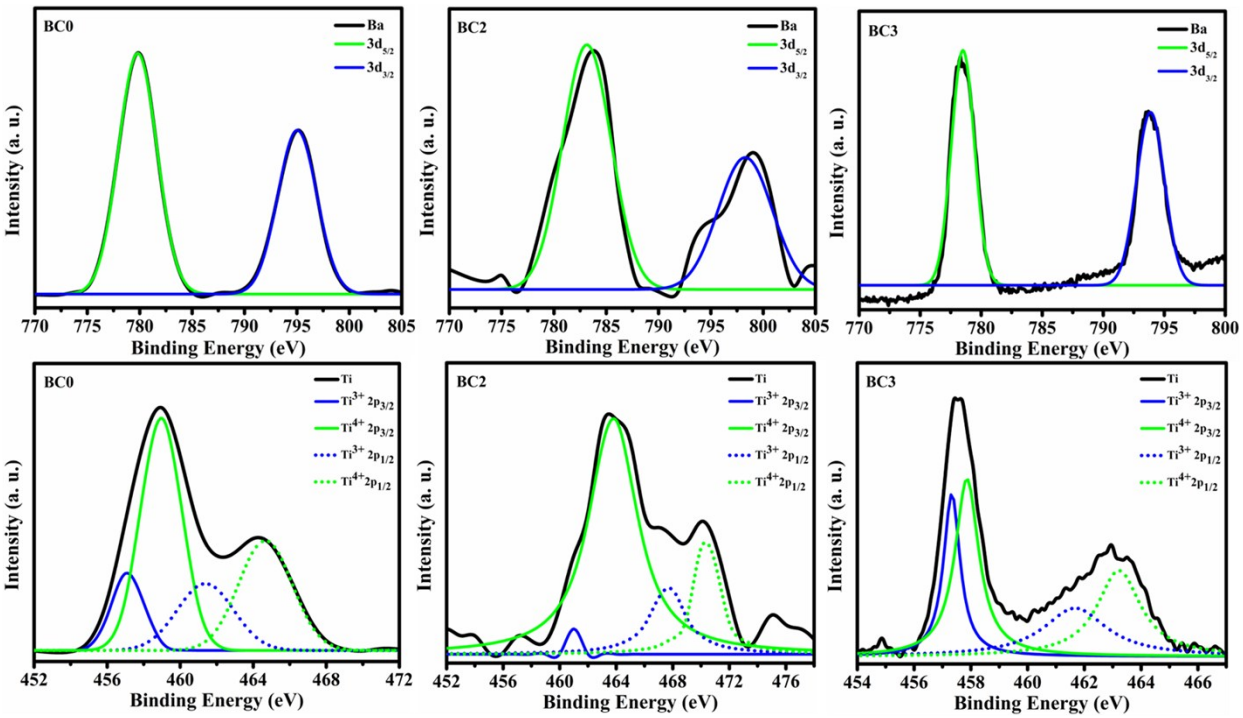

Fig. S2. XPS high resolution scans of Ba-3*d* and Ti-2*p* spectra of BC0, BC2 and BC3 samples.

Sample	Binding Energy (eV)						
	Ti^{4+}		Ti^{3+}		O-1*s*		
	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	L_O	V_O	S_O
BC0	458.9	464.4	457.1	461.4	528.9	530.7	531.9, 534.1
BC2	464.0	470.0	461.0	468.0	530.2	532.2	533.8,535.2
BC3	457.9	463.2	457.3	461.7	528.9	531.4	532.9

Table S1. XPS binding energies of Ti-2*p* and O-1*s* core levels of pristine and Ce doped BT nanoparticles.

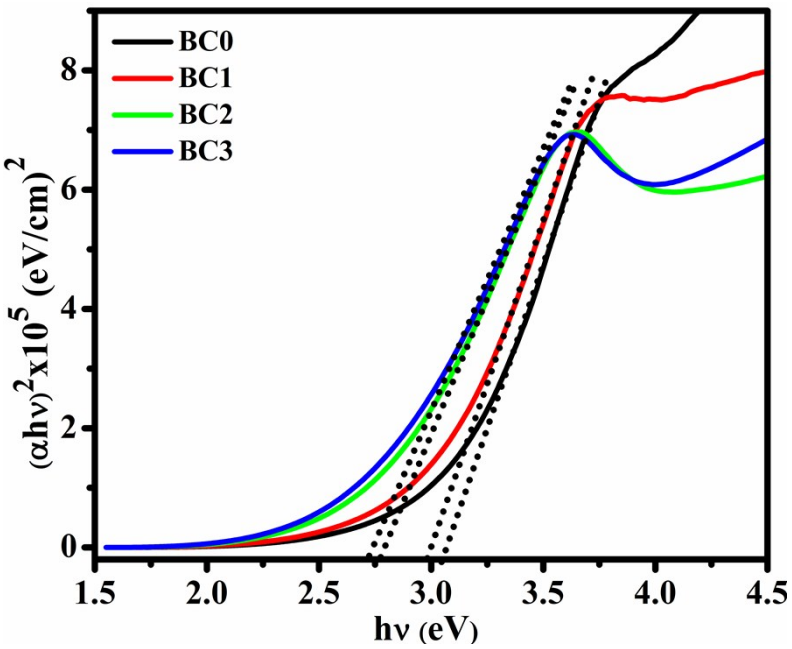

Fig. S3. Tauc plot of pristine and Ce doped BT samples.

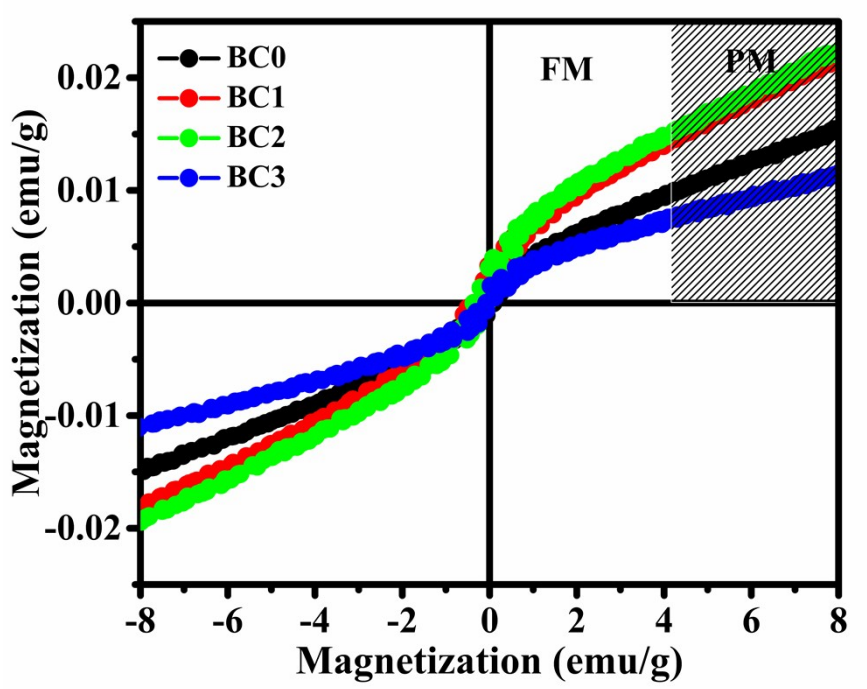

Fig. S4. Room temperature M-H data of pristine and Ce doped BT nanoparticles before the paramagnetic deduction.

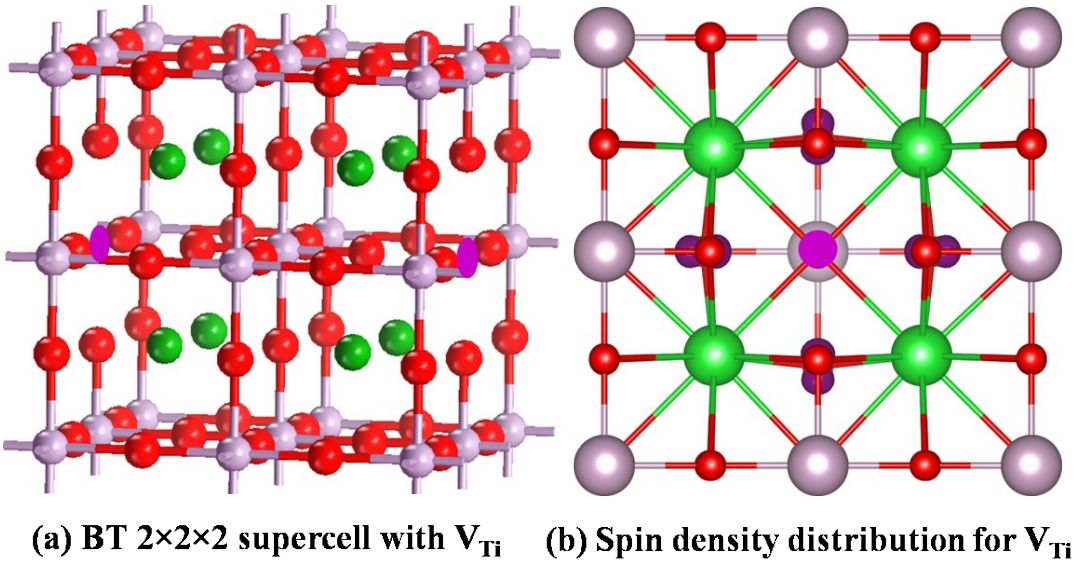

Fig. S5. (a) BT 2×2×2 supercell (spherical balls showing Gray-Ti atoms, Green-Ba atoms, Red-O atoms, Magenta-Ti vacancies) (b) spin density distribution for Ti vacancies (the isosurface value 0.02 e/Å^3).

Optical Nonlinearity Investigations

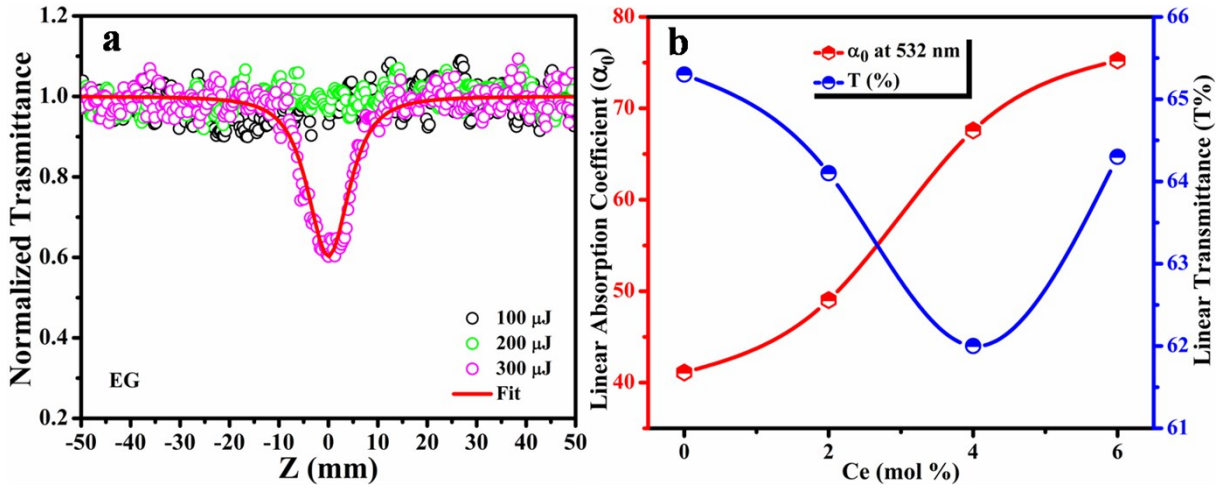

Fig. S6. (a) Open aperture Z-Scan curves of ethylene glycol at different input energies (b) the variation of linear absorption coefficient (α_0) at 532 nm and linear transmittance (T) as a function of Ce concentration.

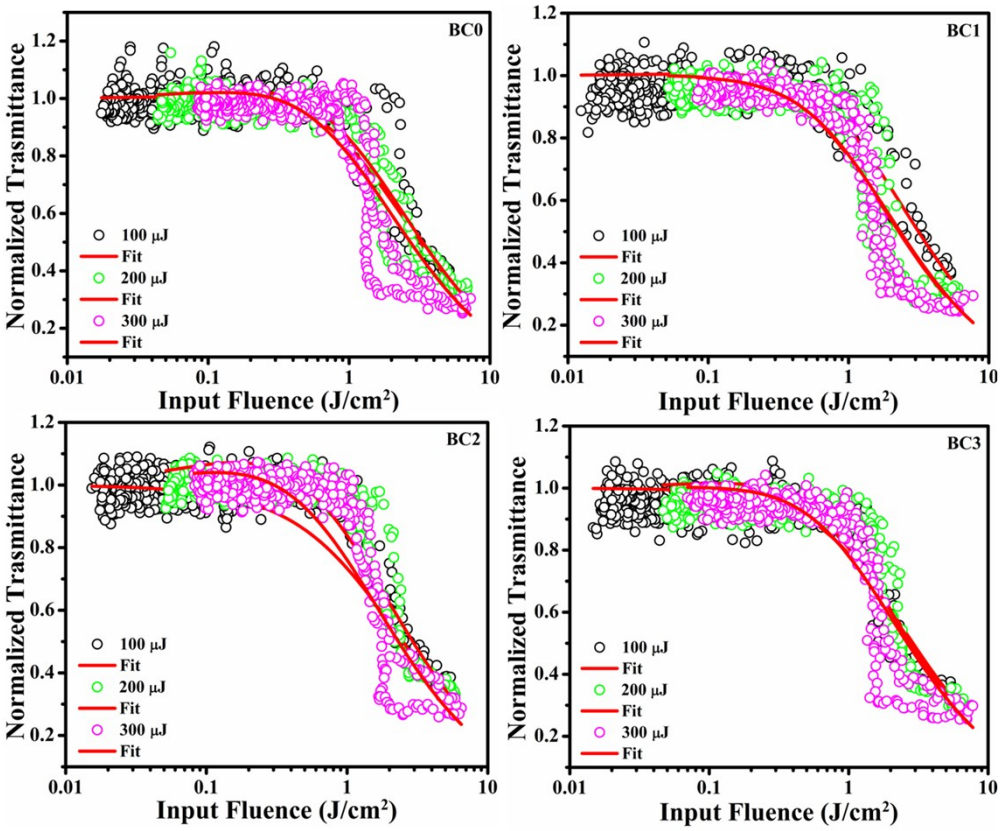

Fig. S7. Optical limiting curves of Ce doped BT nanoparticles at different input energies, spherical balls are experimental data and solid lines are numerical fitting with the nonlinear equations.

The estimation of σ_{TPA}, σ_{GS} and τ,

In the present work, optical absorption of the materials lies between 300 – 600 nm so that the TPA transitions exist under the excitation of 532 nm and the two state rate equations are,

$$\frac{dN_0}{dt} = -\frac{\sigma_{TPA} I^2}{2h\omega_0} N_0 + \frac{1}{\tau} N_1 \qquad (1)$$

$$\frac{dN_1}{dt} = \frac{\sigma_{TPA} I^2}{2h\omega_0} N_0 - \frac{1}{\tau} N_1 \qquad (2)$$

Here, N_0 and N_1 are the ground and excited state carrier density respectively. The total carrier density N is evaluated from,

$$N = \frac{\text{Sample Concentration * Avogadro Number}}{\text{Molecular Weight}} \quad (3)$$

TPA cross section (σ_{TPA}), the ground state absorption cross section (σ_{GS}) and excited state life time (τ) are calculated using the upcoming relations,

$$\sigma_{TPA} = \frac{hc\beta_{TPA}}{N\lambda} \quad (4)$$

$$\sigma_{GS} = \frac{-\log T_0}{NL} \quad (5)$$

$$\tau = \frac{hc}{\lambda \sigma_{GS} I_S} \quad (6)$$

Here, c, λ, T_0 and N are speed of light, wavelength, normalized transmittance in the linear regime and total number of active molecules ($5.939\times10^{17}cm^{-3}$) respectively.

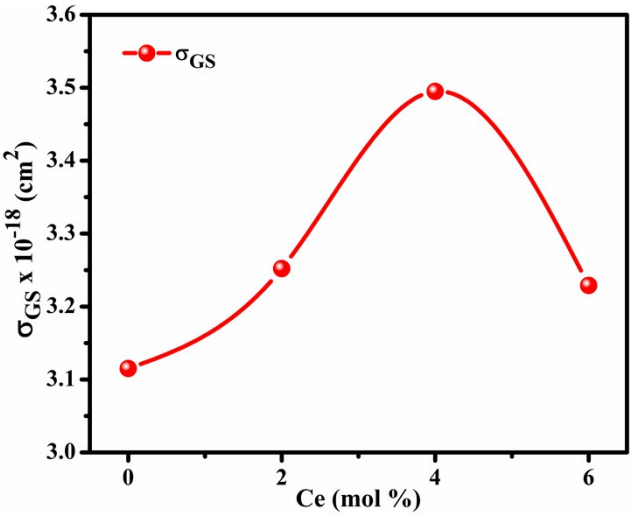

Fig. S8. Ground state absorption cross section (σ_{GS}) as a function of Ce concentration.