Upconversion photoluminescence of Ho$^{3+}$-Yb$^{3+}$ doped barium titanate nanocrystallites: Optical tools for structural phase detection and temperature probing

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Authors have explored the photo-physical properties of Ho$^{3+}$-Yb$^{3+}$ doped BaTiO$_3$ nanocrystals and proposed an intuitive method to probe temperature and crystal phase structure of the matrix. Structural phase change of doped crystals was analyzed in terms of their X-ray diffraction, and it was confirmed through second harmonic generation. We give insights on upconversion of energy of light-emission in Ho$^{3+}$-Yb$^{3+}$: BaTiO$_3$ nanocrystals upon a 980 nm laser-light excitation and subsequently, the excited state dynamics were studied with the help of dependence of upconversion luminescence on excitation power and measuring-temperature. To understand the nature of occupancies of the Ho$^{3+}$ ions at the Ti- and Ba-sites, we performed site-selective, time-resolved spectroscopic measurements at various crystal phases. Based on the lifetime analysis, it is inferred that the Ho$^{3+}$ ions are present at two types of sites in barium titanate lattice. One of those is the 6-coordinated Ti-site of low symmetry, while the other one is the 12-coordinated Ba-site of higher symmetry. The upconversion emission of the nanocrystals are found to be temperature-sensitive (12 to 300 K), indicating possible use as a self-referenced temperature probe. An analysis of the temperature dependent emissions from $^5$F$_4$ and $^5$S$_2$ levels of Ho$^{3+}$ ions, gives a maximum value of temperature sensitivity ~ 0.0095 K$^{-1}$ at 12 K. Furthermore, we observe a sharp change in the luminescence intensity at ~180 K due to a ferroelectric phase change of the sample. The correlation of upconversion luminescence with the results of X-ray diffraction and second harmonic generation at different crystal phases implies that the frequency upconversion may be used as a probe of structural change of the lattice.

Ferroelectric titanates of a perovskite ABO$_3$ structure (where A and B are usually divalent and tetravalent cations, respectively) are widely used in many applications due to their excellent dielectric, magnetic and electro-optic properties$^{1-4}$. In general, a perfect perovskite has a cubic unit cell of a simple crystal structure of a CaTiO$_3$-mineral perovskite. Here, the tolerance factor ($T_f$) governs the nature of distortions from its ideal shape, e.g., a rhombohedral or an orthorhombic GdFeO$_3$-type crystal structure is observed on effectively small $T_f \leq 1$, while polytypic structures turn up at $T_f > 1$. The wide range of physical properties of ABO$_3$-type oxides are mainly dependent on the relative sizes of the ions, electronic configuration of the ions, dopants and substituents$^5,6$. For example, Pandey et al. have investigated structure and electronic/magnetic properties of such oxides BiFeO$_3$ – PbTiO$_3$, BiFeO$_3$-BaTiO$_3$, etc. in this series$^{7,8}$. Small ABO$_3$ crystallites are particularly used in liquefied petroleum gas sensing and humidity sensing$^9-12$. Further, barium titanate (BaTiO$_3$) is an important nonlinear optical material which has numerous applications in light modulation, optical memory storage, optical switching and electro-optic phase modulator$^{13-16}$. Additionally, the high photorefractive sensitivity of barium titanate is beneficial for photonic applications$^{15,16}$. Relation between phase transition and crystallite size of BaTiO$_3$ is studied in many theoretical and experimental works$^{17-20}$, which show that five phases, namely, rhombohedral, orthorhombic, tetragonal, cubic and hexagonal.

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appear at different temperatures. A low temperature phase change is reported at ~183 K \(^{31}\). Considering radius of a rare-earth ion \(\text{R}^{3+}\) is within Ba\(^{2+}\) (1.35 Å) and Ti\(^{4+}\) (0.68 Å), the Ba\(^{2+}\) -site (A-site) is preferred to be occupied by a larger \(\text{R}^{3+}\) such as Nd\(^{3+}\) (1.08 Å) and La\(^{3+}\) (1.15 Å), while the intermediate ones such as Er\(^{3+}\) (0.89 Å) and Ho\(^{3+}\) (0.90 Å) may replace both the A- and B- sites \(^{22,23}\). Ba\(\text{TiO}_3\) is a good optical host suitable for doping \(\text{R}^{3+}\) ions due to its low phonon cut-off frequency with excellent chemical and mechanical stability, which suits for upconversion luminescence. On the other hand, upconversion luminescence is an optical non-linear anti-Stokes process, which features conversion of low energy photons into high energy by utilizing the quantum mechanically forbidden 4\(f\rightarrow 4f\) optical transitions of \(\text{R}^{3+}\) ions while doped in crystallite host materials\(^{34-37}\). Over the past decade, researchers have shown extensive range of advanced applications of upconversion nanoparticles, spanning from background noise-free biological imaging, theranostics, drug-delivery to photo-voltaic devices, and photochemical reactions\(^{38-39}\). To date, several excellent reviews on \(\text{R}^{3+}\) doped upconversion luminescence have been published to summarize the progress in this field along with demonstration of advanced applications\(^{40,43}\). The long-lived intermediate energy levels of the \(\text{R}^{3+}\) ions are favorable to achieve unique upconversion emission. The electronic transitions within a 4\(p\) shell of \(\text{R}^{3+}\) ions greatly rely upon their site-symmetry in the crystal lattice of the host materials due to the difference in sensitivity to the crystal field. Therefore, the \(\text{R}^{3+}\) ions and their positions in different crystal structures may give distinct photoluminescence properties, and thus the knowledge of crystal structure of a given material may be realized by analyzing its luminescence behavior. Despite this interest, the explanation on the site symmetry of \(\text{R}^{3+}\) ions in \(\text{BaTiO}_3\) through luminescence measurements and the effect of phase transition on upconversion properties have not been studied in depth. Recently, the phase transition induced by high pressure in \(\text{Eu}^{3+}\) : \(\text{Bi}_2\text{WO}_6\) was investigated by Maczka \textit{et al.} by utilizing the variation of emission intensity in downconversion luminescence measurements of \(\text{Eu}^{3+}\) ions\(^{8}\). Here, \(\text{Bi}_2\text{WO}_6\) undergoes two phase transitions near 3.4 and 6.2 GPa pressure what is clearly reflects in the \(\text{Eu}^{3+}\) light-emission. In a separate study, Yao \textit{et al.} \(^{22}\) measured luminescence properties in the transition of phase structure of \(\text{Er}^{3+}\) doped \(\text{Pb(Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)-\text{PbTiO}_3\) from a rhombohedral to a morphotropic phase boundary, consecutively to a tetragonal phase on increasing \(\text{PbTiO}_3\) content in this example. However, none of the earlier studies\(^{26-28}\) has taken into consideration studying such materials as a structural probe, and a major concern is that the basic luminescence properties in terms of excited state dynamics at steady-state or time-resolved mode with the crystal phase transition have not been addressed so far.

In this work, we report on the comprehensive upconversion properties of \(\text{Ho}^{3+}\)-Yb\(^{3+}\) : \(\text{BaTiO}_3\) nanocrystals. We have further characterized the structural phases by using not only the X-ray diffraction (XRD) patterns but also second harmonic generation (SHG). The temperature dependent population variation of \(\text{T}_4\) and \(\text{S}_2\), \(\text{Ho}^{3+}\)-levels has been employed for phosphorescence intensity ratio based low-temperature thermometry. The variation of site-occupancy of \(\text{Ho}^{3+}\) ions in \(\text{BaTiO}_3\) of different phases is also investigated based on time-resolved spectroscopic analysis. This study suggests a general approach for sensibly probing crystal phase of this compound.

### Results and Discussion

#### Structural properties.

The \(\text{Ho}^{3+}\)-Yb\(^{3+}\) doped \(\text{BaTiO}_3\) samples, prepared by a wet-chemical precipitation method (\textit{Methods and analyses}), were annealed at three different temperatures 873, 1173 and 1473 K for 6h and were abbreviated as c-BT (cubic) q-BT (quasi-cubic) and t-BT (tetragonal), respectively, according to their XRD patterns. Figure 1(a) presents the XRD patterns of c-BT, q-BT and t-BT of \(\text{Ho}^{3+}\)-Yb\(^{3+}\) doped \(\text{BaTiO}_3\). Following their positions and relative intensities, the individual XRD peaks can be indexed as in the standard cards (ICDD card no. 75-0461) for c- and t-Ba\(\text{TiO}_3\) structures\(^{39-41}\). The c-Ba\(\text{TiO}_3\) structure with the \(\text{Pm}3\text{m}\) space group gives lattice parameters \(a = 4.013 \text{ Å}\), while the t-BT sample with space group \(\text{P4mm}\) gives \(a = 3.994 \text{ Å}\) and \(c = 4.022 \text{ Å}\). Tsur \textit{et al.}\(^{22,23}\) have reported that \(\text{Ho}^{3+}\) can occupy both A-site or B-site (known as amphoteric behavior), whereas Yb\(^{3+}\) occupies B-site mainly because of its better stability in this site in \(\text{BaTiO}_3\). They have considered thermodynamics and \(\text{T}_4\) value to predict the \(\text{R}^{3+}\) occupancy in perovskites. An average crystallite size calculated by a well-known Scherrer formula\(^{42}\) was found to be 33, 39 and 54 nm (with an error bar \(\pm 3 \text{ nm}\) for the c-BT, q-BT and t-BT specimens, respectively. The patterns reveal that an increasing calcination temperature is promoting average crystallite size in a thermally promoted growth of small crystallites. The size of c-phase increased from 33 to 39 nm as the calcination temperature was raised from 873 K to 1173 K. The t-phase exhibits increased from 45.19° and 2\(\theta\) \(\approx 45.51°\) in (200) and (002) planes of \(\text{Ho}^{3+}\)-doped \(\text{BaTiO}_3\). The specimen prepared at 1173 K owes the onset of t-phase formation. Looking closely to these two peaks, one can readily ascertain the existence of two phases in the q-BT. It is believed that as a result of cell elongation in the c-axis due to a ferroelectric transition at high temperature, the t-phase reforms over the c-phase. Co-existence of crystal phases in a similar perovskite material- barium titanate stannate was reported by Mueller \textit{et al.}\(^8\) and the phenomenon was interpreted in terms of mechanically clamped c- and t-phases. A phase transition \(c \rightarrow t\)-Ba\(\text{TiO}_3\) in a similar range of calcining temperature was reported by Sengodan \textit{et al.}\(^{41}\).

An analysis of XRD patterns on evolution of cubic, quasi-cubic and tetragonal lattice parameters with annealing temperature reveals due shifts in peak positions towards lower 2\(\theta\) values. This results in a noticeable change of the unit cell volume as sintering temperature is increased from 873 K to 1473 K. What’s more, the effect of annealing temperature on the Ba\(\text{TiO}_3\) lattice is reflected in the ratio of their lattice parameters (Fig. 1c). The tetragonality
in terms of $c/a$ ratio for the three samples - c-BT, q-BT and t-BT are calculated as 1, 1.005 and 1.007, unveiling intriguing correlation of increase in $c/a$ ratio with lattice expansion$^{44}$. The evolution of crystallite size of Ho$^{3+}$-Yb$^{3+}$:BaTiO$_3$ with annealing temperature is shown in Figure S1. It increases with increasing annealing temperature. Scanning electron microscopic (SEM) images (Figure S1) reveals that the small crystallites are joined one another in small assemblies. The results are similar to those of Er$^{3+}$-Yb$^{3+}$ doped BaTiO$_3$ synthesized using the same procedure in our earlier study$^{16}$. The energy-dispersive X-ray spectra for t-BT and c-BT are shown in Figure S2.

Optical properties. The optical absorption spectrum (Figure S3) of Ho$^{3+}$-Yb$^{3+}$:BaTiO$_3$ powder in diffuse reflection mode shows a strong absorption in the Stark components of $^2F_{7/2}$ level of Yb$^{3+}$ ions at around 980 nm. The other R$^{3+}$ absorption bands at 524, 655 and 800 nm are attributed to $^5F_4$ $^5S_2$ $\leftarrow$ $^5I_8$, $^5F_5$ $\leftarrow$ $^5I_8$ and $^5I_5$ $\leftarrow$ $^5I_8$ transitions of Ho$^{3+}$ ions. Upon 980 nm laser-light excitation, the t-BT exhibits intense green (538 and 548 nm) and red (655 nm) frequency upconversions in the $^5F_4$ $^5S_2$ $\leftarrow$ $^5I_8$ and $^5F_5$ $\leftarrow$ $^5I_8$ transitions, respectively, as shown in Fig. 2a and Figure S4. More details of mechanisms on the upconversion processes and photophysical pathways involved here are provided in the Supplementary Information.

Laser pulse energy dependent upconversion properties. In order to unravel the nature of upconversion processes, i.e., the number of photons involved in a particular transition in the upconversion emission, the pump power dependent upconversion (Figure S5a) was studied in a simplified model. As known from theoretical analysis, the slope of the logarithmic plot of pump power vs. intensity accounts the number of photons participated in a particular upconversion process$^{45}$. In addition, to understand the mechanism and illustrate the experimental findings in Ho$^{3+}$-Yb$^{3+}$ doped BaTiO$_3$, the population mechanism of $^5F_4$, $^5S_2$ and $^5F_5$ levels have been inevitably established by solving the steady-state rate equations at an unsaturated stage of population of the ions. In the present case, the absorption cross-section of Yb$^{3+}$ ions at 980 nm is much higher over the Ho$^{3+}$ value$^{28}$. Therefore, the steady-state rate equations of Ho$^{3+}$-Yb$^{3+}$ in BaTiO$_3$, according to Fig. 2b can be set as follows:

$$\frac{dN_{Ho,1}}{dt} = 0 = W_2 N_{Ho,2} + W_{11} N_{Ho,5} - W_{11} N_{Ho,1} - \rho_{p} \sigma_{t} N_{Ho,1} - K_{p} N_{Ho,1} N_{Yb,1} + W' N_{Ho,3} N_{Yb,0}$$

(1)

$$\frac{dN_{Ho,0}}{dt} = 0 = K_{p} N_{Ho,0} N_{Yb,1} + \rho_{p} \sigma_{t} N_{Ho,0} - W_{2} N_{Ho,2} - K_{p} N_{Ho,2} N_{Yb,1} - \rho_{p} \sigma_{t} N_{Ho,2}$$

(2)

Figure 1. (a) XRD patterns of Ho$^{3+}$-Yb$^{3+}$:BaTiO$_3$ synthesized at 873 K (c-BT), 1173 K (q-BT) and 1473 K (t-BT), (b) magnified XRD peaks around $2\theta$ = 45.71°, and (c) variation of lattice parameters with increasing processing temperature, with a c $\rightarrow$ t-phase transition.
where, $N_{Ho,i}$ ($i = 0, 1, 2, 3, 4, 5$) are the density of population of the levels $5I_{8}, 5I_{7}, 5I_{6}, 5I_{4}, 5F_{5}$ and $5F_{4}/5S_{2}$, respectively. The population densities of $2F_{5/2}$ (ground state) and $2F_{7/2}$ (excited state) of Yb$^{3+}$ ions are expressed as $N_{Yb,i}$ ($i = 0, 1$). $W_{1}, W_{2}, W_{4}$ and $W_{5}$ are the non-radiative decay rates of $5I_{7}, 5I_{6}, 5F_{5}$ and $5F_{4}/5S_{2}$ levels, while the radiative decay rates for the red, green and NIR emissions are expressed as $W'_{red}, W'_{green}$ and $W'_{NIR}$ from the levels $5F_{2}$ and $5F_{4}/5S_{2}$. The decay rates of Yb$^{3+}$ ions' $2F_{5/2} \rightarrow 2F_{7/2}$ is $W_{Yb}$, while the energy transfer (ET) rates to Ho$^{3+}$ are $K_{1}, K_{2}$ and $K_{3}$ corresponding to ET-1, ET-2, ET-3, respectively, as shown in Fig. 2b. The energy back transfer (EBT) from Ho$^{3+}$ to Yb$^{3+}$ is indicated by using $W_{EBT}$ as an energy back transfer rate. The absorption cross-section of Ho$^{3+}$ (between ‘i’ and ‘j’) and Yb$^{3+}$ (between $2F_{5/2}$ and $2F_{7/2}$) are represented by $\sigma_{ij}$ and $\sigma_{Yb}$, respectively, and the laser pump constant is $\rho_{P}$, which is dependent on incident pumping energy. The Eqs. (1) and (3) are associated with red upconversion emission, while the green upconversion emission is correlated with Eqs. (2) and (4). The frequency upconversion of Ho$^{3+}$-Yb$^{3+}$ is relatively cumbersome due to the involvement of the Ho$^{3+}$ to Yb$^{3+}$ back energy-transfer followed by emission from Yb$^{3+}$. Therefore, the challenges in solving the rate equations are realized by neglecting the less impact terms in the equations. Since the Yb$^{3+}$ ions have much higher absorption cross-section at 980 nm than the Ho$^{3+}$ ions, the terms corresponding to ground state absorption (GSA) and excited state absorption (ESA) can be ruled out. In view of the fast multi-phonon relaxation between $5I_{4}$ and $5I_{5}$ levels, the $5I_{4}$ level can be considered as a short-lived level.

When the excitation pulse energy is low, the spontaneous decay of Ho$^{3+}$ ions at the levels $5I_{6}$ and $5I_{7}$ are dominant through the energy-transfer processes ET-2 and ET-3. As a consequence, the relevant terms from Eqs. (2) and (1) can be omitted. Furthermore, the EBT is insignificant compared to the direct photon absorption of 980 nm wavelength by the Yb$^{3+}$ ions ($2F_{7/2}$ to $2F_{5/2}$), allowing us to neglect the relevant term of EBT. From Eq. (3), we get,
structure in a solid material. The local $R_3$ wherein the XRD patterns and infrared bands did not indicate countable difference among the samples.

creation of charge carriers in c-BT, q-BT and t-BT can be responsible for the tailored upconversion emission, emission, the maximum emission intensity is noted for the t-BT phase. Effects of grain-growth and elimination/Interestingly, the red emission is decreased in intensity over the green one (Figure S6a). In view of the overall material extensively at various measuring-temperatures, as discussed as follows.

This type of variation is usually attributed to laser induced heating of the material, which led us to investigate the version spectra (Fig. 3) show largely enhanced upconversion emission intensity in the c
light excited frequency upconversion emission properties in its different crystal phases. The comparative upconversion of energy of its light emission. Electronic transitions of the R3
variants of tailored light-emission in terms of a tailored local LaVO4:Er3 counterpart monoclinic phase, which is evidently due to a difference in the local structure. They have interpreted the origin of tailored light-emission in terms of a tailored local LaVO4:Er3 structure. Not many reports are available on the upconversion emission in a phase transition suitable to compare these results more meticulously in terms of tailored charge carriers. Qualitatively, as the structure symmetry decreases in the t-BaTiO3, the Ho3+ doped sites acquire a larger perturbation field, which in turn arise in an enhanced electronic transition probability in the form of a duly enhanced light emission as observed in this example.

In accordance to the previous section- the solutions of the rate equations at low pump power (LP) and high pump power (HP), the ratios of Eqs. (7) to (8) and Eqs. (9) to (10) can be presented as

$$\frac{I_G}{I_K} \bigg|_{LP} = \frac{W_3N_{Ho,5}}{W_4N_{Ho,4}} = \frac{W_5}{W_4} \left(1 + \frac{W_4}{W_5} \right).$$

(11)
In this scenario, a considerable phenomenon is that the Ho$^{3+}$ ions at the $5F_{4}/5S_{2}$ levels depopulate radiatively at the $5I_{8}$ and $5I_{7}$ levels, producing the green and NIR emission bands and the branching ratio for these two emissions is a significant factor accounting in their intensities. In this context, we have calculated the ratio of green to NIR emission for the three specimens (Figure S6b), which reflects that the intensity increasing in both the emission bands almost linearly and, therefore, branching of Ho$^{3+}$ ions' populations at the $5F_{4}/5S_{2}$ level is not responsible for a change in a ratio of green to red emission band ($I_{G}/I_{R}$). Thus, based on the results illustrated in the rate equation model, an increased $I_{G}/I_{R}$ ratio could be due to several combined effects (i) a decrease of non-radiative decay from $5F_{4}/5S_{2}$ to $5F_{5}$, (ii) an increase of non-radiative decay from $5F_{5}$ to $5I_{4}$ in a $c \rightarrow t$-BaTiO$_3$ phase transition, and (iii) an induced crystal field on the Ho$^{3+}$ doped sites.

**Effect of temperature on upconversion emission and temperature sensing.** In order to understand the Ho$^{3+}$-Yb$^{3+}$:BaTiO$_3$ properties at temperatures below room temperature, we have further investigated the upconversion emission as a function of temperature over 12 to 300 K (Fig. 4a). The emission intensity is increased by a large amount at low temperatures due to a deactivation of non-radiative channels. A closer observation of intensities of green and red emissions at selective temperatures reveals that at ~ 180 K, there is a sharp jump in their values, as shown in Figure S7. This abnormal intensity change in these upconversion emission bands at this specific temperature could be associated to a structural change in BaTiO$_3$ with its ferroelectric phase transition and Ho$^{3+}$ crystal field symmetry is altered in the transition. Recently, Zuo and coworkers$^{48}$ have reported a similar investigation of Er$^{3+}$-emission intensity change at Curie transition temperature (395 K) of the BaTiO$_3$ matrix. Figure S7 also illustrates that the upconversion emission from $3F_{4}$ (538 nm) level is notably suppressed, while it is increased remarkably from the $5S_{2}$ (548 nm) level. The $3F_{4}$ state is quenched thermally to $5S_{2}$ what is it contributes an enhanced $5S_{2} \rightarrow 5I_{4}$ emission on cooling the sample. Alternatively, as the temperature increases, the intensities of 538 nm and 548 nm bands tend to be equal at ~ 260 K (Figure S7) and it anticipates that at higher temperature ($\geq$ 300 K), the 538 nm band will be starting raising its intensity on hot phonons, which help to populate Ho$^{3+}$ ions in the $3F_{4}$ level from the $5S_{2}$ level. However, the ratio 538 nm/548 nm (Fig. 4b) is not affected due to the phase transition, which infers that the influence of thermal quenching is more effective than that of the phase transition for the $3F_{4}/5S_{2}$ levels. Additionally, the temperature dependent emissions from $3F_{4}$ and $5S_{2}$ levels reflect that this material could be utilized for non-contact thermometry. Therefore, to investigate its temperature sensing ability, its temperature dependent upconversion emission spectra were inspected over 12 K to 300 K. The $3F_{4}$ and $5S_{2}$ levels of Ho$^{3+}$ are closely located so as to thermally exchange couple each other. Thus, the variations of relative intensities of these bands were studied at different temperatures. It is observed that the overall intensity increases as the sample cools down with no any shift in the two bands. The ratio of intensities of 538 nm and 548 nm emission bands is seen to be increasing in the sample warming from 12 K to 300 K. The variation of relative intensities of these two emission bands at different temperatures was calculated and the graph is shown in Fig. 4b.

The fluorescence intensity ratio (FIR) of the two bands can be written as$^{49,50}$,

$$\frac{I_{G}}{I_{R}}_{up} = \frac{W_{5}}{W_{5} + W_{5I_{8}}} \left[ 1 + \frac{W_{5}}{W_{4}} \right].$$

(12)
Figure 4. (a) Temperature dependent upconversion spectra of t-BT, (b) plot of ln(FIR) against temperature, and (c) variation of absolute sensitivity with temperature.

\[ F I R = \frac{I_{538}}{I_{548}} = B \exp \left( \frac{\Delta E}{kT} \right), \]  

where, \( I_{538} \) and \( I_{548} \) are the integrated intensities corresponding to the \( ^5F_4 \rightarrow ^5I_8 \) and \( ^5S_2 \rightarrow ^5I_8 \) transitions, respectively; \( B \) is dependent on radiative probabilities, degeneracies and emitted photon energies of the associated levels; \( \Delta E \) is the energy gap between the \(^5F_4\) and \(^5S_2\) levels; \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Figure 4b shows the variation of FIR with temperature. The fitting of experimental data according to Eq. (13), gives \( B = 0.75 \pm 0.01 \) and \( \Delta E = 120 \pm 10 \text{ cm}^{-1} \).

Being an important parameter of sensor materials, the sensitivity (absolute) has been calculated as the rate of change of FIR with temperature and can be described as:\(^{51,52}\)

\[ S = \frac{\partial (\text{FIR})}{\partial T} = \text{FIR} \times \frac{\Delta E}{kT^2}, \]

where all the terms have their usual meanings as defined in Eq. (13). The values of FIR and \( \Delta E \) as obtained above were used to calculate the S-value. The sensor sensitivity, as presented in Fig. 4c as a function of temperature, confirms that the sensitivity of the material is reasonably good and it decreases rapidly as temperature rises towards room temperature. A maximum value of \( S \approx 0.0095 \text{ K}^{-1} \) is thus found at 12 K, which is decreased to 0.0002 K\(^{-1}\) at 300 K. Eventually, the material is very well sensitive to temperature especially at low temperatures. A similar trend of thermal S variation was observed for YVO\(_4\):Ho\(^{3+}\)/Yb\(^{3+}\) as on excited by an ultraviolet light of 266 nm wavelength in our recent studies\(^ {28}\).  

Site-selective and phase dependent time-resolved luminescence. In 1965, a preliminary report\(^ {53}\) on emission spectra of Sm\(^{3+}\) in BaTiO\(_3\) had described two separate series of spectral bands in the Sm\(^{3+}\) present in two nonequivalent sites in the lattice of Ba\(^{2+}\) and Ti\(^{4+}\) sites. Therefore, in order to examine the variation of lifetime of the green upconversion (\(^5F_2/5S_2\)) and red upconversion (\(^5F_3\)) emitting levels and to light on the site selective occupancy of Ho\(^{3+}\) ions in a BaTiO\(_3\) lattice, the time-resolved spectroscopic measurements were conducted by exciting the selective specimens with a 980 nm laser-light. The streak camera images (survey spectra) related to the \(^5F_2/5S_2 \rightarrow ^5I_8\) and \(^5F_3 \rightarrow ^5I_8\) transitions of Ho\(^{3+}\) ions are portrayed in Fig. 5. The decay profiles of \(^5F_2/5S_2\) and \(^5F_3\) levels (Fig. 6) can be described in terms of an empirical relation as follows:\(^ {54}\)

\[ I(t) = I_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \]

where \( I(t) \) and \( I_0 \) are the upconversion intensities at time ‘t’ and ‘0’ (zero), respectively, with \( A_1 \) and \( A_2 \) as the fitting parameters at fast \( \tau_1 \) and slow \( \tau_2 \) components of the luminescence lifetimes. The values of decay times so calculated are summarized in Table 1 for c-BT, q-BT and t-BT samples.
The fraction \((\phi)\) of site-occupancy of \(\text{Ho}^{3+}\) ions of a characteristic lifetime value can be determined in a formula\(^\text{16,55}\),

\[
\phi = \frac{A_l \tau_l}{\sum_{i=1,2} A_l \tau_l} \times 100. \tag{16}
\]

The short-lived and long-lived components of lifetime can be interpreted by considering the existence of two types of emitting sites in a \(\text{Ho}^{3+}-\text{Yb}^{3+}: \text{BaTiO}_3\) sample. The \(\text{Ho}^{3+}\) (ionic size: 0.901 Å) can occupy the \(\text{Ba}^{2+}\) and \(\text{Ti}^{4+}\) sites with two unequal co-ordinations at the two sites; which in turn adapt different modulated lifetimes. As we know, the co-ordination numbers of \(\text{Ba}^{2+}\) and \(\text{Ti}^{4+}\) ions thereby are 12 and 6, respectively (Figure S8), which render a large difference in ionic size of \(\text{Ho}^{3+}\) and 12-coordinated \(\text{Ba}^{2+}\) sites, so as \(\text{Ho}^{3+}\) occupied \(\text{Ba}^{2+}\) sites form largely distorted octahedrons.

Conversely, if a produced defect in a charge difference is large, the local site is expected to lose its inversion symmetry. Nonetheless, while a \(\text{Ho}^{3+}\) ion occupies a 6-coordinated \(\text{Ti}^{4+}\) site, the ionic size difference is smaller over the former one and results in a lesser lattice distortion. In general, a comparatively short component of lifetime is associated with a low symmetric position of largely relaxed electronic transition rules, while a long component of lifetime is usually attributed to a relatively high symmetric position owing to the forbidden 4f-4f transitions\(^\text{55}\). Therefore, in this purview, it is proposed that the short component of lifetime arises in \(\text{Ho}^{3+}\) occupied \(\text{Ti}^{4+}\) sites (6-coordinated), while the long component of lifetime arises in \(\text{Ho}^{3+}\) occupied \(\text{Ba}^{2+}\) sites (12-coordinated). The fraction of \(\text{Ho}^{3+}\) ions at \(\text{Ba}^{2+}\) sites is calculated as 73% leaving behind a residual 27% value that in the \(\text{Ti}^{4+}\) sites in a c-BT sample. Further, as the \(\text{Ho}^{3+}\) site-occupancy reorder in a phase transition, it becomes 64% and 36% in the respective sites in a t-BT sample. A due change in the coordination numbers with a crystal phase is responsible for switching the site-occupancy, which eventually tunes local crystal fields around

Figure 5. Streak camera evolved images of \(\text{Ho}^{3+}-\text{Yb}^{3+}: \text{BaTiO}_3\) in c-BT, q-BT and t-BT phases.
It is also possible that part of Ho$^{3+}$ ions occupies Ti$^{4+}$ interstitial sites and some others occupy the surfaces in the small crystallites. The site occupancy of Sm$^{3+}$ ions is reported in a similar SrZrO$_3$ host$^{55}$ in which Sr$^{2+}$ sites serve as a minor and Zr$^{4+}$ sites as a major host of Sm$^{3+}$ dopants. In another example, Eu$^{3+}$ ions doped in $\alpha$-Zn$_2$P$_2$O$_7$$^{56}$ yield short and long lifetimes as they order at two differently coordinated Zn-sites.

Second harmonic generation. In SHG, two identical photons effectively combine giving rise to a single photon of twice the energy of the initial value. Nanocrystals exhibiting SHG are nowadays emerging in a versatile optical probe$^{57}$. These nanocrystals are comprised of non-centrosymmetric crystallites and their overall contribution from the asymmetric unit cells give the SHG. Using SHG, BT nanocrystals have recently been demonstrated in stem cell labelling with high contrast images$^{58}$. Thus, a phase transformation in Ho$^{3+}$-Yb$^{3+}$: BaTiO$_3$ is not probed only in terms of its XRD but also its second harmonic signal. The magnitude of eccentricity of distortion in the crystal system is correlated with the intensity of the SHG signal. The SHG under a 1064 nm laser-light excitation for three BT specimens, which were annealed at 873 K (c-BT), 1173 K (q-BT) and 1473 K (t-BT), are shown in Fig. 7.

The presence of a green light at 532 nm in a half of the IR excitation wavelength supports the exploration of a non-linear effect in the BT samples. A markedly enhanced SHG signal intensity is exhibited for t-BT specimen. No such signal is visible in c-BT in view of its center of symmetry. As an eccentric distortion rises-up, the SHG turns-up in a t-BT phase. Our results of SHG, energy-upconversion of luminescence, and XRD patterns are consistent one another, and thus infer that our approach would lend itself for the use of a ‘structural probe’ employing the upconversion luminescence for identifying a crystal phase of the Ho$^{3+}$-Yb$^{3+}$ doped BTs.

### Table 1.

| Energy state | Lifetime components | Ho$^{3+}$-Yb$^{3+}$: BaTiO$_3$ | c-BT (μs) | q-BT (μs) | t-BT (μs) |
|--------------|---------------------|-----------------------------|-----------|-----------|-----------|
| $^5\text{F}_2/\text{S}_2$ | $\tau_1$ | 63.5 | 37.5 | 28.8 |
| | $\tau_2$ | 175.3 | 143.5 | 135.6 |
| $^3\text{F}_4$ | $\tau_1$ | 54.2 | 34.5 | 28.9 |
| | $\tau_2$ | 155.5 | 133.5 | 124.6 |

Figure 6. Time-resolved luminescence decay transients of $^5\text{F}_2/\text{S}_2$ and $^3\text{F}_4$ levels of Ho$^{3+}$ in Ho$^{3+}$-Yb$^{3+}$: BaTiO$_3$ upon a 980 nm laser-light excitation at room temperature. $\tau_{1,2}$ values in the insets are in μs.
Conclusions

In conclusion, upconverted light emission from Ho\(^{3+}\)-Yb\(^{3+}\): BaTiO\(_3\) is studied with the steady-state and time-resolved photoluminescence properties. The green to red emission intensity ratio varies across a phase transition of the crystallites on a due change in Ho\(^{3+}\) positions in the final lattice, with modified population of the Ho\(^{3+}\) energy levels. The experimental results on the number of photons involved in the upconversion processes were described in support with the theoretical approach of the rate equations. Effect of thermal annealing of the samples has been illustrated based on the Ho\(^{3+}\) emission spectra and the rate equations. It is found that the SHG signal intensity is a measure of eccentricity present in the non-centro-symmetric BaTiO\(_3\) crystals. Further, an analysis of decay time of \(^5F_4/5S_2\) and \(^5F_5\) levels exhibits double decay characteristic of these levels. The Ho\(^{3+}\) occupancies of 73% and 27% found in the Ba\(^{2+}\) and Ti\(^{4+}\) sites in a cubic phase get modified to 64% and 36%, respectively, as it transforms to a tetragonal phase. The temperature dependent luminescence of this material can be used as a low-temperature probe, with a sensitivity as much as 0.0095 K\(^{-1}\) found at 12 K. Furthermore, consistent with XRD and SHG results, this work suggests a general approach to use upconversion luminescence of these samples in identifying their crystal structure and phase transitions.

Methods and analyses

Synthesis of Ho\(^{3+}\)-Yb\(^{3+}\): BaTiO\(_3\) small crystallites. A doped BaTiO\(_3\) with Ho\(^{3+}\)-Yb\(^{3+}\) ions, was prepared via a wet-chemical co-precipitation method of an optimized composition, 96.8 mol% BaTiO\(_3\) + 0.2 mol% Ho\(_2\)O\(_3\) + 3.0 mol% Yb\(_2\)O\(_3\), suitable for the upconversion emission\(^{28,46}\).

In a typical reaction batch\(^{16,39}\), BaCO\(_3\), acetic acid (CH\(_3\)COOH), titanium tetra-isopropoxide C\(_{12}\)H\(_{28}\)O\(_4\)Ti, ytterbium acetate Yb(CH\(_3\)COO)\(_3\), and holmium acetate Ho(CH\(_3\)COO)\(_3\) of purity better than 99% were used as raw materials. A 1.5 g of barium carbonate was dissolved in 15 mℓ of acetic acid and warmed on a hot-plate of a magnetic stirrer at 80 °C, and then, cooled down to room temperature. Required amounts of 0.2 mol% of holmium acetate were added to this precursor in a homogeneous solution. As a source of Ti\(^{4+}\) ions, 2.0 mℓ titanium tetra-isopropoxide was mixed in the above solution and stirred on a magnetic stirrer for 1 h. At the final stage, 10 mℓ of distilled water was added to this solution for precipitating small slurries capping the cations of hydroxides, which were recovered and finally washed repeatedly in ethanol. So obtained sample was dried in ambient atmosphere over days and then annealed at 873, 1173 and 1473 K for 6 h, here after called as c-BT, q-BT and t-BT, respectively.

Light-emission and other measurements. The XRD patterns were measured on a Bruker D8 Advance X-ray diffractometer using Cu-K\(_\alpha\) (1.5405 Å) radiation. The absorption spectrum was taken in a diffuse reflectance mode using a Lambda 950, UV-Vis-NIR spectrophotometer (Perkin Elmer). The upconversion emission spectra at different pulse energies were recorded using a 980 nm diode laser on SP2300 grating spectrometer (Princeton Instruments, USA)\(^{31}\). The measurements of temperature-dependent upconversion spectra from 12 K to 300 K were performed on a SPEX 1000 M spectrometer\(^{28}\). A He-closed-cycle refrigerator at 10\(^{-7}\) mbar pressure was used to cool down the sample in a chamber. The time-resolved spectroscopic measurements were carried out under excitation at a 980 nm laser-light by a Ti-sapphire laser, Mira 900-F (Coherent) pumped by Verdi 10–532 nm laser with an experimental set up consisting of a streak camera (Hamamatsu C10910), a synchronous delay generator (Hamamatsu C10647-01), water-cooled CCD (Hamamatsu Orca R2), and a delay unit (Hamamatsu C1097-05), as used in our earlier studies\(^{46,28}\). Furthermore, a chopper wheel at 200 Hz frequency was employed for generating laser ‘pulses’. The SHG measurements were performed using a 1064 nm Nd-YAG laser of a pulse width of 7 ns (laser model: SplitLight 600, InnoLas Laser GmbH, Germany). A suitable filter was used to block 1064 nm radiation to pass at the CCD detector.
Data availability
The experimental data is available upon request from the corresponding author.

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Author contributions
M.K.M. prepared the Ho$^{3+}$/Yb$^{3+}$ doped BaTiO$_3$ samples. M.K.M. and K.K. performed the upconversion measurements. M.K.M., T.K. and U.V. carried out time-resolved spectroscopic measurements and M.K.M. performed the analysis. U.V. and H.H. supervised the work.

Competing interests
The authors declare no competing interests.

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