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# Interplay between local distortion at lattice sites with optical and electrical properties of $\text{Eu}^{3+}$ -doped $\text{MNbO}_3$ ( $\text{M} = \text{Na}$ and $\text{K}$ ) compounds†

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Local distortion at lattice sites plays a pivotal role in determining many important physical properties. In the present study, our focus has been to examine such crucial roles for the optical and ferroelectric properties in  $\text{MNbO}_3$  ( $\text{M} = \text{Na}$  and  $\text{K}$ ) compounds. This study on dual property has significant importance in view of the potential application for piezophotonic devices; herein, an effort has been made to develop compounds with the simultaneous control of such properties in the desired range. For the optical properties, we doped  $\text{Eu}^{3+}$  ions, which not only give efficient red emission but also act as a spectroscopic probe for the local structure investigation. It was observed from a photoluminescence (PL) study that the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound is a pink-colour-emitting phosphor material while the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound is a single phase white-light-emitting material. It was also observed that doping  $\text{Eu}^{3+}$  ions had a significant impact on ferroelectric properties of these compounds. While such doping increased the remnant polarization of  $\text{NaNbO}_3$ , the impact was completely reversed in  $\text{KNbO}_3$ . A PL study confirmed that the local structure surrounding the  $\text{Eu}^{3+}$  ion in  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  compounds was different, and there was a more distorted environment surrounding the  $\text{Eu}^{3+}$  ion in the  $\text{NaNbO}_3$  compound. It was confirmed that  $\text{Eu}^{3+}$  ions, which exist in an asymmetric environment, have a major contribution among the PL lifetime components in the  $\text{NaNbO}_3$  compound. On the other hand in the  $\text{KNbO}_3$  compound,  $\text{Eu}^{3+}$  ions, which exist in a comparatively more symmetric environment, make the major contribution. From the PL study, we also conclude that  $\text{Eu}^{3+}$  ions preferably occupy the Na-site in  $\text{NaNbO}_3$  compound, which may distort the nearby  $\text{NbO}_6$  more and are responsible for a higher polarization. On the contrary in  $\text{KNbO}_3$  compound, majority of  $\text{Eu}^{3+}$  ions prefer symmetrical octahedral sites, which may not have an additional impact on the distortion of the  $\text{NbO}_6$  octahedron. Further, it was also observed from the extended X-ray absorption fine structure (EXAFS) study that upon  $\text{Eu}^{3+}$  doping the distortion parameter  $\sigma^2$  increased for Nb–O bonds in  $\text{NaNbO}_3$  compounds, while it decreased in  $\text{KNbO}_3$  compounds.

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## 1.0 Introduction

The demand for smart materials with multiple properties is ever increasing. There is an emerging trend to combine electrical properties with optical properties to meet potential applications in light emitting diodes, photocells or solar cells, and photon detectors.<sup>1–4</sup> This is the basis of various electro-optical devices,

such as piezo-photonic devices, which are based on the combination of piezoelectric and photoluminescence properties.<sup>5,6</sup> In such materials, the strain-induced piezopotential can stimulate photon emission without additional excitation energy, such as light and electricity.<sup>7</sup> Piezophotonic effects based on mechano-luminescent materials have applications in e-signature systems, visible wearable electronic devices, *etc.*<sup>7</sup> Oxide perovskites with the general formula  $\text{ABO}_3$ , with A being the larger cation (alkaline-earth or rare-earth metal) and B a smaller cation (transition metal), have extensive applications in optoelectronics, solar cells, light emitting diodes, and devices based on the photo-refractive effect, or ferroelectric and dielectric constants.<sup>8–14</sup> The core structure of these compounds consists of a three-dimensional (3D) network of corner-shared  $\text{BO}_6$  octahedra and A atoms occupy the hole created by these octahedra. Niobate-based

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perovskite materials, such as (Na/KNbO<sub>3</sub>), are potential environment friendly lead-free piezoelectric materials with a wide range of potential applications, such as storage devices, sensors, and generators.<sup>12–14</sup> The interesting feature of this class of compounds is that larger A-cations and smaller B-cations can be flexibly accommodated by distorting the compound's ideal cubic crystal structure. Several properties, such as ferroelectricity and piezoelectricity, can be suitably tuned by simply replacing the ions at their lattice sites. The research interest in environmentally friendly niobate perovskite is continuously increasing as it can replace lead zirconate titanate (PZT) in various application areas.<sup>13,15</sup> The structural order–disorder in these compounds plays an important role in the evolution of various optical and electrical properties. The cationic and anionic vacancies can alter the electronic structure, which has a tremendous impact on various physical properties.<sup>11,12</sup> Such vacancies can be controlled by adopting a suitable synthesis method. It has been reported that submicron-sized particles may crystallize in the polar space group *Pmc*2<sub>1</sub>, which is an alternative setting of *P*2<sub>1</sub>*ma*, and hence such compounds can be potentially ferroelectric.<sup>16,17</sup> Different polymorphs arise due to the octahedral tilting of the perovskites, which is very common in this class of compounds and is an intrinsic property of perovskites. The tilting is determined by the relative sizes and nature of the A- and B-site cations, and a detailed description about the various tilt systems was provided by Glazer *et al.*<sup>18,19</sup> Johnston *et al.* recorded the spectrum of <sup>93</sup>Nb MQMAS NMR and observed a degree of additional broadening, which suggested that Nb<sup>5+</sup> cations have some positional disorder and that they lie significantly off-centre from the centrosymmetric positions towards an edge of the octahedron in a polar manner, *i.e.* in the “*P*2<sub>1</sub>*ma*” polymorph.<sup>20</sup> Thus, the greater the positional disorder due to tilting of the octahedron, the greater the polarisation. However, it is of great interest to investigate the impact on the electrical properties when an aliovalent ion is doped. This is because the positional disorder of Nb<sup>5+</sup> cations in the NbO<sub>6</sub> octahedron is highly dependent on the relative sizes of A and B cations.<sup>18,19</sup>

Further, if the dopant ion is a luminescent ion itself, then the materials can truly behave as multifunctional or smart materials, having both electrical and optical properties. A few studies on the optical properties of undoped NaNbO<sub>3</sub> due to structural order–disorder have been reported recently.<sup>12</sup> On the other hand, the dopant-mediated optical properties are mostly related to the PL properties of lanthanides-doped NaNbO<sub>3</sub>.<sup>21–23</sup> Among the lanthanides, the Eu<sup>3+</sup> ion is widely used as a dopant ion to develop red-coloured phosphors.<sup>24–29</sup> A few works on the luminescence properties of Eu<sup>3+</sup>-doped NaNbO<sub>3</sub> and KNbO<sub>3</sub> matrices have also been reported separately.<sup>30,31</sup>

Distortion at the lattice site in the perovskite class of materials plays a huge role in deciding the physical properties of such materials and is of great importance to understand how the doping of a luminescent ion, such as Eu<sup>3+</sup> ion, can influence the local distortion; in particular, concerning the first coordination shell. This will have a direct impact on both the optical and electrical properties. However, no reports are

available towards that direction in NaNbO<sub>3</sub> and KNbO<sub>3</sub> matrices. The f–f transitions of Eu<sup>3+</sup> ions are forbidden in nature both by spin and parity selection rules. However, in an asymmetric or distorted environment, the transitions become partially allowed due to a relaxation in the selection rules. Especially, the electrical dipole (ED) transition (<sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub>) is hypersensitive to the local structure, making the Eu<sup>3+</sup> ion as the best candidate for structural study. Since K and Na atoms have different ionic radii, it is expected that the local distortion will be different in NaNbO<sub>3</sub> and KNbO<sub>3</sub>. Time-resolved emission spectroscopy can provide significant information in this regard. Using this technique, it is possible to separate the emission profile of Eu<sup>3+</sup> ions in different lattice sites of NaNbO<sub>3</sub> and KNbO<sub>3</sub>, which will greatly help to understand the difference in the local environment.<sup>25,26</sup> Such a study on the isolation of different Eu<sup>3+</sup> components at different lattice site has not been reported yet. Another advanced technique that is very useful to study the local structure is X-ray absorption spectroscopy or extended X-ray absorption fine structure (EXAFS) analysis. Such a study can give significant information about the local structure. Only a single report of an X-ray absorption spectroscopic study on an Eu<sup>3+</sup>-doped NaNbO<sub>3</sub> compound is available.<sup>32</sup> However, a comprehensive study on Eu<sup>3+</sup> doping in NaNbO<sub>3</sub> and KNbO<sub>3</sub> matrices separately would give a clearer picture about the doping-induced distortion in ABO<sub>3</sub>-type perovskites.

Although there are many reports on the electrical and optical properties of NaNbO<sub>3</sub> and KNbO<sub>3</sub> matrices available in the literature, a comprehensive report on the lattice site distortion upon doping Eu<sup>3+</sup> ions and the immediate consequences on the optical and electrical properties are significantly missing. However, such a study would be very much helpful not only to develop multifunctional materials but it may also shed light on how to control the multiple physical properties simultaneously. In this work, we prepared both undoped and Eu<sup>3+</sup>-doped NaNbO<sub>3</sub> and KNbO<sub>3</sub> compounds separately, and then performed optical and electrical property studies on these. In the electrical property study, for the first time, we observed that in the case of the NaNbO<sub>3</sub> matrix, there was an enhancement of the remnant polarization upon Eu<sup>3+</sup> doping. However, the other compound, *i.e.* KNbO<sub>3</sub>, showed a completely different picture and the remnant polarization was found to be decreased. In the PL study, the Eu<sup>3+</sup>-doped NaNbO<sub>3</sub> compound was found to be pink-colour emitting, while the Eu<sup>3+</sup>-doped KNbO<sub>3</sub> compound showed near white light emission. The bluish and green emissions from the host KNbO<sub>3</sub> in combination with the red emission from Eu<sup>3+</sup> ions resulted in such white light emission. Such single-phase, white-light-emitting phosphors are always of tremendous importance since they can overcome the problem faced by white light LEDs, which are typically made of three different colour phosphors (red, green and blue). Such phosphors have many advantages, such as a higher colour rendering index (CRI), tuneable correlated colour temperature (CCT), and pure Commission Internationale de l'Eclairage (CIE) chromaticity coordinates.<sup>33</sup> Using time-resolved photoluminescence spectroscopy (TRPS), the host emission along with various Eu<sup>3+</sup> components were isolated and a clear picture of the transition lines of



$\text{Eu}^{3+}$  ions was obtained, which otherwise was not possible due to the overlap with the intense host emission. It was observed that for the  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  compound, three different  $\text{Eu}^{3+}$  components were present, wherein the long-lived component made a significantly lower contribution. On the contrary, in the  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3$  compound, the long-lived component was found to be the major contributor. From the EXAFS study, it was found that the structural disorder parameter was different in the  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  matrices. Combining all these experimental observations, our main objective was to present a complete picture on how a luminescent dopant ion (here  $\text{Eu}^{3+}$ ) can influence the local distortion at the lattice site, particularly in the first coordination shell, which would have a significant impact on both the optical and electrical properties. Such a comprehensive study will certainly give future direction not only to developing efficient multifunctional materials but also to tuning and controlling their physical properties.

## 2.0. Synthesis and characterisation of the compounds using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR)

### $\text{NaNbO}_3(\text{s})$

$\text{NaNbO}_3(\text{s})$  (where 's' stands for solid sample) was synthesized through a solid-state route by heating an equimolar mixture of 0.2119 g of  $\text{Na}_2\text{CO}_3(\text{s})$  and 0.5316 g of  $\text{Nb}_2\text{O}_5(\text{s})$  at 900 °C in a high-purity Ar atmosphere (to obtain, 99.999% pure argon gas was passed through silica gel, metallic calcium and  $\text{P}_2\text{O}_5(\text{s})$  in order to remove the bulk moisture, oxygen and trace moisture, respectively) for 100 h with intermediate grinding after 20 h time interval. Before initiating the heating procedure, the starting materials were ground thoroughly for 1 h so that homogeneous mixtures were formed. The final temperature of 900 °C was reached through many heating steps and in each step the temperature was raised by 100 °C at a heating rate of

5 °C  $\text{min}^{-1}$ . After completing the heat treatment procedure at 900 °C, the sample mixture was cooled down to room temperature in the same experimental condition at a cooling rate of 5 °C  $\text{min}^{-1}$ . When the synthesis procedure was completed, the sample was stored in vacuum in order to avoid any contamination. Formation of the pure compound was confirmed by matching the XRD pattern with the reported one in JCPDS file No. 77-0873, as shown in Fig. 1a.

### $\text{Eu}^{3+}$ -doped $\text{NaNbO}_3(\text{s})$

A homogeneous and stoichiometric mixture of 0.0070 g  $\text{Eu}_2\text{O}_3(\text{s})$ , 0.2097 g  $\text{Na}_2\text{CO}_3(\text{s})$  and 0.5316 g  $\text{Nb}_2\text{O}_5(\text{s})$  was heated in order to synthesize 1.0 mol%  $\text{Eu}_2\text{O}_3(\text{s})$ -doped  $\text{NaNbO}_3(\text{s})$  in a high-purity argon atmosphere at 900 °C for 100 h. A similar heat treatment process was also followed for this compound as described for pure  $\text{NaNbO}_3(\text{s})$ . The purification of argon gas was also the same as mentioned before. The characterization of the sample was carried out by the X-ray diffraction technique and the spectrum is given in Fig. 1b. It can be seen from the spectrum of this  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  that there was a shift of the XRD patterns towards the higher two theta side in comparison to the undoped compound. This is only possible when  $\text{Eu}^{3+}$  ions are substituted at a position of a bigger cation to reduce the cell parameters; which are inversely related to the two theta value. The small impurity peaks around  $2\theta = 30^\circ$  for both the undoped and doped compound may be due to  $\text{Nb}_2\text{O}_5$ .

### $\text{KNbO}_3(\text{s})$

$\text{KNbO}_3(\text{s})$  was synthesized through the solid-state route by heating a homogeneous (1:1) mixture of 0.2764 g  $\text{K}_2\text{CO}_3(\text{s})$  and 0.5316 g  $\text{Nb}_2\text{O}_5(\text{s})$  at 900 °C for 100 h in a high-purity Ar gas atmosphere with heat treatment similar to that for  $\text{NaNbO}_3$ . After completing the heat treatment, the sample mixture was cooled down to room temperature, like for  $\text{NaNbO}_3$ , and then the sample was stored in vacuum in order to avoid any contamination. The purification process of Ar gas was the same as discussed earlier. Formation of the compound was

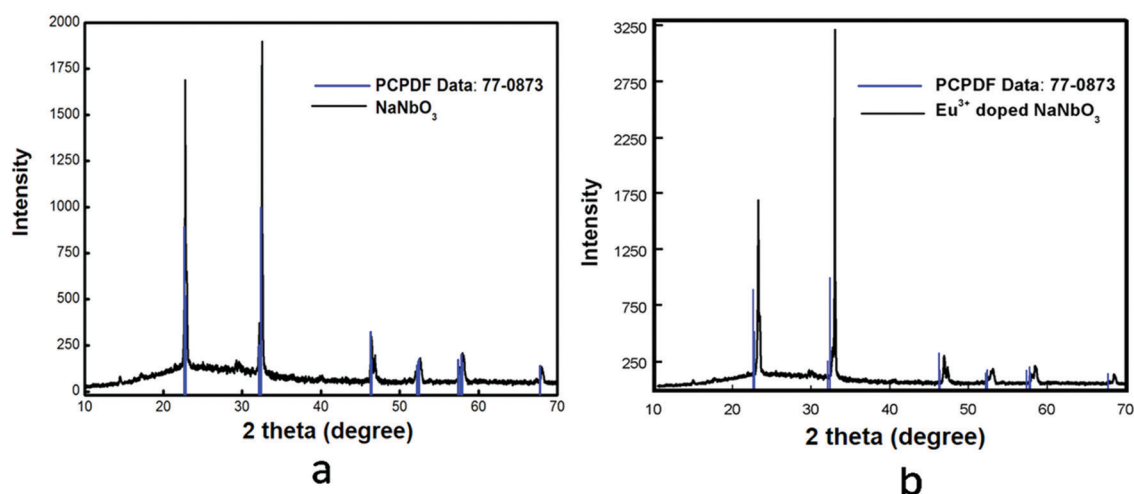


Fig. 1 Powder X-ray diffraction patterns of: (a)  $\text{NaNbO}_3$  and (b)  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$ .



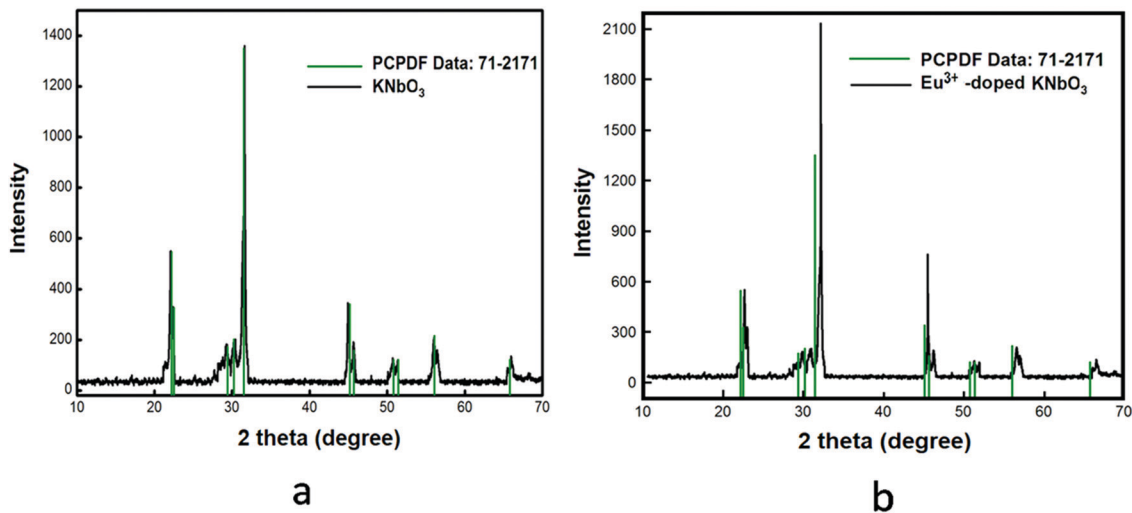


Fig. 2 Powder X-ray diffraction patterns of: (a)  $\text{KNbO}_3$  and (b)  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3$ .

confirmed by matching the XRD pattern with the reported one in JCPDS file No. 71-2171, as shown in Fig. 2a.

### $\text{Eu}^{3+}$ doped $\text{KNbO}_3(\text{s})$

1.0 mol%  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3(\text{s})$  compound was prepared by heating a homogeneous and stoichiometric mixture of 0.0070 g  $\text{Eu}_2\text{O}_3(\text{s})$ , 0.2736 g  $\text{K}_2\text{CO}_3(\text{s})$  and 0.5316 g  $\text{Nb}_2\text{O}_5(\text{s})$  at 900 °C in a high-purity Ar environment for 100 h with the same heating conditions as described for pure  $\text{KNbO}_3(\text{s})$ . The characterization of the sample was carried out using the X-ray diffraction technique and the XRD pattern is given in Fig. 2b. For this  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3$  compound too, there was a slight shift of the XRD patterns towards a higher two theta value.

### FTIR study

The FTIR spectra of undoped and  $\text{Eu}^{3+}$ -doped niobates are presented in Fig. 3. For both the  $\text{KNbO}_3$  and  $\text{NaNbO}_3$  compounds,

the absorption peaks in the range of 500–1000  $\text{cm}^{-1}$  were due to the  $\text{NbO}_6$  octahedron.<sup>34,35a</sup> The band around 534  $\text{cm}^{-1}$  was due to the edge-shared  $\text{NbO}_6$  octahedron, while the band around 628  $\text{cm}^{-1}$  represented the O–Nb–O stretching vibration ( $\nu_3$  mode) in the corner-shared  $\text{NbO}_6$ . A weak band around 860  $\text{cm}^{-1}$  could be observed for all of the compounds, which was due to existence of a carbonate group.<sup>35b</sup>

*Note:* The instrumental details are given in the ESI.†

## 3.0. Results and discussion

### 3.1. Photoluminescence (PL) study

$\text{NaNbO}_3$  and  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  ( $\text{Eu}^{3+}:\text{NaNbO}_3$ ). The emission spectrum of the undoped  $\text{NaNbO}_3$  compound with an excitation wavelength of 230 nm is given in Fig. 4a, which shows multiple emission bands at around 425, 480, 540 and 630 nm. Such emission bands must have originated from  $\text{NbO}_6$

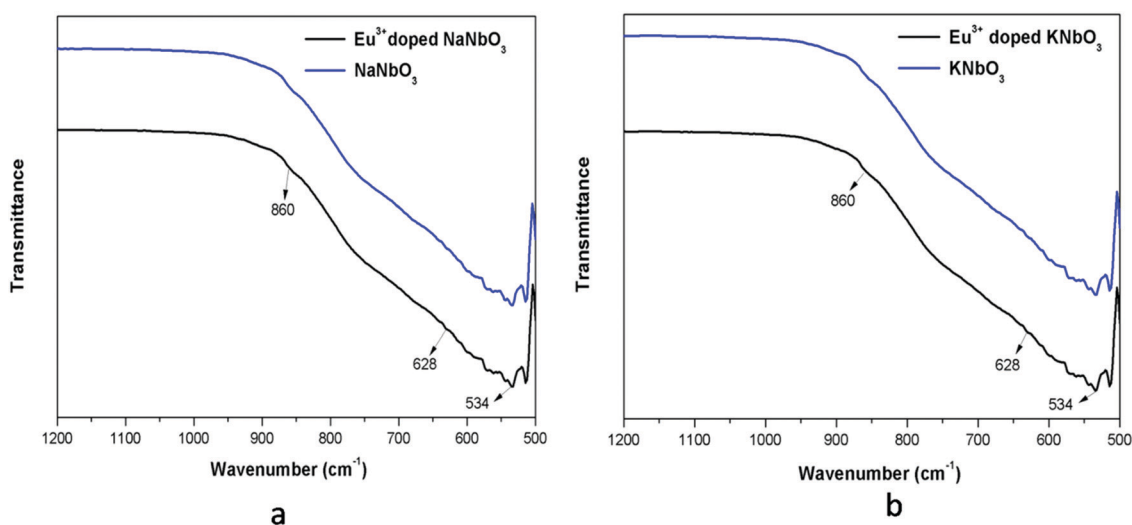


Fig. 3 FTIR spectra of: (a) undoped and  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  and that of (b)  $\text{KNbO}_3$ .





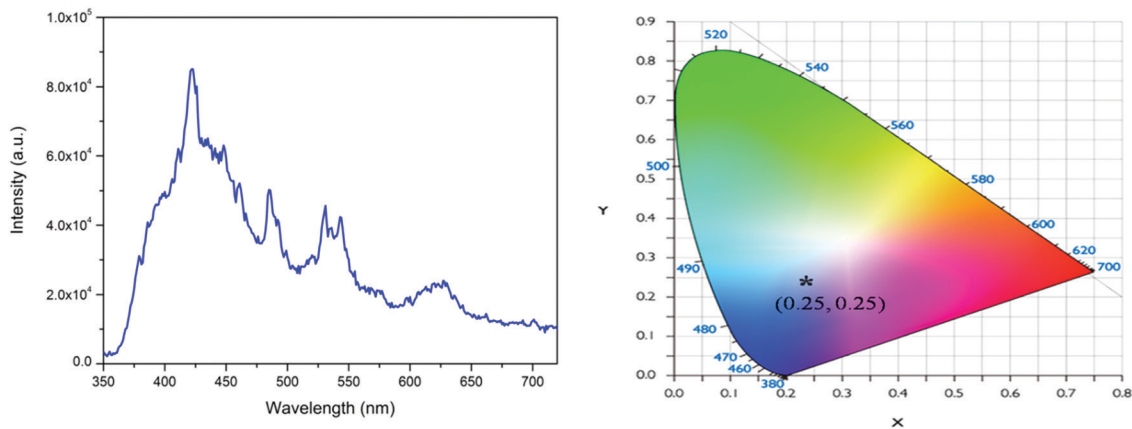


Fig. 4 (a) Emission spectrum of  $\text{NaNbO}_3$  at 230 nm excitation and (b) its CIE colour coordinates.

octahedra<sup>12a</sup> and various defect centres, such as the different types of oxygen vacancies associated with the  $\text{NbO}_6$  octahedron, which create several trap states (shallow and deep trap states) inside the band gap of the materials, as reported earlier.<sup>12b</sup> These oxygen vacancies are mostly singly charged ( $\text{V}_\text{O}^+$ ) or doubly charged ( $\text{V}_\text{O}^{2+}$ )<sup>12b</sup> and are associated with the  $\text{NbO}_6$  octahedron and originate due to structural order–disorder transition. The bluish 425 nm band could be attributed to  $\text{NbO}_6$  octahedron, while the bands in the green and yellow regions might be due to defect centres.<sup>12a,b</sup> The CIE colour coordinates of this compound were calculated following the earlier procedures<sup>36</sup> and they are presented in Fig. 4b, which show that the compound was a blue-light-emitting material.

The PL excitation spectrum of  $\text{Eu}^{3+}:\text{NaNbO}_3$  is given in the ESI† (Fig. S1), which showed that there were multiple excitation peaks present in the 210–300 nm and 350–450 nm regions, with the peaks in the 350–450 nm range being the most intense. The excitation peaks in the 350–450 nm range could be attributed to the characteristic excitation bands of  $\text{Eu}^{3+}$  ion, arising due to the f–f transitions. The peaks in the 210–300 nm range were due to the charge-transfer (CT) transitions from the p orbital of oxygen to the empty d orbital of the  $\text{Eu}^{3+}$  ion and to the empty 4d orbital of the  $\text{Nb}^{5+}$  ion in the  $\text{NbO}_6$  groups.<sup>25,26</sup> Since we aimed to investigate both host- and dopant-induced emission, the emission spectra were recorded with the charge-transfer excitation for the doped compounds. Fig. 5 shows the PL emission spectrum of  $\text{Eu}^{3+}:\text{NaNbO}_3$  with CT excitation, which was composed of both the host's emission and the prominent characteristics transition lines of  $\text{Eu}^{3+}$  ions. The orange  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  (594 nm) and the red  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  (614 nm) transition lines of the  $\text{Eu}^{3+}$  ion, which correspond to magnetic dipole (MD) transition and electric dipole (ED) transition were clearly visible in the spectrum. In addition, the emission line at 715 nm ( ${}^5\text{D}_0\text{--}{}^7\text{F}_4$ ) was also visible. The calculated colour coordinates for this compound are presented in the inset of Fig. 5, which shows that the compound was a pink-colour-emitting phosphor material. Generally,  $\text{Eu}^{3+}$ -doped compounds are red in nature; however, in the present case, the prominent blue emission from the host in combination with the red emission from  $\text{Eu}^{3+}$

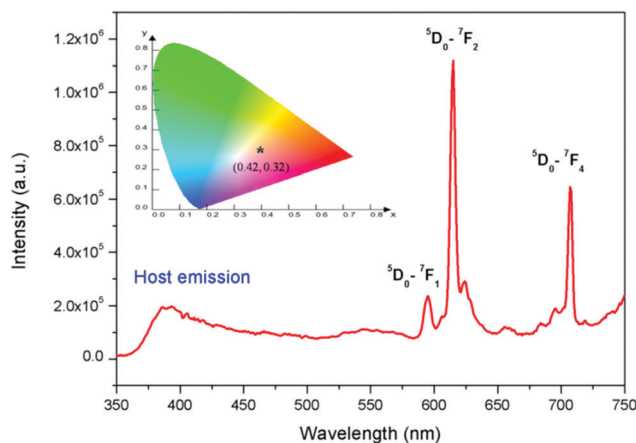


Fig. 5 Emission spectrum of  $\text{Eu}^{3+}:\text{NaNbO}_3$  at 250 nm excitation wavelength and its CIE colour coordinates (inset).

ions gave rise to the pink colour. It is well known that the relative intensity ratio of the ED and MD lines (*i.e.* ED/MD), which is also known as the asymmetric ratio (A), measures the degree of distortion from the inversion symmetry around the  $\text{Eu}^{3+}$  ion.<sup>25–27</sup> Thus, the higher intensity ED line indicated that the dopant  $\text{Eu}^{3+}$  ion was situated at a lattice site within a highly distorted environment. This distortion occurs due to the size and charge differences of the  $\text{Eu}^{3+}$  ion with the two host cations, *i.e.*  $\text{Na}^+$  and  $\text{Nb}^{5+}$ . The respective ionic radii were 0.94 Å for the 6-co-ordinated  $\text{Eu}^{3+}$ , 1.12 Å for the 9-co-ordinated  $\text{Eu}^{3+}$  (maximum reported Shannon radius of a  $\text{Eu}^{3+}$  ion), 1.39 Å for the 12-co-ordinated  $\text{Na}^+$  and 0.64 Å for the 6-co-ordinated  $\text{Nb}^{5+}$  ion. Thus from an ionic radius point of view, the  $\text{Eu}^{3+}$  ions are more likely to replace the bigger sized  $\text{Na}^+$  ions since the size difference with the smaller  $\text{Nb}^{5+}$  ion is more. This was also supported by the XRD pattern of the  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  compound, which showed a shift of the pattern towards the higher two theta side and that is only possible when a smaller dopant ion replaces a bigger lattice ion. The other factor that can induce more distortion into the lattice site is the charge imbalance. Since there will



be a charge difference of two at any of the two lattice sites in this matrix when a  $\text{Eu}^{3+}$  ion is doped, defect centres with opposite charges must have to originate as a counterbalance. Such defect centres might be close or far from the lattice sites and the distance will determine the amount of induced distortion in the lattice site. However, there is always a possibility that a few percentages of  $\text{Eu}^{3+}$  ions may also replace the smaller  $\text{Nb}^{5+}$  ions from the respective lattice site and in such a case there will be two different kinds of  $\text{Eu}^{3+}$  ions (one at a Na-site and another at a Nb-site). Lifetime study can provide significant information in this context, which is discussed later.

**$\text{KNbO}_3$  and  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3$  ( $\text{Eu}^{3+}:\text{KNbO}_3$ ).** Fig. 6 presents the emission spectra of undoped  $\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  compounds at 250 nm excitation wavelength. The excitation spectrum of  $\text{Eu}^{3+}:\text{KNbO}_3$  is provided in the ESI† (Fig. S2). It can be seen that for the undoped compound there was a broad emission band consisting of several emission components. Such a broad emission band must have originated from  $\text{NbO}_6$  octahedron and several defect centres associated with it, as observed in the case of  $\text{NaNbO}_3$ .<sup>12</sup> Upon doping with  $\text{Eu}^{3+}$  ions, in addition to the host emission, peaks due to  $\text{Eu}^{3+}$  ions also appear in the spectrum. Here the emission intensity arising due to the host and  $\text{Eu}^{3+}$  are comparable unlike that in  $\text{Eu}^{3+}:\text{NaNbO}_3$ , where the host emission was suppressed upon  $\text{Eu}^{3+}$  doping. One possibility is the energy transfer from the host to the dopant ion in  $\text{NaNbO}_3$ , since the 395 nm excitation peak of  $\text{Eu}^{3+}$  matches the bluish emission of the  $\text{NbO}_6$  octahedron. However, such an energy-transfer mechanism may not exist in  $\text{KNbO}_3$ , as evident from the intense host emission. Later, we discuss how the site occupancy of  $\text{Eu}^{3+}$  ions is different in  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  and this might be one reason. In  $\text{Eu}^{3+}:\text{KNbO}_3$ ,  $\text{Eu}^{3+}$  ions prefer to occupy Nb sites, which may create additional oxygen-vacancy-related defects. Since  $\text{NbO}_6$  octahedra connect to each other *via* corner sharing through the oxygen linkage, any oxygen vacancy can quench the blue

emission of the  $\text{NbO}_6$  octahedron. On the other hand in  $\text{NaNbO}_3$ , the  $\text{Eu}^{3+}$  ions prefer to occupy  $\text{Na}^+$  sites which results in two additional positive charges in the matrix. Thus the possibilities of the formation of positively charged oxygen vacancies are less and instead there will be the creation of negatively charged defects. Further, from the respective intensity of the ED and MD lines of  $\text{Eu}^{3+}$  ions, it can be inferred that the asymmetry ratio is less in  $\text{KNbO}_3$  compared to that in  $\text{NaNbO}_3$  and that the  $\text{Eu}^{3+}$  ions have a more symmetrical environment in  $\text{KNbO}_3$ . We also calculated the CIE colour coordinates as shown in Fig. 6-ii, which suggested that upon doping a  $\text{Eu}^{3+}$  ion, the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound behaved as a white-light-emitting material. This was due to the mixing of the red emission of  $\text{Eu}^{3+}$  ions with the blue and green emissions from the host. Since the host showed a very prominent emission in the blue and green regions unlike in  $\text{NaNbO}_3$ , the realization of white light emission was possible in the single-phase  $\text{Eu}^{3+}$ -doped  $\text{KNbO}_3$  compound, which offers many advantages over the others.<sup>33</sup> The host emission also behaved as a white light. It is worth mentioning here that the emission spectra of both the compounds ( $\text{Eu}^{3+}:\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{NaNbO}_3$ ) at 395 nm excitation wavelength (characteristic excitation wavelength of  $\text{Eu}^{3+}$  ions) were also recorded and are provided in the ESI† (Fig. S3 and S4). This was to check whether the ratio of the ED and MD lines followed a similar trend as observed with the 250 nm excitation. It was observed that the ratio of ED and MD lines followed a similar trend. Interestingly, we observed that the splitting pattern of the emission line at 715 nm ( ${}^5\text{D}_0-{}^7\text{F}_4$ ) was different in  $\text{Eu}^{3+}:\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{NaNbO}_3$ . This also suggested that the lattice site occupancy or the surrounding environment of the  $\text{Eu}^{3+}$  ion was different in these compounds. Now for both the doped compounds, there were multiple cationic sites wherein  $\text{Eu}^{3+}$  ions could get distributed. Two major factors that will determine the dopant ion's distributions are: (a) the size difference and (b) the charge differences between the dopant ions and host's cations.

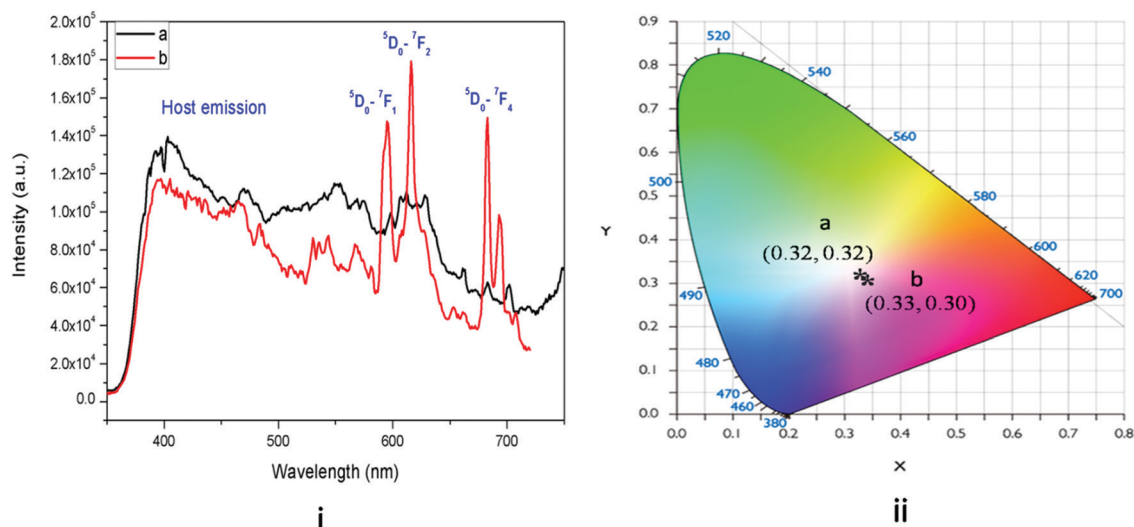


Fig. 6 (i) Emission spectra of: (a) undoped and (b)  $\text{Eu}^{3+}:\text{KNbO}_3$  at 250 nm excitation and (ii) its CIE colour coordinates.



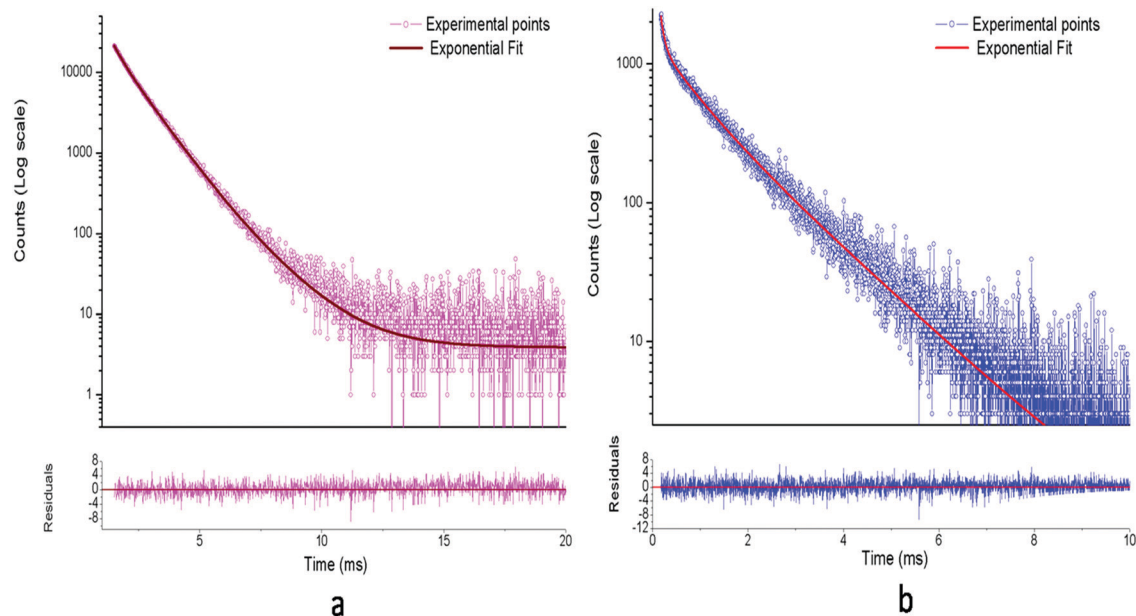


Fig. 7 Photoluminescence decay profiles of: (a)  $\text{Eu}^{3+}:\text{NaNbO}_3$  and (b)  $\text{Eu}^{3+}:\text{KNbO}_3$  at an excitation wavelength of 395 nm and emission wavelength of 615 nm.

A PL lifetime study is the most suitable technique to obtain information about the existence of different  $\text{Eu}^{3+}$  environments.

**PL lifetime study.** The respective decay curves of  $\text{Eu}^{3+}:\text{NaNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  are given in Fig. 7. It could be observed that both compounds followed a tri-exponential behaviour as mentioned in eqn (1)

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \quad (1)$$

where  $I(t)$  is the intensity,  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  are the emission decay times, and  $A_1$ ,  $A_2$  and  $A_3$  are their relative weightings. These lifetime values with their respective magnitudes are given in Table 1.

From Table 1, it can be seen that three different emitting components existed for the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound and the 2nd lifetime component (0.96 ms) with the intermediate lifetime value had the highest contribution. On the contrary, in the case of  $\text{Eu}^{3+}:\text{KNbO}_3$ , the long-lived component (1.38 ms) had the highest contribution among the three components. Since f-f transitions of  $\text{Eu}^{3+}$  ions are forbidden in nature and only in an asymmetric environment do they become partially allowed, the short lifetime value must be associated with a distorted or asymmetric environment of  $\text{Eu}^{3+}$  ions, while the long-lived component may be associated with a more symmetric environment.<sup>25,26</sup> Thus for  $\text{Eu}^{3+}:\text{NaNbO}_3$ , the  $\tau_3 = 1.69$  ms is attributed to  $\text{Eu}^{3+}$  ions in a more symmetrical environment

while  $\tau_2 = 0.96$  ms is attributed to  $\text{Eu}^{3+}$  ions in an asymmetrical environment. In  $\text{ABO}_3$  type of perovskite, the B-atom resides in a symmetrical octahedron, *i.e.*  $\text{BO}_6$ . On the other hand, the A-atom with twelve co-ordinations has a relatively more asymmetrical environment. Further, since this site is created by the corner sharing of oxygen atoms from the surrounding 8  $\text{BO}_6$  octahedra, which are very often tilted due to the slight mismatch of the ionic radii of A and B atoms, the 12 oxygen atoms are not symmetrically co-ordinated towards the A atom. Therefore we may attribute the long-lived lifetime ( $\tau_3 = 1.69$  ms) component to the  $\text{Eu}^{3+}$  ion at the Nb site, while the other component with a lower lifetime value ( $\tau_2 = 0.96$  ms) may be attributed to  $\text{Eu}^{3+}$  ion at the asymmetric Na site. The  $\tau_1 = 0.33$  ms lifetime component, which makes the very least contribution among the three, might be due to  $\text{Eu}^{3+}$  ion present in a highly asymmetric environment or close to an impurity or defect centre that acts as a quencher. In the FTIR spectra, we could observe the presence of small carbonate impurity, which may quench the excited state. However, since the contribution is very much less, we believe that such a  $\text{Eu}^{3+}$  ion will not have any significant impact on the physical properties of the materials. The fact that the percentage of the  $\tau_2 = 0.96$  ms component is more in the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound indicates that most of the  $\text{Eu}^{3+}$  ions are placed in a distorted environment. From the emission spectra too, it is clear that the intensity of the ED line is very high compared to the MD line, resulting in an asymmetric ratio of  $A > 1$ .

On the contrary in the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound, the contribution from the long-lived component ( $\tau_2 = 1.38$  ms) is more than from the short-lived components ( $\tau_1 = 0.07$  ms &  $\tau_2 = 0.61$  ms), which suggests that most of the  $\text{Eu}^{3+}$  ions exist in a symmetrical environment, here at Nb sites. Considering the respective ionic radii of  $\text{K}^+$  ( $r_{\text{K}^+} = 1.64$  Å) and  $\text{Eu}^{3+}$  ions ( $r_{\text{Eu}^{3+}} = 1.12$  Å for

Table 1 Photoluminescence lifetime values of the  $\text{Eu}^{3+}$ -doped niobate compounds

Compound	$\tau_1$ in millisecond	$\tau_2$ in millisecond	$\tau_3$ in millisecond
$\text{Eu}^{3+}:\text{NaNbO}_3$	0.33 (6%)	0.96 (80%)	1.69 (14%)
$\text{Eu}^{3+}:\text{KNbO}_3$	0.07 (4%)	0.62 (25%)	1.38 (71%)



9 co-ordination), it is more likely that  $\text{Eu}^{3+}$  ions do not prefer to replace a much bigger ion like  $\text{K}^+$  unlike the  $\text{Na}^+$  ion in  $\text{Eu}^{3+}:\text{KNbO}_3$ . The fact that the lifetime value of the long-lived component ( $\tau_2 = 1.38$  ms) is less compared to that in  $\text{Eu}^{3+}:\text{KNbO}_3$  can be explained on the basis of oxygen vacancies associated with the  $\text{NbO}_6$  octahedron. If  $\text{Eu}^{3+}$  ions replace  $\text{Nb}^{5+}$  ions, oxygen vacancies will be created, which can quench the excited state. The  $\tau_2 = 0.62$  ms component might be due to  $\text{Eu}^{3+}$  ions close to an impurity centre, like a carbonate. Another possibility is that the long-lived component is due to  $\text{Eu}^{3+}$  ions placed at Nb sites with a fewer defect centres, while the short-lived component is due to  $\text{Eu}^{3+}$  ions at similar sites but with a higher number of defect centres. We believe that the  $\tau_1 = 0.07$  ms is not due to the  $\text{Eu}^{3+}$  ions as it rarely shows a lifetime value in this order due to forbidden nature of the f-f transition. Rather, it will be some defect related component, and here, in  $\text{KNbO}_3$ , it can be seen that the host has an emission band around 600 nm. The fact that the defect centres play an important role in the lifetime value of the  $\text{Eu}^{3+}$  ions is also reflected in the lower intensity of the  $\text{Eu}^{3+}$  ion's characteristic lines (ED & MD) in  $\text{Eu}^{3+}:\text{KNbO}_3$  compared to that in  $\text{Eu}^{3+}:\text{NaNbO}_3$ . The few defect centres in the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound may quench the excited state *via* a nonradiative pathway, thereby reducing both the lifetime and intensity from  $\text{Eu}^{3+}$  ions. Now if we critically view the emission profile, then it can be concluded that the intensity ratio, *i.e.* the ED/MD, or the asymmetric ratio is very

low compared to that in the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound. However, due to the significant contribution from the host emission, it is difficult to get a clear picture about the characteristics of the emission lines. The best way is to isolate the individual spectra by giving different delay times once all of them are excited in the TRES study. In this way, we found that the lifetime values of the host emission at 400, 440, 470 and 550 nm were 11.22, 10.78, 10.87 and 11.03  $\mu\text{s}$ , respectively, which were less than that of the  $\text{Eu}^{3+}$  ion. The decay profiles of these emission wavelengths are given in the ESI† (Fig. S5–S8). Therefore, a systematic TRES study at different delay times can provide a clearer picture about the host emission as well as the emission from  $\text{Eu}^{3+}$  ions.

**Time-resolved emission spectroscopy (TRES) study of  $\text{Eu}^{3+}:\text{KNbO}_3$ .** TRES analysis of the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound was carried out following similar procedures as demonstrated in our earlier work.<sup>37</sup> The TRES spectra at different delay times are given in Fig. 8. It can be seen that with increasing the delay time, the spectral features are changed gradually. At a smaller delay time, such as at 0.050 ms, the spectrum is composed of both the host emission as well as the emission from  $\text{Eu}^{3+}$  ions. However, as we kept on increasing the delay time, the host emission started disappearing. This was due to the lower lifetime value of the host emission. At 0.5 ms delay time, the host emission had completely disappeared, and if we properly subtract it from the TRES spectrum at 0.050 ms delay time,

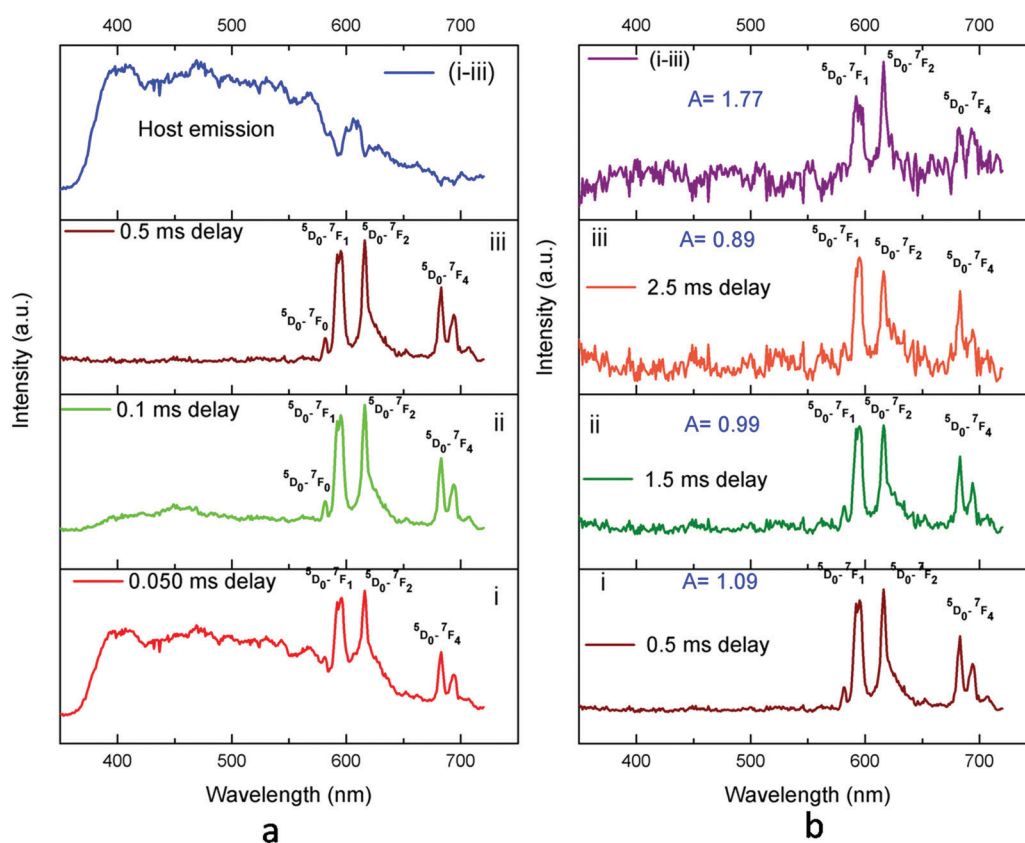


Fig. 8 TRES spectra of  $\text{Eu}^{3+}:\text{KNbO}_3$  at different delay times.





a clear picture of the host emission profile can be obtained, as given in the top of Fig. 8a. Now at 0.5 ms delay time, the spectral features of the  $\text{Eu}^{3+}$  ion is clearly visible and the ED and MD lines are almost equally intense, with ED being slightly higher intense. However, as we further increased the delay time, a complete different picture was observed, and at higher delay time such as at 2.5 ms delay, the MD line was found to be more intense with an asymmetric ratio of  $<1$ . This was due to the fact that at this time delay the spectrum was only composed of the long-lived  $\text{Eu}^{3+}$  component with a lifetime value of 1.39 ms. This  $\text{Eu}^{3+}$  ion occupied a symmetrical lattice site and thus the MD line was more intense. The emission spectrum of the  $\text{Eu}^{3+}$  ion existing in an asymmetric site can be obtained if we subtract the TRES spectrum at 2.5 ms from that at 0.5 ms. At 0.5 ms delay time, the emission spectrum was composed of both the short-lived and long-lived components and at 2.5 ms delay time (which is more than three times the lifetime value of the short-lived component), the short-lived component must have been decayed completely. The emission spectrum of the short-lived component is given at the top of Fig. 8b, which had an asymmetry ratio of  $A = 1.77$ . While for the long-lived component in Fig. 8b-iii, it is clearly visible that  $A < 1$  owing to the less intense ED line. Therefore, from these observations in the lifetime and TRES studies, it was confirmed that the local structure around the  $\text{Eu}^{3+}$  ion in  $\text{Eu}^{3+}:\text{KNbO}_3$  was more symmetric in nature compared to that in  $\text{Eu}^{3+}:\text{NaNbO}_3$ , where it was asymmetric. We further confirmed this observation later by EXAFS study.

Another way to understand the local distortion is to understand the site symmetry from the Stark splitting pattern of the characteristics lines of  $\text{Eu}^{3+}$  ions as described elsewhere.<sup>38</sup> However, to understand such symmetry, the splitting patterns must be clearly visible. From the emission spectra of the  $\text{Eu}^{3+}$  ions, we saw that the  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  line existed for both the

compounds but with a higher intensity for the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound. The existence of a  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  line indicated that  $\text{Eu}^{3+}$  existed at a low-symmetry site without an inversion centre. The  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  line is only allowed with the 10 site symmetries, *i.e.*  $C_s$ ,  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_6$ ,  $C_{2v}$ ,  $C_{3v}$ ,  $C_{4v}$  and  $C_{6v}$  respectively.<sup>38</sup> From the Stark splitting pattern (Fig. S9, which is given in the ESI†), we observed that the site symmetry of  $\text{Eu}^{3+}$  ion in  $\text{NaNbO}_3$  might be  $C_{4v}$ . Although, the  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$  line was clearly visible in the emission spectrum of  $\text{Eu}^{3+}$  ions in  $\text{KNbO}_3$ , the splitting of other peaks was not clear to us and hence we did not calculate the site symmetry for the case of  $\text{KNbO}_3$ . However, the symmetry must be among the 10 mentioned symmetries. This also suggested that although the MD line had good intensity in  $\text{Eu}^{3+}:\text{KNbO}_3$ , the Nb site was not purely symmetric in nature, *i.e.* it was a site with inversion symmetry. This might be due to the fact that the defect centres, such as oxygen vacancies, created some asymmetric environment surrounding the Nb site as stated earlier. Now, let us see what happened to the electrical properties of  $\text{KNbO}_3$  and  $\text{NaNbO}_3$  when  $\text{Eu}^{3+}$  ion was doped, which was another important physical property investigated in this present work.

### 3.2. Electrical properties

The ferroelectric ( $P$ - $E$ ) hysteresis loops of the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound at room temperature and at different electrical fields are shown in Fig. 9a, wherein it is clearly visible that the polarisation is at a maximum at a field of  $5 \text{ kV cm}^{-1}$ . A similar observation was also found for the  $\text{NaNbO}_3$  samples. The compound showed saturation in polarization and also a concave region in the  $P$ - $E$  plot, which suggested that it is truly ferroelectric in nature.<sup>39</sup> The ferroelectric ( $P$ - $E$ ) hysteresis loops for undoped  $\text{NaNbO}_3$  and  $\text{Eu}^{3+}:\text{NaNbO}_3$  compounds at a field of  $5 \text{ kV cm}^{-1}$  are shown in Fig. 9b. From the plot, we measured the respective remnant polarization of both these samples and they

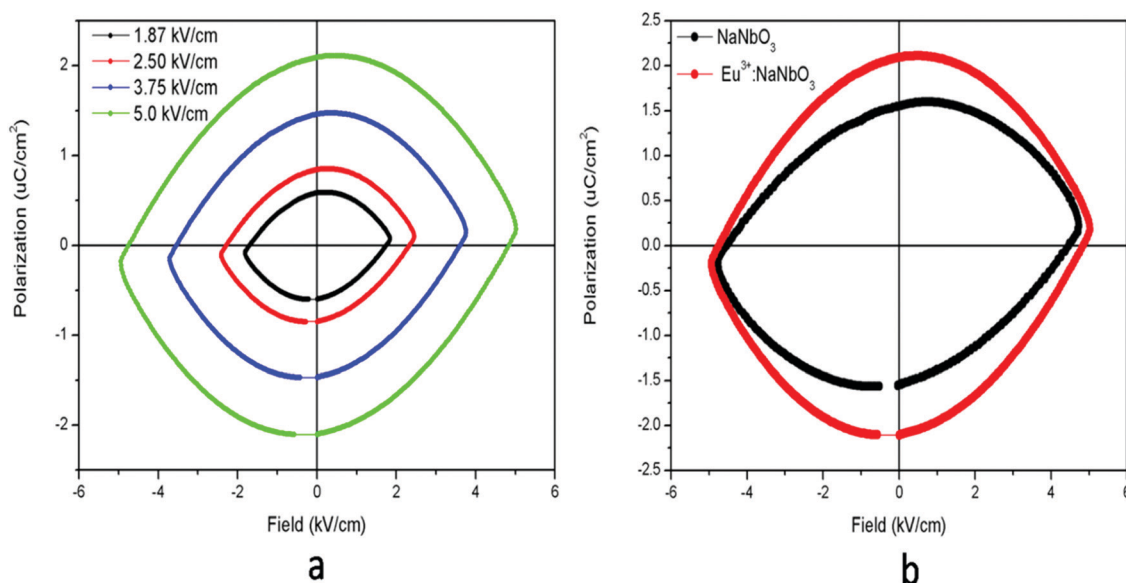


Fig. 9 Ferroelectric ( $P$ - $E$ ) hysteresis loops for: (a)  $\text{Eu}^{3+}:\text{NaNbO}_3$  at room temperature under different electrical fields, and (b) for undoped  $\text{NaNbO}_3$  and the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound at a field of  $5 \text{ kV cm}^{-1}$ .



were  $\text{Pr} = 1.65 \mu\text{C cm}^{-2}$  for  $\text{NaNbO}_3$  and  $\text{Pr} = 2.16 \mu\text{C cm}^{-2}$  for  $\text{Eu}^{3+}:\text{NaNbO}_3$ . Thus, there was an enhancement of the polarization value when  $\text{Eu}^{3+}$  ions were doped. Interestingly, the  $\text{KNbO}_3$  series of compounds showed a reverse trend and the ferroelectric ( $P$ - $E$ ) hysteresis loops of  $\text{Eu}^{3+}:\text{KNbO}_3$  and  $\text{KNbO}_3$  are presented in Fig. 10. Here, although the undoped  $\text{KNbO}_3$  compound showed a ferroelectric hysteresis loop; upon doping with  $\text{Eu}^{3+}$  ions, the compound showed very weak ferroelectric behaviour. We also measured the leakage current density of these compounds. The leakage current density vs electric field plot for  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  compounds are presented in Fig. 11, which suggests that the leakage current was less in the case of the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound at any point of the field compared to the undoped  $\text{NaNbO}_3$  compound. On the other hand, in the  $\text{KNbO}_3$  series of compounds, the leakage current density was found to increase when a  $\text{Eu}^{3+}$  ion was doped. Thus, there must be two different factors that are responsible for such behaviour. Earlier reports on the crystal structure of  $\text{NaNbO}_3$  suggested that, due to the octahedral tilting of the perovskites, which is very common in this class of compounds and an intrinsic property of perovskites, the  $\text{Nb}^{5+}$  cations have some positional disorder and they lie significantly off-centre from the centrosymmetric positions towards an edge of the octahedron in a polar manner, in the " $P_{21}ma$ " polymorph.<sup>20</sup> Such an off-centre position of the  $\text{Nb}^{5+}$  cations is mainly

responsible for the polar character of the compound. Now, doping an impurity ion, such as  $\text{Eu}^{3+}$  ion, with a different size must increase the positional disorder due to change in the tilting of the octahedron. In  $\text{NaNbO}_3$ , the respective ionic radii of the  $\text{Na}^+$ ,  $\text{Nb}^{5+}$  and  $\text{Eu}^{3+}$  ions were in the order  $r_{\text{Nb}^{5+}} = 0.64 \text{ \AA}$  (6 co-ordinated)  $<$   $r_{\text{Eu}^{3+}} = 0.94 \text{ \AA}$  (6 co-ordinated) and  $1.12 \text{ \AA}$  (9 co-ordinated)  $<$   $r_{\text{Na}^+} = 1.39 \text{ \AA}$  (12 co-ordinated). However in  $\text{KNbO}_3$ , the respective ionic radii of  $\text{K}^+$ ,  $\text{Nb}^{5+}$  and  $\text{Eu}^{3+}$  ions were in the order  $r_{\text{Nb}^{5+}} = 0.64 \text{ \AA}$  (6 co-ordinated)  $<$   $r_{\text{Eu}^{3+}} = 0.94 \text{ \AA}$  (6 co-ordinated) and  $1.12 \text{ \AA}$  (9 co-ordinated)  $<$   $r_{\text{K}^+} = 1.64 \text{ \AA}$  (12 co-ordinated). Thus the substitution of  $\text{Eu}^{3+}$  at  $\text{K}^+$  sites may lead to the shrinkage of the  $\text{KNbO}_3$  lattice. On the other hand, the substitution at the  $\text{Nb}^{5+}$  site (B site) will definitely expand the unit cell volume. A study on the changes of the lattice parameters due to the substitution of lanthanides, such as  $\text{Er}^{3+}$ , at the lattice sites of  $\text{KNbO}_3$  was reported earlier using XRD and it was concluded that  $\text{Er}^{3+}$  may go to both K and Nb sites.<sup>40</sup> In our present cases too, we observed a shift in the XRD patterns towards a higher two theta side in  $\text{NaNbO}_3$  and since two theta is inversely related to the lattice parameters, it can be assumed that the majority of the  $\text{Eu}^{3+}$  dopant ions are substituting for the larger sized  $\text{Na}^+$  ions. However, the shift was less in the case of  $\text{KNbO}_3$  and, as discussed earlier, the major portion of the  $\text{Eu}^{3+}$  ions had the possibility to go to the  $\text{Nb}^{5+}$  site as observed in the PL lifetime study. Generally XRD does not give accurate information at the atomic scale unlike PL and EXAFS studies, which are very useful to extract such information. From the PL lifetime and TRES study, we already concluded that in  $\text{KNbO}_3$ , the majority of  $\text{Eu}^{3+}$  ions prefer to go to the Nb site, while in  $\text{NaNbO}_3$ , they have a preference for the Na site. Now as far as the ferroelectric property is concerned, substitution at only Na or K sites may have a direct impact on the ferroelectric property, since the off-centring of  $\text{Nb}^{5+}$  cations from the centrosymmetric positions in the  $\text{NbO}_6$  octahedron is the main reason for such a property and the substitution at Na or K sites may alter the off-centre position of  $\text{Nb}^{5+}$  cations. Therefore, the substitution of  $\text{Eu}^{3+}$  ions at Na sites might be the reason for the enhanced remnant polarization in  $\text{NaNbO}_3$ , since such substitution may help to increase the off-centring parameter. The fact that substitution at the Na site in  $\text{NaNbO}_3$  may induce more disorder was also supported by an earlier EXAFS study.<sup>32</sup> On the other hand in  $\text{KNbO}_3$ , since most of the  $\text{Eu}^{3+}$  ions go to comparatively more symmetric Nb sites, such off-centring might be reduced, and might thereby reduce the remnant polarization. Let us now try to explain the increase in ferroelectric properties by Goldschmidt's tolerance factor ' $t$ ', which is defined as  $t = R_{\text{A-O}}/\sqrt{2} (R_{\text{B-O}})$ , where  $R_{\text{A-O}}$  and  $R_{\text{B-O}}$  are A-O and B-O bond lengths in  $\text{ABO}_3$  perovskite. As per various studies, tilting of the  $\text{BO}_6$  octahedron in  $\text{ABO}_3$ -type perovskites appears when  $t$  is below 1, while tilts do not exist when  $t \geq 1$ .<sup>41</sup> The  $t$  values for  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  were 0.96 and 1.06, respectively.<sup>42</sup> In  $\text{NaNbO}_3$ , the tilting of  $\text{NbO}_6$  octahedra occurs due to the relatively small size of Na atoms ( $r_{\text{Na}^+} = 1.39 \text{ \AA}$ ), which are placed in the 12-fold-coordinated cavities between the  $\text{BO}_6$  octahedra. On the other hand in  $\text{KNbO}_3$ , due to the larger size of K cations ( $r_{\text{K}^+} = 1.64 \text{ \AA}$ ), they fit well inside the cavities and

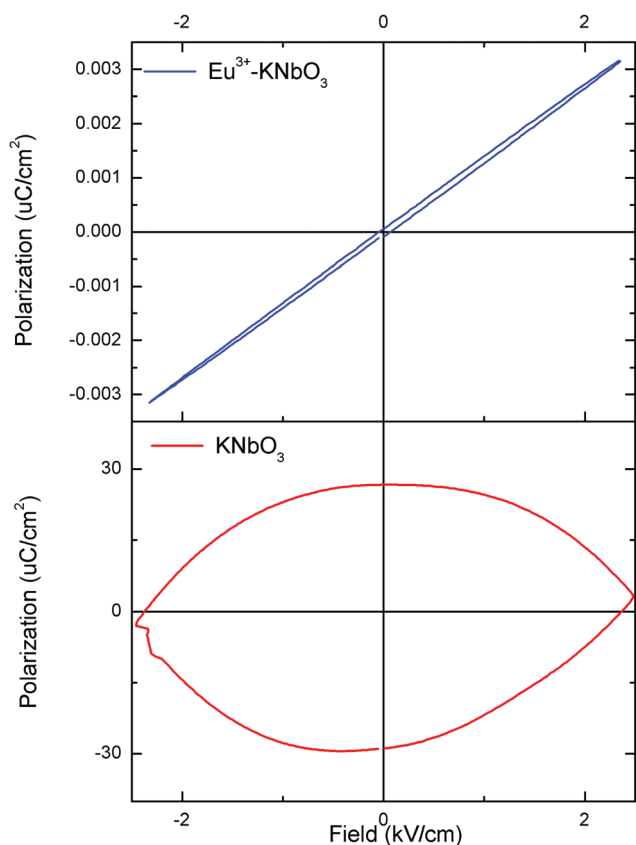


Fig. 10 Ferroelectric ( $P$ - $E$ ) hysteresis loops for undoped  $\text{KNbO}_3$  and the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound at a field of  $5 \text{ kV cm}^{-1}$ .



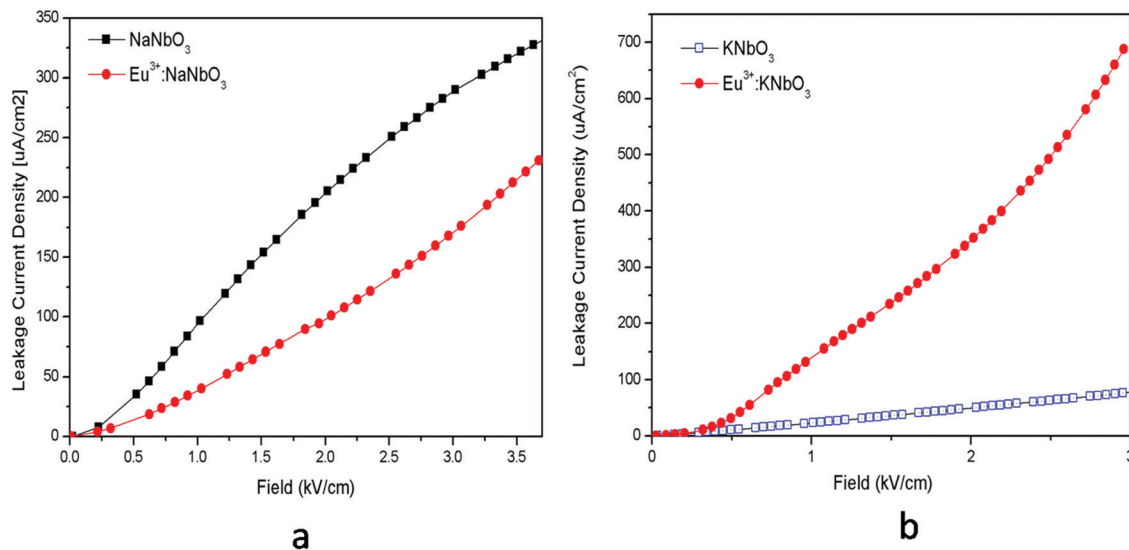


Fig. 11 Leakage current density vs. field for: (a)  $\text{NaNbO}_3$  and  $\text{Eu}^{3+}:\text{NaNbO}_3$  compounds and for (b)  $\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  compounds.

the tilting of the  $\text{NbO}_6$  octahedron is not present. This was also reflected in the higher intensity of the MD line of  $\text{Eu}^{3+}$  ions in  $\text{KNbO}_3$ , suggesting a more ordered structure compared to  $\text{NaNbO}_3$ . Therefore, the observed ferroelectric property of  $\text{KNbO}_3$  was purely due to the inherent off-centre of  $\text{Nb}^{5+}$  from the centrosymmetric positions and tilting played no role in further increasing such an off-centre position of  $\text{Nb}^{5+}$  ions, like in  $\text{NaNbO}_3$ . In  $\text{NaNbO}_3$ , as smaller sized  $\text{Eu}^{3+}$  ions are doped at the Na site, the  $t$  values might be further reduced from the value of 0.96 and this increases the tilting of  $\text{NbO}_6$  octahedra, which makes the  $\text{Nb}^{5+}$  ions more off-centred from the centrosymmetric positions. On the contrary in  $\text{KNbO}_3$ , the larger sized  $\text{Eu}^{3+}$  ions may be preferably placed at  $\text{Nb}^{5+}$  sites, since the size difference with  $\text{K}^+$  ions is more here. These larger size  $\text{Eu}^{3+}$  ions in the place of smaller sized  $\text{Nb}^{5+}$  ions may reduce the off-centring of  $\text{Nb}^{5+}$  ions in the nearby  $\text{NbO}_6$ . To get more evidence we carried out an EXAFS study.

The leakage current density can be explained based on defect centres. It could be observed that for both the  $\text{Eu}^{3+}:\text{NaNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  compounds, there was a prominent host emission band along with the  $\text{Eu}^{3+}$  ion's emission. These host emission bands were created due to the presence of several oxygen vacancies or defect centres, which may create many shallow or deep trap states inside the band gap as reported earlier.<sup>12</sup> It was also observed that the host emission peaks maxima were mostly comparable to that of the  $\text{Eu}^{3+}$  ion's emission in  $\text{Eu}^{3+}:\text{KNbO}_3$ ; while in  $\text{Eu}^{3+}:\text{NaNbO}_3$ , although the host's emission bands were clearly visible, their intensity was less compared to the  $\text{Eu}^{3+}$  ion's emission. This indicates that there are more defect centres being created due to  $\text{Eu}^{3+}$  doping in  $\text{KNbO}_3$  compared to that in  $\text{NaNbO}_3$ . Now it is worth mentioning here that these defect centres might be due to the oxygen vacancies,<sup>12</sup> which can be created only when a  $\text{Eu}^{3+}$  ion substitutes at a  $\text{Nb}^{5+}$  site. These defects may increase the ionic conductivity, which causes a higher leakage current density. Therefore, from both saturation polarisation and leakage current density observation, it could be

concluded that while  $\text{Eu}^{3+}$  doping may enhance the  $\text{NaNbO}_3$  compound's performance for application in storage devices, the same doping may reduce such performance for the  $\text{KNbO}_3$  compound.

### 3.3. X-ray absorption spectroscopy studies of undoped and $\text{Eu}^{3+}:\text{NaNbO}_3$ and $\text{Eu}^{3+}:\text{KNbO}_3$ compounds

Extended X-ray absorption fine structure (EXAFS) techniques were performed on  $\text{Eu}^{3+}:\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{NaNbO}_3$  samples at the Nb K-edge and Eu  $L_3$  edge to probe the local structure. The measurements were carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 200 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.<sup>43,44</sup> This beamline operates in the energy range of 4 KeV to 25 KeV. The beamline optics consists of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si(111) ( $2d = 6.2709 \text{ \AA}$ )-based double-crystal monochromator (DCM). The second crystal of DCM is a sagittal cylinder used for horizontal focusing, while a Rh/Pt coated bendable post mirror facing down is used for vertical focusing of the beam at the sample position. Rejection of the higher harmonics content in the X-ray beam was performed by detuning the second crystal of DCM. In the case of the Nb K edge, XAS measurements were performed in transmission mode and for the Eu  $L_3$  edge, the measurements were done in fluorescence mode.

The local structure around the absorbing atom was obtained from the quantitative analysis of the EXAFS spectra. The EXAFS spectrum was obtained from the absorption spectrum using the following method. In order to take care of the oscillations in the absorption spectrum,  $\mu(E)$  was converted to the absorption function  $\chi(E)$ , defined as follows:<sup>45</sup>

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)} \quad (2)$$



where,  $E_0$  is the absorption edge energy,  $\mu_0(E_0)$  is the bare atom background and  $\Delta\mu_0(E_0)$  is the step in  $\mu(E)$  value at the absorption edge. The energy-dependent absorption coefficient  $\chi(E)$  was converted to the wave-number-dependent absorption coefficient  $\chi(k)$  using the relation,

$$K = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (3)$$

where,  $m$  is the electron mass.  $\chi(k)$  is weighted by  $k^2$  to amplify the oscillation at high  $k$  and the  $\chi(k)k^2$  functions are Fourier transformed in  $R$  space to generate the  $\chi(R)$  versus  $R$  spectra in terms of the real distances from the centre of the absorbing atom. The set of EXAFS data analysis programmes available within the Demeter software package were used for the EXAFS data analysis.<sup>46</sup> This included background reduction and Fourier transform to derive the  $\chi(R)$  versus  $R$  spectra from the absorption spectra (using ATHENA software), generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of the experimental data with the theoretical spectra using ARTEMIS software.

**Eu<sup>3+</sup>:NaNbO<sub>3</sub>.** The normalised absorption spectra at the Nb K edge and Eu L<sub>3</sub> edge are shown in Fig. 12 for NaNbO<sub>3</sub> and Eu<sup>3+</sup>:NaNbO<sub>3</sub>. The  $\chi(R)$  versus  $R$  plots were generated using Fourier transform from the  $\mu(E)$  versus  $E$  spectra following the methodology as described above and are shown in Fig. 13, which shows the phase-uncorrected spectra, where the coordination peak in the Fourier transform spectra appeared at a slightly lower  $R$  compared to the actual bond length. For quantitative information, experimental  $\chi(R)$  versus  $R$  plots were

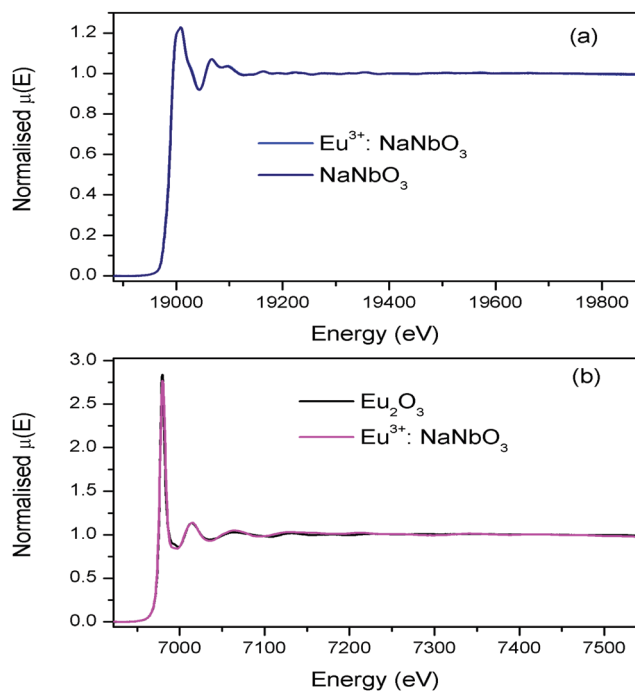


Fig. 12 (a) Nb K-edge normalised absorption spectra of NaNbO<sub>3</sub> and Eu<sup>3+</sup>:NaNbO<sub>3</sub>; (b) Eu L<sub>3</sub> edge normalised absorption spectra of Eu<sub>2</sub>O<sub>3</sub> and Eu<sup>3+</sup>:NaNbO<sub>3</sub>.

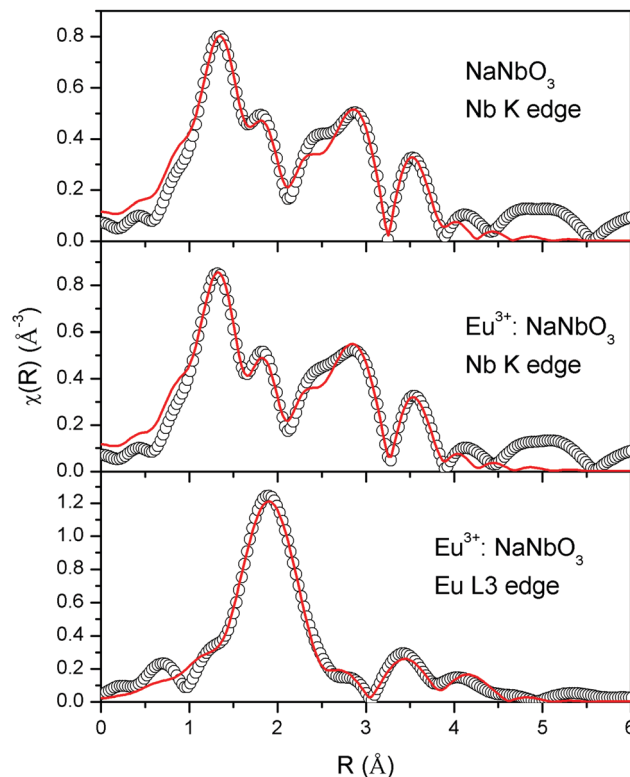


Fig. 13 Fourier transformed EXAFS spectra of NaNbO<sub>3</sub> and Eu<sup>3+</sup>:NaNbO<sub>3</sub>. The experimental spectra are represented by scatter points and the theoretical fit is represented by the solid line.

Table 2 Bond lengths, coordination numbers and disorder factors obtained by EXAFS fitting at the Nb K-edge and Eu L<sub>3</sub> edge of Eu<sup>3+</sup>:NaNbO<sub>3</sub>

NaNbO <sub>3</sub> Nb edge	Eu <sup>3+</sup> :NaNbO <sub>3</sub> Nb edge			Eu <sup>3+</sup> :NaNbO <sub>3</sub> Eu edge						
	Path	$R$ (Å)	$N$ $\sigma^2$	Path	$R$ (Å)	$N$ $\sigma^2$	Path	$R$ (Å)	$N$ $\sigma^2$	
Nb–O	1.86	2	0.0152	1.86	2	0.0151	Eu–O	2.32	2	0.0011
Nb–O	1.93	2	0.0024	1.91	2	0.0027	Eu–O	2.46	4	0.0053
Nb–O	2.12	2	0.0024	2.12	2	0.0027	Eu–Na	3.66	3	0.0151
Nb–Na	3.39	5	0.010	3.37	5	0.010	Eu–Nb	4.31	6	0.0188
Nb–Nb	3.82	6	0.0256	3.81	6	0.0254				
Nb–O	4.14	6	0.0135	4.12	6	0.0112				

fitted with theoretical plots, generated using the structural parameters (atomic coordination and lattice parameters) of NaNbO<sub>3</sub> obtained from the ICSD data base.<sup>47,48</sup> The bond length and disorder factor ( $\sigma^2$ ) were the fitting parameters obtained during the above analysis. The fitting results are shown in Table 2 and the fitted spectra are plotted in Fig. 13. The doublet peak between 1 Å and 2 Å was a contribution of three oxygen coordination distances at 1.86, 1.93 and 2.12 Å, respectively. The second doublet peak between 2–3.25 Å was contribution of Nb–Na coordination at a distance of 3.39 Å. The third coordination peak at 3.5 Å was contribution of Nb–Nb, Nb–O and multiple scattering paths. Similarly, the Nb coordination behaviour was also obtained for Eu<sup>3+</sup>:NaNbO<sub>3</sub> (middle panel). The Fourier transform EXAFS spectrum of the Eu L<sub>3</sub>





edge is shown in Fig. 13 (lower panel). The first coordination peak is a contribution of two oxygen coordination shells at 2.32 and 2.46 Å. This Eu–O bond distance was larger than the Nb–O bond length. This was expected due to the relatively larger ionic radius of  $\text{Eu}^{3+}$ . The second peak at 3.5 Å was a contribution of Eu–Na and Eu–Nb coordination with a large distortion (larger  $\sigma^2$ ).

**$\text{Eu}^{3+}:\text{KNbO}_3$ .** The normalised absorption spectra at the Nb K edge and Eu  $L_3$  edge are shown in Fig. 14 for  $\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  compounds. The  $\chi(R)$  versus  $R$  plots generated using Fourier transform from the  $\mu(E)$  versus  $E$  spectra following the methodology as described above are shown in Fig. 15, which shows the phase-uncorrected spectra, where the coordination peak in the Fourier transform spectra appeared at a slightly lower  $R$  compared to the actual bond length. For quantitative information, experimental  $\chi(R)$  versus  $R$  plots were fitted with theoretical plots generated using the structural parameters (atomic coordination and lattice parameters) of  $\text{KNbO}_3$  obtained from the ICSD data base.<sup>49</sup> The fitting results are shown in Table 3 and the fitted spectra are plotted in Fig. 15. The Fourier transform EXAFS spectra of  $\text{KNbO}_3$  showed a multiple number of coordination peaks. The first doublet peak between 1 and 2 Å was due to a contribution of three oxygen coordination at the distances of 1.87, 2.04 and 2.08 Å. The triplet peak between 3.5 and 4.25 Å was due to a contribution of Nb–K, Nb–Nb and multiple scattering paths. The coordination peaks were similar for  $\text{Eu}^{3+}:\text{KNbO}_3$ . The Fourier

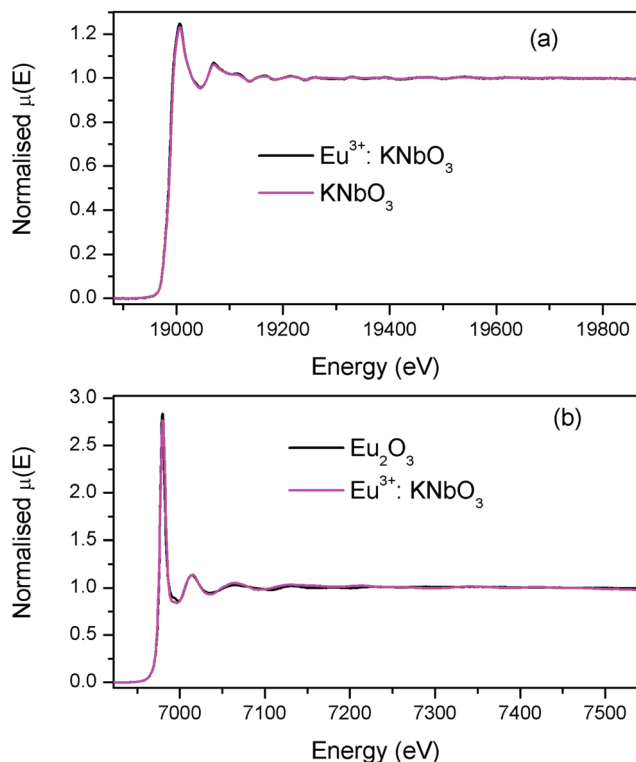


Fig. 14 (a) Nb K-edge normalised absorption spectra of  $\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$ ; (b) Eu  $L_3$  edge normalised absorption spectra of  $\text{Eu}_2\text{O}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$ .

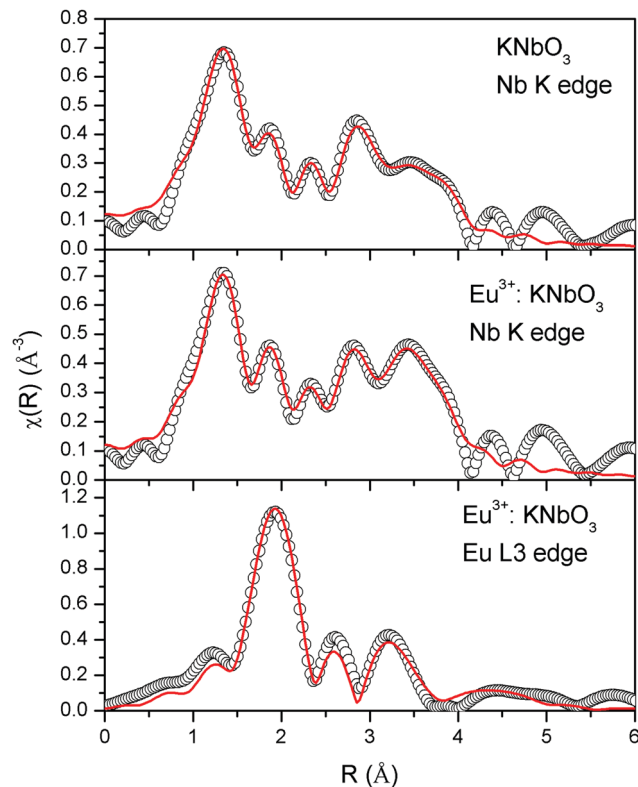


Fig. 15 Fourier transformed EXAFS spectra of  $\text{KNbO}_3$  and  $\text{Eu}^{3+}:\text{KNbO}_3$  compounds. The experimental spectra are represented by scatter points and the theoretical fitting is represented by the solid line.

Table 3 Bond lengths, coordination numbers and disorder factors obtained by EXAFS fitting at the Nb K-edge and Eu  $L_3$  edge of  $\text{Eu}^{3+}:\text{KNbO}_3$

Path	$\text{KNbO}_3$ Nb edge				$\text{Eu}^{3+}:\text{KNbO}_3$ Nb edge				$\text{Eu}^{3+}:\text{KNbO}_3$ Eu edge			
	$R$ (Å)	$N$	$\sigma^2$		$R$ (Å)	$N$	$\sigma^2$		Path	$R$ (Å)	$N$	$\sigma^2$
Nb–O	1.87	2	0.0030		1.88	2	0.0012		Eu–O	2.45	4	0.0017
Nb–O	2.04	2	0.0142		2.04	2	0.0015		Eu–O	2.71	2	0.0010
Nb–O	2.08	2	0.0091		2.09	2	0.0045		Eu–K	3.82	6	0.0185
Nb–K	3.60	6	0.0017		3.62	6	0.011		Eu–Nb	4.57	6	0.0201
Nb–Nb	3.83	6	0.0010		3.89	6	0.0010					
Nb–O	4.43	4	0.0089		4.40	4	0.0087					

transform EXAFS spectra at the Eu  $L_3$  edge is shown in Fig. 15 (lower panel). The first peak at 2.0 Å is a contribution of two Eu–O coordination at 2.45 and 2.71 Å. The second and third peaks were fitted with Eu–K and Eu–Nb coordination at 3.82 and 4.57 Å, respectively. The obtained Eu–O bond length was relatively larger than the Nb–O bond length due to the larger ionic radius of the  $\text{Eu}^{3+}$  ion.

From the observed parameters from the EXAFS study as included in Tables 2 and 3, it can be seen that the distortion parameter  $\sigma^2$  for the Nb–O bonds were greater for the  $\text{NaNbO}_3$  compounds than the  $\text{KNbO}_3$  compounds, which supports the higher polar character of the  $\text{NaNbO}_3$  compounds compared to the  $\text{KNbO}_3$  compounds. Further in  $\text{NaNbO}_3$ , upon  $\text{Eu}^{3+}$  doping, the  $\sigma^2$  value for some of the Nb–O bonds was found to increase slightly. This confirmed that  $\text{Eu}^{3+}$  ions induced more distortion



in  $\text{NaNbO}_3$ , leading to a higher polar character. On the contrary in  $\text{KNbO}_3$ , upon  $\text{Eu}^{3+}$  doping, the  $\sigma^2$  value for some of the Nb–O bonds was found to decrease significantly. This suggests that the compounds became less distorted. Thus, the EXAFS results strongly support our conclusion that it is the preference of site occupancy of the  $\text{Eu}^{3+}$  dopant ion that changes the local distortion in these compounds, thereby controlling their electrical properties.

## 4.0 Conclusion

Undoped and  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  compounds were synthesised through a solid-state method followed by their characterisation using XRD, FTIR, PL, electrical and EXAFS studies. The PL study revealed that the  $\text{Eu}^{3+}:\text{NaNbO}_3$  compound was a pink-colour-emitting phosphor, where the bluish emission from the host in combination with the red emission from the  $\text{Eu}^{3+}$  ion gave rise to the pink colour. On the contrary, the  $\text{Eu}^{3+}:\text{KNbO}_3$  compound was a white-light-emitting material and such a single-phase white-light-emitting material has several advantages over the others. Host emission in this compound is very prominent and superimposed with the  $\text{Eu}^{3+}$  ion's emission, making it difficult to analyse the characteristics peaks of the  $\text{Eu}^{3+}$  ion. However, with the help of TRES study, it was possible to isolate both the host and  $\text{Eu}^{3+}$  ion's emission and a clear picture about the transition lines of the  $\text{Eu}^{3+}$  ions were observed. From the respective transition lines (ED and MD) and their variation in  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  compounds, it was observed that the asymmetric character surrounding the  $\text{Eu}^{3+}$  ion was greater in  $\text{NaNbO}_3$ , while it was less in  $\text{KNbO}_3$ . Further, from the PL lifetime study, it was observed that multiple  $\text{Eu}^{3+}$  components existed in both the compounds. However, the distribution of  $\text{Eu}^{3+}$  ions was greater in the asymmetric environment in the  $\text{NaNbO}_3$  compound, while in case of  $\text{KNbO}_3$ , they preferably went into the symmetric environment. We concluded that in  $\text{NaNbO}_3$ , most of the  $\text{Eu}^{3+}$  ions go to the Na lattice site, while in  $\text{KNbO}_3$ , they go to the K site. Electrical study of these compounds showed that they were ferroelectric in nature and the  $\text{Eu}^{3+}$  doping had a huge impact on the remnant polarization. In the  $\text{Eu}^{3+}$ -doped  $\text{NaNbO}_3$  compound, the polarization value was found to increase upon  $\text{Eu}^{3+}$ -ion doping. However, for the  $\text{KNbO}_3$  compound, there was a drastic decrease in the remnant polarization from the undoped compound. Tilting of the  $\text{NbO}_6$  octahedron, which arose due to the mismatch of the size of A and B cations in  $\text{ABO}_3$ -type perovskites made the  $\text{Nb}^{5+}$  cation relatively off-centre from the centrosymmetric position in the  $\text{NbO}_6$  octahedron and responsible for such ferroelectric behaviour. More, the distortion in  $\text{NbO}_6$  octahedron impacted more the polarisation characteristics. From EXAFS study, it was observed that the distortion parameter  $\sigma^2$  for the Nb–O bonds of the  $\text{NbO}_6$  octahedron in  $\text{NaNbO}_3$  compounds was increased when  $\text{Eu}^{3+}$  ions were doped. On the contrary, the same was decreased in  $\text{KNbO}_3$ . Thus, we concluded that the  $\text{Eu}^{3+}$  ion's substitution at the Na site induced more distortion in nearby  $\text{NbO}_6$  octahedra and was responsible for the increase in remnant polarization. On the contrary, in  $\text{KNbO}_3$ ,

$\text{Eu}^{3+}$ -ion substitution at the Nb site basically reduced the distortion in nearby  $\text{NbO}_6$  octahedra compared to that in the undoped compound and thus led to a decrease in polarization.

## Conflicts of interest

All the authors hereby declare that they have no conflicts of interest.

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