

# Anion Effect on the Thermometric Properties of Near-Infrared Emitting $Mn^{5+}$ -Activated $Sr_5(PO_4)_3X$ ( $X = F, Cl, Br$ ) Apatite Phosphors

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**Near-infrared emitting  $Mn^{5+}$ -activated phosphors are recently recognized as promising thermal sensors for biological applications. However, guidelines to predict suitable hosts with optimal temperature sensing ability are still missing. In this view, the indirect effect of the different halides on the  $3d^2$  electrons of the  $Mn^{5+}$  ions in different  $Sr_5(PO_4)_3X$  apatites ( $X = F, Cl$ , and  $Br$ ) is deeply investigated through a combined experimental and theoretical approach. The temperature dependence of the PL and decay curves allows to simultaneously get information about the electron-phonon coupling and the potential application as optical thermometers, showing promising results in terms of relative sensitivity. Boltzmann-based and lifetime-based thermometry ensure a unique reliability, and the simultaneous use of the ratio between the emission originating from the  $^3T_1$  and  $^1E$  excited states and the split components of the  $^1E$  ( $E_1$  and  $E_2$ ) state allows to enlarge the temperature range of applicability of the thermometers from cryogenic to high temperature. The local  $[PO_4]^{3-}$  tetrahedral geometry in the halide apatites drives their thermometric properties, showing interesting results in terms of sensitivity, particularly for the bromide  $Sr_5(PO_4)_3Br:Mn^{5+}$  phosphor. Moreover, the high quantum efficiencies estimated at room temperature support the potential use in real applications of this family of NIR phosphors.**

## 1. Introduction

$Mn^{5+}$  ions stabilized in insulating host materials have been attracting a lot of interest for a long time due to their optical properties exploited for pigments and investigated as promising near-infrared (NIR) lasers. Indeed, intense and bright colours ranging from blue to green can be obtained by incorporating  $Mn^{5+}$  into tetrahedral sites of phosphates, vanadates, and arsenides.<sup>[1-5]</sup>  $Mn^{5+}$  ions are characterized by a  $3d^2$  electron configuration, isoelectronic to  $Ti^{2+}$ ,  $V^{3+}$ ,  $Cr^{4+}$ , and  $Fe^{6+}$ . As in the case of the small  $Fe^{6+}$ ,  $Mn^{5+}$  ions have a strong preference for the tetrahedral  $MnO_4^{3-}$  configuration.<sup>[6]</sup> Since the first detailed spectroscopic report about the luminescence of  $Mn^{5+}$  ions in  $Ca_2PO_4Cl$  spodiosite and  $Ca_5(PO_4)_3Cl$  apatite by J. D. Kingsley et al. 60 years ago,<sup>[7]</sup>  $Mn^{5+}$ -activated phosphors were thoroughly investigated demonstrating the presence of a strong charge transfer in the absorption/excitation

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spectra in addition to the typical d-d transitions.<sup>[8–16]</sup> Considering the ionic radii, the oxidation state, and the tetrahedral coordination, the most common hosts reported so far are phosphates and vanadates. However, silicates and germanates such as  $\text{Y}_2\text{SiO}_5$ ,<sup>[17]</sup>  $\text{M}_2\text{SiO}_4$  with  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ,<sup>[12,18]</sup> and  $\text{Ba}_2(\text{Si},\text{Ge})\text{O}_4$ ,<sup>[19]</sup> or aluminates such as  $\text{YAlO}_3$  perovskite<sup>[20,21]</sup> were also reported. The sharp NIR emission originated from the spin-forbidden  $^1\text{E} \rightarrow ^3\text{A}_2$  transition makes these materials particularly appealing for NIR lasers<sup>[22–26]</sup> with  $\text{Ba}_3(\text{VO}_4)_2:\text{Mn}^{5+}$  being the first example of  $\text{Mn}^{5+}$ -activated material showing laser action.<sup>[27]</sup> More recently, a renewed interest has been demonstrated in this family of phosphors for applications as NIR-II contrast agents,<sup>[28]</sup> narrow-band NIR LEDs,<sup>[29]</sup> and luminescent thermal sensing.<sup>[19, 30–37]</sup>

The use of luminescence signals to probe temperature is particularly promising due to the possibility of a remote technology, with suitable sensitivity, good thermal resolution, reproducibility, and unique reliability.<sup>[38–40]</sup> Among the wide variety of techniques for thermal sensing, involving the use of a peak broadening, shift, intensity, or lifetime variation, the use of the ratiometric concept employing the ratio between the signals from two excited states or the temperature dependence lifetimes of the excited states are well recognized among the most reliable ones. The so-called Boltzmann thermometers rely on the Boltzmann law between the populations of two thermally coupled excited states, which have been widely investigated for materials doped with  $\text{Er}^{3+}$ ,<sup>[41,42]</sup>  $\text{Nd}^{3+}$ ,<sup>[43,44]</sup> and  $\text{Cr}^{3+}$ ,<sup>[45,46]</sup> demonstrating their reliable applicability in a wide range of technological fields. Moreover, the interest in temperature sensing through luminescence signals is becoming particularly important not only from an academic point of view, with examples of applications to probe intracellular temperature,<sup>[47,48]</sup> temperature of catalytic processes,<sup>[49–51]</sup> and in microfluidic,<sup>[52]</sup> to name a few.

In this framework,  $\text{Mn}^{5+}$ -doped phosphors have been recently recognized as promising thermal probes working in the biological windows (BWs) with the additional advantage with respect to other NIR emitting materials, such as  $\text{Nd}^{3+}$  or  $\text{Er}^{3+}$ -doped systems, to be characterized by broad and efficient excitations also falling into the BWs, particularly suitable for biological applications. In addition,  $\text{Mn}^{5+}$ -activated nanoparticles have been demonstrated to resist photochemical degradation.<sup>[28,53]</sup> However, no general rules for the prediction and design of effective  $\text{Mn}^{5+}$ -activated phosphors for NIR thermometry have been reported so far, remaining a challenge. With the aim to bridge this gap, in this work we investigate the correlation between the local tetrahedral  $\text{MnO}_4^{3-}$  site, the electronic structure, and the thermometric properties of the  $\text{Sr}_5(\text{PO}_4)_3\text{X}:\text{Mn}^{5+}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) halide apatites, considered as prototypes. A combined experimental and theoretical approach is used to try to disclose the local structure-optical relationship, allowing the optimization of the sensitivity and the expansion of the temperature range of applicability.

## 2. Results and Discussion

With the aim of optimizing the luminescent properties, at first, a series of  $\text{Sr}_5(\text{P}_{1-y}\text{Mn}_y\text{O}_4)_3\text{X}$  phosphors ( $\text{X} = \text{F}, \text{Cl}$ , and  $\text{Br}$ ) with  $y = 0.0000, 0.0010, 0.0100, 0.0125, 0.0166, 0.0250$ , and  $0.0500$  was prepared by molten-salt synthesis. The stabilization of the strontium halogen apatite structure was confirmed for all samples by X-ray powder diffraction (XRPD) (Figure S1a-c, Supporting In-

formation) while the photoluminescence emission (PL) intensity signals as a function of the Mn content showed that the best PL is obtained for the samples with  $y = 0.0166$  in bromide, chloride, and fluoride samples (from now labelled as  $\text{Sr}_5(\text{PO}_4)_3\text{X}:\text{Mn}^{5+}$ ). These materials were considered as prototypes to evaluate the effect of the local crystal structure in these series of halide apatites on the thermometric performance in the NIR window.

### 2.1. Crystalline Structure and Local Tetrahedral Site Investigation

The XRPD patterns of the three apatites show a good matching with the ICSD references of the hexagonal structure ( $P6_3/m$  space group, No. 176) in terms of diffraction peaks position (ICSD#95737 for  $\text{Sr}_5(\text{PO}_4)_3\text{F}$ , ICSD#2089 for  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ , and ICSD#253054 for  $\text{Sr}_5(\text{PO}_4)_3\text{Br}$ ), although an evident difference in terms of relative peak intensities for the fluoride and chloride apatites is observed (Figure 1a-c). In order to elucidate this behavior, Rietveld refinements, including the March-Dollase approach to consider possible preferred orientations along the (001) direction, were performed (see Experimental Section).<sup>[54,55]</sup> A March-Dollase parameter of 1.00, 1.12, and 1.60 was obtained through the Rietveld refinement for the bromide, chloride, and fluoride samples, respectively. The  $c$ -axis preferential orientation suggested for the fluoride and chloride agrees with the conventional habitus adopted by the apatite crystals, as confirmed by the SEM images of the chloride and fluoride apatites (Figure S2a,b, Supporting Information). It is worth noting that the apatite structures are characterized by a single tetrahedral  $[\text{PO}_4]^{3-}$  site for the substitution of  $\text{Mn}^{5+}$  ions (Figure 1d,e). Considering the structures obtained from the Rietveld refinements (see the parameters estimated in Tables S1-S3, Supporting Information), the average  $\langle \text{P}-\text{O} \rangle$  bond length, the polyhedral distortion index  $D$ , and the  $T_d$ -distortion angle  $\delta$  of the tetrahedral  $T_d$  sites were calculated as:<sup>[4,56]</sup>

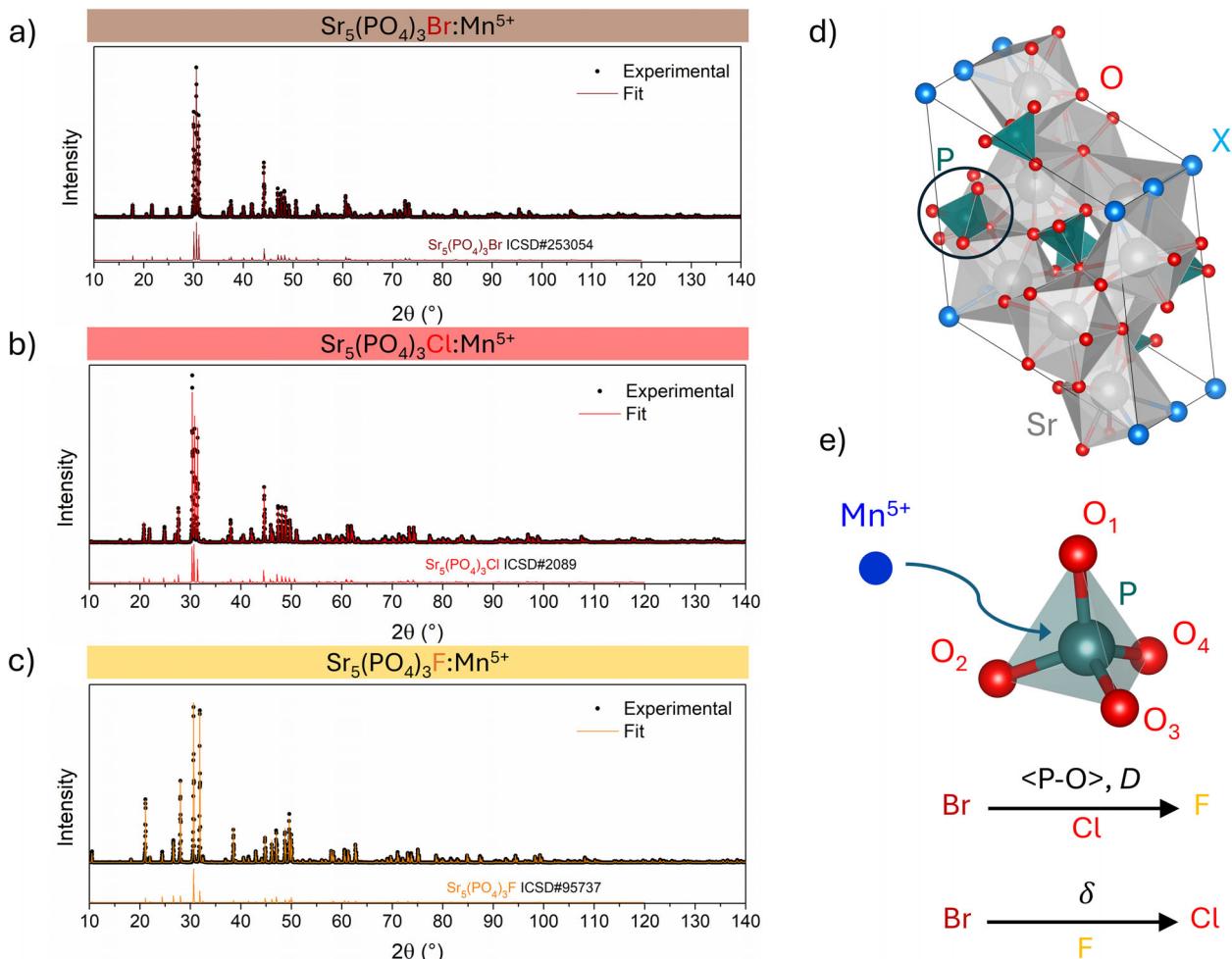
$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}} \quad (1)$$

$$\delta = \frac{1}{6} \sum_{i=1}^6 |\theta_i - 2\theta_t| \quad (2)$$

where  $n = 4$  for the tetrahedral sites,  $l_i$  is the bond length between the central cation and the  $i^{\text{th}}$  coordination ligand,  $l_{av} = \langle \text{P}-\text{O} \rangle$  is the average bond length, and  $2\theta_t$  is the tetrahedral angle. The values calculated for the apatites are summarized in Table 1. The distortion index  $D$  shows a relative increase moving from bromide to chloride and fluoride. On the other hand, the deviation from the  $T_d$  geometry in terms of distortion angle  $\delta$  evidences a different behavior with an increasing value moving from bromide to fluoride and finally chloride.

### 2.2. Optical Properties and Electronic Structure: Tanabe-Sugano Diagram and Exchange Charge Model

Figure 2a shows the room temperature PL and photoluminescence excitation (PLE) spectra of  $\text{Mn}^{5+}$  ions in the samples.



**Figure 1.** a-c) XRPD pattern and Rietveld refinements of the  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  apatites along with ICSD references. d) Crystalline structure of  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  apatites. e) Sketch of the local tetrahedral  $[\text{PO}_4]^{3-}$  site for the stabilization of  $\text{Mn}^{5+}$  ions along with the average  $\langle \text{P}-\text{O} \rangle$  bond length, the distortion index  $D$ , and the distortion angle  $\delta$  as a function of the halide in the apatite structures.

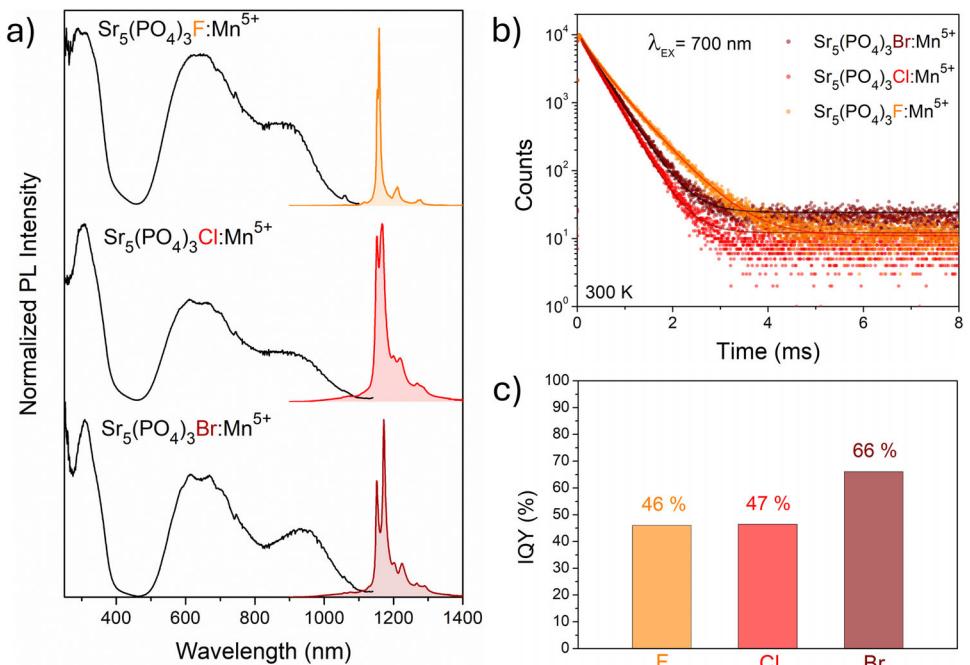
The sharp PL spectra are characteristic of the strong crystal field due to the  $^1\text{E} \rightarrow ^3\text{A}_2$  transitions. The ground state ( $^3\text{A}_2$ ) is non-degenerate, derived from the  $\text{e}^2$  strong field configuration, while the  $^1\text{E}$  excited state has an  $\text{e}^2$  configuration which can be split into two components  $E_1$  ( $E_{z^2}$ ) and  $E_2$  ( $E_{x^2} - E_{y^2}$ ) by the low symmetry ligand field. On the other hand, the excitation spectra are composed by a series of broadbands with at least three main components due to the  $^3\text{A}_2 \rightarrow ^3\text{T}_2$ ,  $^3\text{A}_2 \rightarrow ^3\text{T}_1$  transitions and charge transfer (CT) band around 900, 600, and

300 nm, respectively. It is worth mentioning that all the samples not only emit in the second biological window at  $\approx 1200$  nm, but they can also be efficiently excited in the first biological window<sup>[57]</sup> (from now on, all the measurements are performed exciting at 700 nm). The PL decay curves (Figure 2b) can be fit by a single exponential showing  $^1\text{E}$  excited state lifetimes in the order of hundreds of microseconds (399, 386, and 498  $\mu\text{s}$  for bromide, chloride, and fluoride apatite, respectively) in agreement with the typical values reported in the literature. On the other hand, as summarized in Figure 2c, remarkable internal quantum efficiencies (IQE) of  $46\% \pm 5\%$ ,  $47\% \pm 5\%$  and  $66\% \pm 5\%$  are obtained at room temperature for  $\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Mn}^{5+}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Mn}^{5+}$ , and  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$ , respectively, suggesting effective potential for practical applications.

The analysis of the crystalline environment effect on the Mn<sup>5+</sup> electrons can be performed by means of the Tanabe-Sugano theory by employing the diagram for the  $3\text{d}^2$  configuration in a tetrahedral site corresponding to the Tanabe-Sugano diagram for the  $3\text{d}^8$  octahedral coordination. In this framework, the crystal field strength  $Dq$  and the Racah parameters  $B$  and  $C$  can be

**Table 1.** Polyhedral distortion index  $D$ ,  $\delta$   $T_d$ -distortion angle, crystal field strength  $Dq$ , Racah parameters  $B$  and  $C$ ,  $C/B$  and  $Dq/B$  values for the Mn<sup>5+</sup>-activated halide apatites.

Sample	$D$	$\delta$ [°]	$Dq$ [ $\text{cm}^{-1}$ ]	$B$ [ $\text{cm}^{-1}$ ]	$C$ [ $\text{cm}^{-1}$ ]	$C/B$	$Dq/B$
$\text{Sr}_5(\text{PO}_4)_3\text{F}$	0.048	2.71	1118	438	2614	5.96	2.55
$\text{Sr}_5(\text{PO}_4)_3\text{Cl}$	0.030	4.31	1101	485	2405	4.96	2.27
$\text{Sr}_5(\text{PO}_4)_3\text{Br}$	0.015	2.30	1067	508	2304	4.53	2.10



**Figure 2.** a) PL and PLE spectra, b) PL decay curves exciting at 700 nm and collecting the  ${}^1\text{E}$  emission with the single exponential fit, and c) IQY of the  $\text{Mn}^{5+}$ -doped  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}$ , and  $\text{Br}$ ) apatite phosphors.

evaluated from the spectroscopic analysis using the following equations:

$$10Dq = E({}^3\text{A}_2 \rightarrow {}^3\text{T}_2) \quad (3)$$

$$B = \frac{x^2 - 10x}{15(x-8)} Dq \text{ with } x = \frac{E({}^3\text{A}_2 \rightarrow {}^3\text{T}_1) - E({}^3\text{A}_2 \rightarrow {}^3\text{T}_2)}{Dq} \quad (4)$$

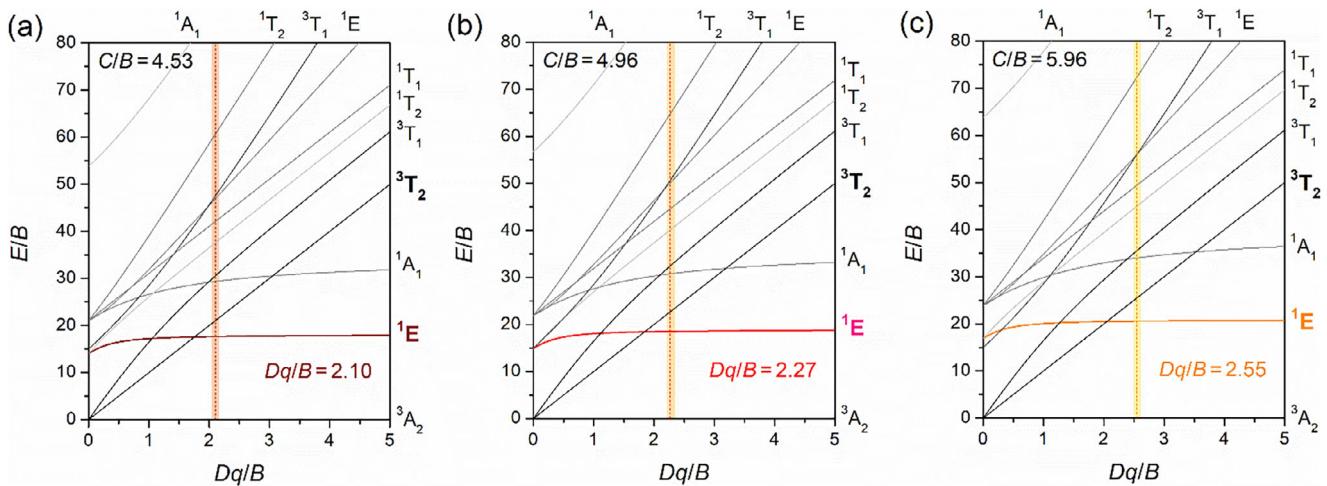
$$C = 0.5 [E({}^3\text{A}_2 \rightarrow {}^1\text{E}) - 10Dq - 8.5B + 0.5\sqrt{400Dq^2 + 40DqB + 49B^2}] \quad (5)$$

A clear blue shift of the low energy PLE broadband assigned to the  ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$  transition is observed moving from the bromo- to the chloro- and fluoro-apatite (Figure 2a) and the same blue shift can be recognized in the  ${}^1\text{E}$  emissions (8632, 8565, and 8532  $\text{cm}^{-1}$  for  $\text{Sr}_5(\text{PO}_4)_3\text{F}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ , and  $\text{Sr}_5(\text{PO}_4)_3\text{Br}$ , respectively). It is interesting to recognize the direct correlation between the energy of the  ${}^1\text{E}$  position and the distortion index  $D$ . The crystal field strength  $Dq$  and Racah parameters  $B$  and  $C$  estimated are also reported in Table 1, showing a relative increase in the  $Dq/B$  values moving from the bromide (2.10) to chloride (2.27), and finally fluoride (2.55) samples.

As demonstrated for other transition metal ions such as  $\text{Cr}^{3+}$ <sup>[58,59]</sup> an accurate comparison of the effect of the crystal field on their energy levels in different hosts based on the Tanabe-Sugano theory can be achieved only by considering the diagrams built for the specific  $C/B$ . The values estimated evidence a large deviation from the original value of 4.50, in particular for the chloride ( $C/B = 4.96$ ) and fluoride ( $C/B = 5.96$ )

samples, in agreement with the larger deviation from the ideal tetrahedral sites demonstrated in terms of both  $D$  and  $\delta$  parameters. Based on the values estimated spectroscopically, the Tanabe-Sugano diagrams for the corresponding  $C/B$  values of the  $3\text{d}^2$  in the tetrahedral sites (corresponding to the  $3\text{d}^8$ ) of the strontium halogen  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  apatites are calculated (Figure 3). Considering the  $Dq/B$  values for the Tanabe-Sugano diagrams plotted for the corresponding  $C/B$ , it is evident that the energy of the  ${}^1\text{E}$  state increases for  $\text{Mn}^{5+}$  ions moving from bromide to chloride and fluoride, in agreement with the PL spectra, and the relative energy gap between the  ${}^1\text{E}$  and  ${}^3\text{T}_2$  levels is also changing but only slightly with respect to the large change predicted by considering the diagram built with  $C/B = 4.50$ .

It must be pointed out that the assignment of the energy position of the broadbands related to the  ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$  and  ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$  transitions is not trivial, leading to values of the crystal field strength  $Dq$  and the Racah parameters  $B$  and  $C$  that are difficult to compare reliably with respect to the literature. In addition, the Tanabe-Sugano theory was developed to describe the splitting of the terms of the free ions for ideal symmetric octahedral or tetrahedral fields (generally defined as cubic crystal fields) being not suitable when large distortions are present. To overcome this limit and go deeper in the investigation of the effect of the local symmetry on the energy levels of  $\text{Mn}^{5+}$  ions, the energy levels and the  $Dq$ ,  $B$ , and  $C$  parameters were calculated by means of the exchange charge model (ECM) of the CF theory<sup>[60-62]</sup> by analysing the experimental spectra and considering the local geometry obtained through the crystalline structure investigation. The results are shown in Figure S3 (Supporting Information), showing a good match between the spectra and the energy levels calculated. Tables S4 and S5 (Supporting Information)



**Figure 3.** Calculated 3d<sup>8</sup> Tanabe-Sugano diagram for the proper C/B values of Mn<sup>5+</sup> in tetrahedral sites for a) Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br:Mn<sup>5+</sup>, b) Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Mn<sup>5+</sup>, and c) Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Mn<sup>5+</sup>.

summarize the crystal field parameters, the Racah parameters, and the energy levels calculated for Mn<sup>5+</sup> ions in the Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>X apatites.

It is worth noting that for an ideal tetrahedral site, the  $B_4^4$  value is 5 times  $B_4^0$  if the crystal field parameters are calculated in the Stevens normalization. However, the  $B_4^4/B_4^0$  ratio is only slightly deviating from this value in the case of the chloride apatite ( $B_4^4/B_4^0 \approx 4$ ), but it is strongly deviating in the case of the fluoride and bromide samples ( $B_4^4/B_4^0 \approx 11$ ).

Due to the unshielded electrons involved in the optical transitions of 3d<sup>2</sup> transition metal ions, the electron-phonon coupling (EPC) plays a critical role in the thermal behavior of their luminescence. To account for the EPC interaction, an effective phonon energy is usually considered. The temperature dependence of the spectral emission shift of the  $^1\text{E} \rightarrow ^3\text{A}_2$  transition in the apatites is investigated in the temperature range of 77–400 K (Figure 4a-c). As the temperature increases from 77 to 400 K, the PL spectra red shift.

The red shift of the zero phonon line (ZPL)  $\Delta E_Z$  is caused by the quadratic interactions of the electrons with acoustic phonons and can be described in the framework of the Debye model as:<sup>[63]</sup>

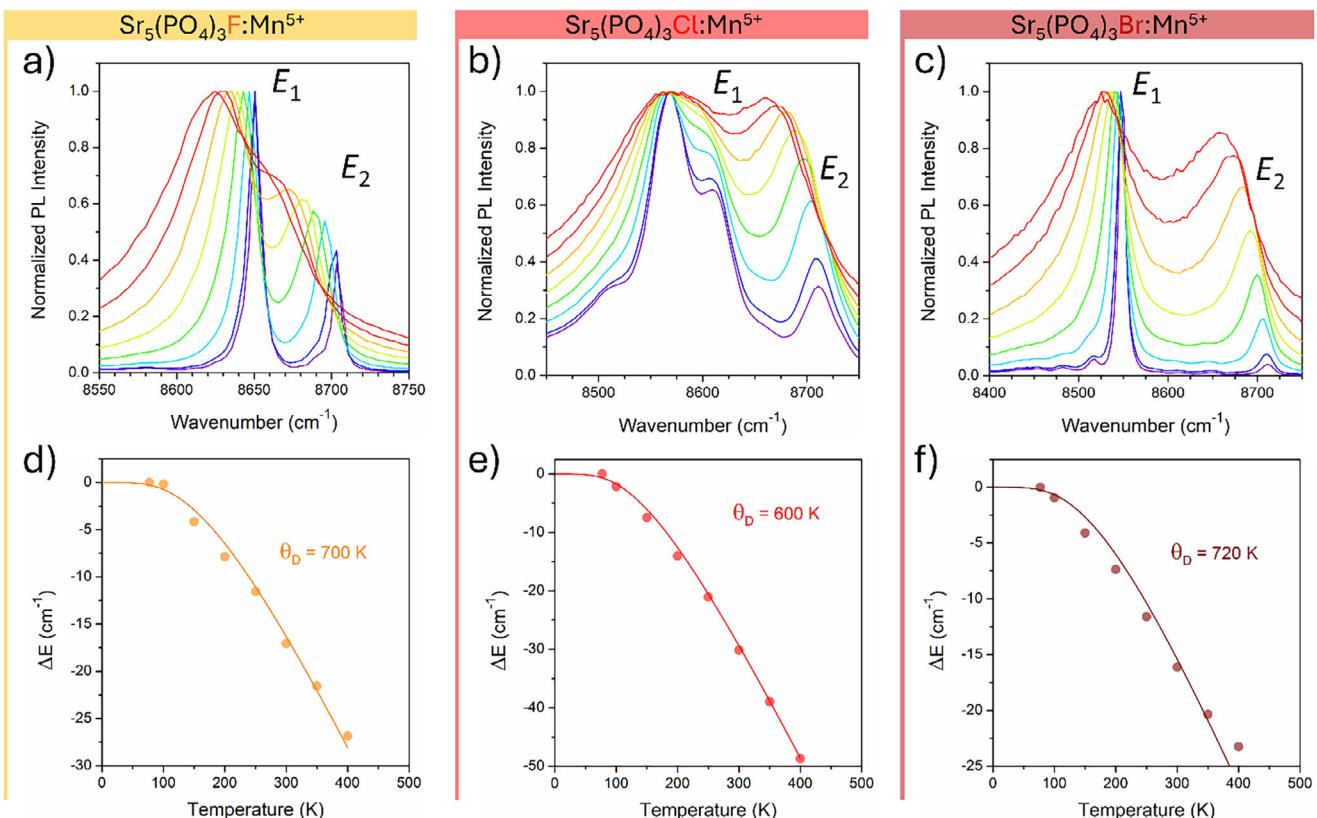
$$\Delta E_Z(T) = \alpha_{EP} \left( \frac{T}{\theta_D} \right)^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \quad (6)$$

where  $\theta_D$  is the Debye temperature,  $\alpha_{EP} = \frac{3k_B\theta_D}{2} \frac{w}{w+1}$  is the electron-phonon coupling parameter (in cm<sup>-1</sup>), and  $w$  is the quadratic coupling constant ( $w > -1$ ). A Debye temperature  $\theta_D$  of 700 K, 600 K, and 720 K can be estimated from the fit of the emission shift for the fluoride, chloride, and bromide-based apatites, respectively (Figure 4d-f). Consequently, the cutoff frequency  $\omega_{\text{cutoff}}$  and the effective phonon energy of Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>X apatites are estimated as  $\hbar\omega_{\text{cutoff}} = k_B \cdot \theta_D$ , giving values of 487 cm<sup>-1</sup>, 417 cm<sup>-1</sup>, and 500 cm<sup>-1</sup> for X = F, Cl, and Br, respectively. These values are slightly lower than those reported for other phosphates such as Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O,<sup>[31]</sup> in agreement with

the effect of halide ions in lowering the phonon energies of materials.

### 2.3. Luminescence Thermometry: From Boltzmann to Lifetime-Based Methods

To access the potential of this family of compounds as optical thermometers, the temperature dependence of the PL spectra was first investigated in the 77–500 K range (Figure 5a-c). The normalized spectra evidence the relative increase between the emission peaks coming from the split components of the  $^1\text{E}$  state (labelled  $E_1$  and  $E_2$ ) as better emphasized in Figure 4a-c. As the temperature increases, the higher lying  $E_2$  state increases with respect to the  $E_1$  state. In addition to this spectral change, as the temperature increases, a growing broadband emission is observed at the base of the  $^1\text{E} \rightarrow ^3\text{A}_2$  transitions. This is assigned to the  $^3\text{T}_2 \rightarrow ^3\text{A}_2$  transition, as reported in other compounds.<sup>[19,31,33,36]</sup> This behavior allows to define two thermometric parameters based on (i) the ratio between the  $^1\text{E}$  components  $LIR_E = I_{E_2}/I_{E_1}$  and (ii) the ratio between the emission originating from the  $^3\text{T}_2$  and  $^1\text{E}$  states  $LIR_{TE} = I_{^3T_2}/I_{^1E}$ . In order to disclose whether the two couples of states used are in thermal equilibrium and, therefore, whether the thermometers follow the Boltzmann law  $LIR = B \cdot \exp(-\Delta E/k_B T)$ , where  $B$  is the electronic constant,  $\Delta E$  the energy gap between the two excited states, and  $k_B$  the Boltzmann constant, the corresponding Boltzmann plots of  $LIR$  versus  $1/T$  were employed (Figure 5d-f). The range of linearity of the thermometers demonstrated their potential and the temperature range of applicability of the Boltzmann thermometers. The thermometers built from the  $^1\text{E}$  split components follow the Boltzmann law in the whole temperature range explored for both the bromide and chloride samples, ensuring a high degree of reliability. In the case of Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Mn<sup>5+</sup>, at temperatures higher than 350 K, the overlap between the emissions originating from the  $^1\text{E}$  split states makes the use of the thermometer difficult. From the linear trends, the energy gap between the  $E_1$  and  $E_2$  energy states  $\Delta E_E$  is calculated to be  $39 \pm 2$ ,



**Figure 4.** a-c) Spectral emission shift of the  ${}^1\text{E}\rightarrow{}^3\text{A}_2$  peaks as a function of temperature in the 77–400 K range and d-f) temperature dependence of the energy shift of the  $E_1$  line of Mn<sup>5+</sup> with fit (solid line) using Equation (6).

$80 \pm 2$ , and  $211 \pm 7$  cm<sup>-1</sup> moving from the fluoride to the chloride and bromide samples, respectively. It is evident that there is a direct correlation between the  $\Delta E_E$  energy gap and the distortion index  $D$  (Table S6, Supporting Information): the smaller the distortion index, the larger the energy gap between the  $E_1$  and  $E_2$  states.

Regarding the thermometers built by considering the ratio between the  ${}^1\text{E}$  and  ${}^3\text{T}_2$ , it must be pointed out that the range of linearity of the Boltzmann law is much narrower than in the case of the  $LIR_E$  (200–500 K for bromide and chloride samples and 250–500 K for the fluoride apatite). This behavior can be explained considering the large energy gap between the excited states, resulting in a weak population of the higher lying  ${}^3\text{T}_2$  state around room temperature. The  $\Delta E_{TE}$  energy gaps are estimated to be  $1160 \pm 15$  cm<sup>-1</sup> for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br:Mn<sup>5+</sup>,  $1000 \pm 10$  cm<sup>-1</sup> for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Mn<sup>5+</sup>, and  $1517 \pm 46$  cm<sup>-1</sup> for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Mn<sup>5+</sup>.

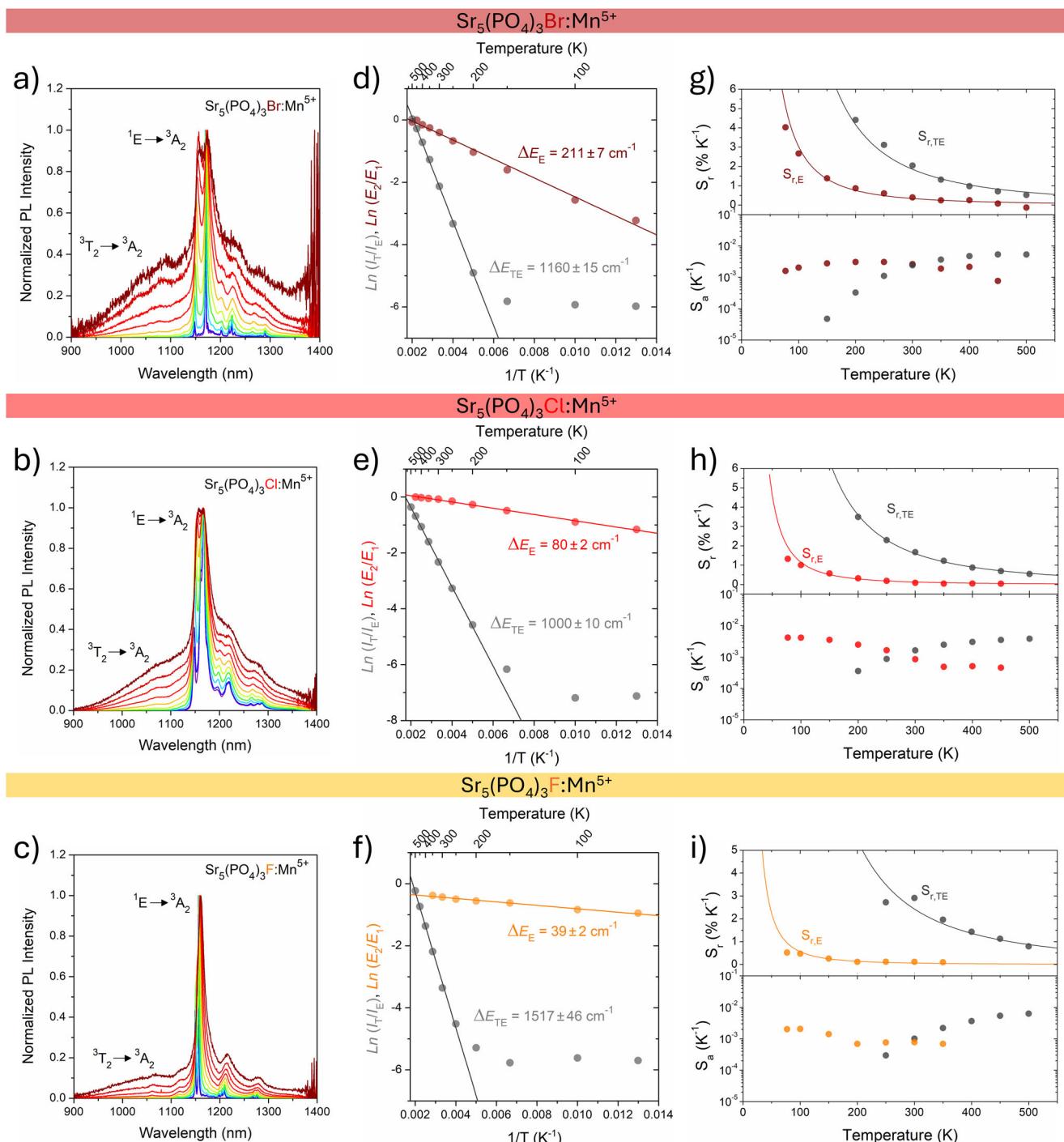
Two of the most important parameters used to discuss the performance of the thermometers are the relative sensitivity ( $S_r$ ), a figure of merit allowing the comparison among the thermometers of different nature, and the absolute sensitivity ( $S_a$ ), defined as

$$S_a = \left| \frac{\partial LIR}{\partial T} \right| \quad (7)$$

$$S_r = \frac{1}{LIR} \left| \frac{\partial LIR}{\partial T} \right| \quad (8)$$

Figure 5g-i show the values of both relative and absolute sensitivities calculated in the range of linearity of the Boltzmann law for the two thermometers. For Boltzmann thermometers  $S_r = \frac{\Delta E}{k_B T^2}$ ; therefore, the difference between the  $S_r$  values for the thermometers built considering  $LIR_{TE}$  and  $LIR_E$  reflects the differences in the energy gap between the couples of excited states. The values of relative sensitivity obtained for the  $LIR_{TE}$ ,  $S_{r,TE}$  are the highest values reported so far for Mn<sup>5+</sup>-doped thermometers (see the comparison with the literature in Table S7, Supporting Information), with values at 300 K of  $2.91\% \cdot \text{K}^{-1}$  for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F:Mn<sup>5+</sup>,  $2.05\% \cdot \text{K}^{-1}$  for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br:Mn<sup>5+</sup>, and  $1.68\% \cdot \text{K}^{-1}$  for Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Mn<sup>5+</sup>. On the other hand, the use of  $LIR_E$  allows to expand the range of temperatures at which the  $S_r$  values are larger than  $1\% \cdot \text{K}^{-1}$  to low temperatures showing unprecedented values in the case of the bromide apatite, where the  $S_{r,E}$  values are all larger than  $1\% \cdot \text{K}^{-1}$  for temperatures lower than 200 K with a maximum values of  $4\% \cdot \text{K}^{-1}$  at 77 K (see Figure 5g).

It is important to recognize that, despite the recent proposal of the use of the  ${}^3\text{T}_2/{}^1\text{E}$  PL intensity ratio for the physiological temperature range,<sup>[31,33,36]</sup> the large energy gap between the  ${}^1\text{E}$  and  ${}^3\text{T}_2$  excited states allows to only weakly populate the higher lying  ${}^3\text{T}_2$  state around room temperature resulting in a weak broadband emission often emphasized by a logarithmic scale, making this strategy not particularly reliable due to the low signal-to-noise ratio. A similar situation is well known in the case of the Nd<sup>3+</sup>-activated thermometers based on the ratio between the  ${}^4\text{F}_{5/2}\rightarrow{}^4\text{I}_{9/2}$  and  ${}^4\text{F}_{3/2}\rightarrow{}^4\text{I}_{9/2}$  transitions.<sup>[64,65]</sup> Therefore, the

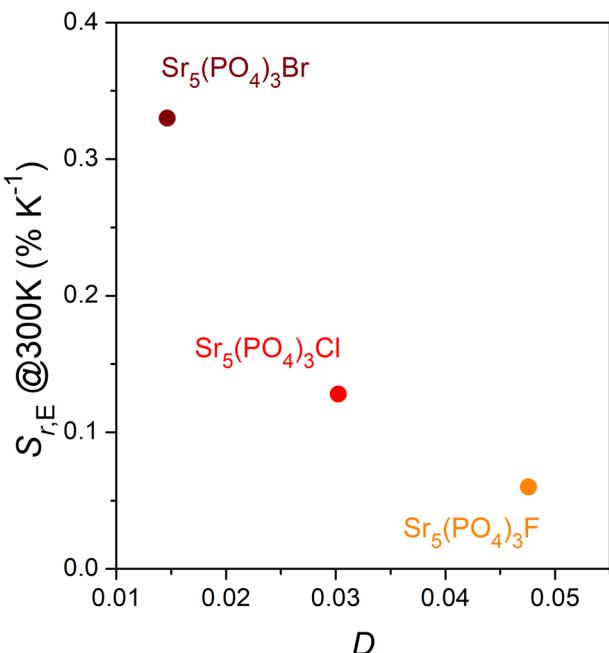


**Figure 5.** a-c) Normalized temperature-dependent PL spectra. d-f) Boltzmann plot for the thermometric parameters built considering the ratio between the  $^3\text{T}_2$  and  $^1\text{E}$  states ( $L\text{IR}_{\text{TE}}$ ) and between  $E_2$  and  $E_1$  levels ( $L\text{IR}_E$ ) along with the fit of the linear ranges. g-i) Absolute and relative sensitivities for the  $L\text{IR}$ -based thermometers and theoretical  $S_r$  (solid line) considering the corresponding  $\Delta E$  estimated.

possibility to simultaneously use the  $^3\text{T}_2/{}^1\text{E}$  and  $E_2/E_1$  intensity ratio allows for expanding the temperature window of application of the thermometers in the whole temperature range explored. This makes the thermometers useful not only for biological applications but also for low and high temperatures, with relative

sensitivities of both the  $L\text{IR}_{\text{TE}}$  and  $L\text{IR}_E$  thermometers, particularly promising for  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$ .

Looking for correlations between the sensitivities and geometric parameters that could be easily extrapolated from crystalline structure databases, such as the polyhedral distortion index  $D$



**Figure 6.** Correlation between the relative sensitivity  $S_{r,E}$  at 300 K and the distortion index  $D$ .

and the angle distortion index  $\delta$ , an inverse correlation between  $S_{r,E}$  and the distortion index  $D$  can be observed (Figure 6).

Despite the reliability and the promising results obtained for the *LIR*-based technique using the  $^3T_2$ - $^1E$  and  $E_1$ - $E_2$  excited state couples, it was demonstrated that the luminescence spectral shapes can be strongly affected by the biological environment with a clear limit in their applicability in the biological field.<sup>[66]</sup> In this view, the use of lifetimes is preferred. Therefore, the temperature dependence of the PL decay curves is investigated (Figure 7a-c). The decays were fitted with a single exponential to extrapolate the lifetime of the excited state. The Mott-Seitz model (single-barrier energy gap model) was employed to describe the temperature dependence of the lifetime

$$\tau(T) = \frac{\tau_0}{1 + C \cdot \exp\left(\frac{-\Delta E_{nr}}{k_B T}\right)} \quad (9)$$

where  $\tau_0$  is the radiative luminescence lifetime,  $C = k_{nrad}/k_{rad}$  is the ratio between the non-radiative and radiative decay rates,  $\Delta E_{nr}$  is the energy gap between the emitting level and the closest lower-lying energy level, and  $k_B$  is the Boltzmann constant. The fit of the temperature-dependent lifetime measurements (Figure 7d-f) allows to estimate an energy barrier of  $1485 \pm 75 \text{ cm}^{-1}$ ,  $1430 \pm 60 \text{ cm}^{-1}$ , and  $1315 \pm 90 \text{ cm}^{-1}$  for the bromide, chloride, and fluoride apatites, respectively.

The  $\Delta E_{TE,\tau}$  value obtained for the  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Mn}^{5+}$  sample of  $1430 \pm 60 \text{ cm}^{-1}$  is, within the errors, the same reported by Oetliker et al.<sup>[6]</sup> ( $1450 \text{ cm}^{-1}$ ), ensuring the reliability of the analysis.

As for the *LIR*-based thermometers, the absolute sensitivity  $S_{a,\tau} = |\frac{\partial \tau}{\partial T}|$  and the relative sensitivity  $S_{r,\tau} = \frac{1}{\tau} |\frac{\partial \tau}{\partial T}|$  were calculated as reported in Figure 7g-i.

A relative sensitivity  $S_{r,\tau}$  of  $0.42\% \cdot \text{K}^{-1}$  was reported at 300 K for  $\text{Ba}_3(\text{VO}_4)_2$ ,<sup>[34]</sup>  $0.35\% \cdot \text{K}^{-1}$  for  $\text{Ba}_5(\text{VO}_4)_3\text{Cl}$ ,<sup>[36]</sup>  $0.30\% \cdot \text{K}^{-1}$  for  $\text{Ba}_3(\text{PO}_4)_2$ ,<sup>[32]</sup> and  $0.40\% \cdot \text{K}^{-1}$  for  $\text{Sr}_3(\text{PO}_4)_2$ .<sup>[32]</sup> As summarized in Table S7 (Supporting Information), the values of  $0.61\% \cdot \text{K}^{-1}$  estimated at 300 K for both  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Mn}^{5+}$  are the highest reported in literature for the NIR emitting  $\text{Mn}^{5+}$ -doped thermometers.

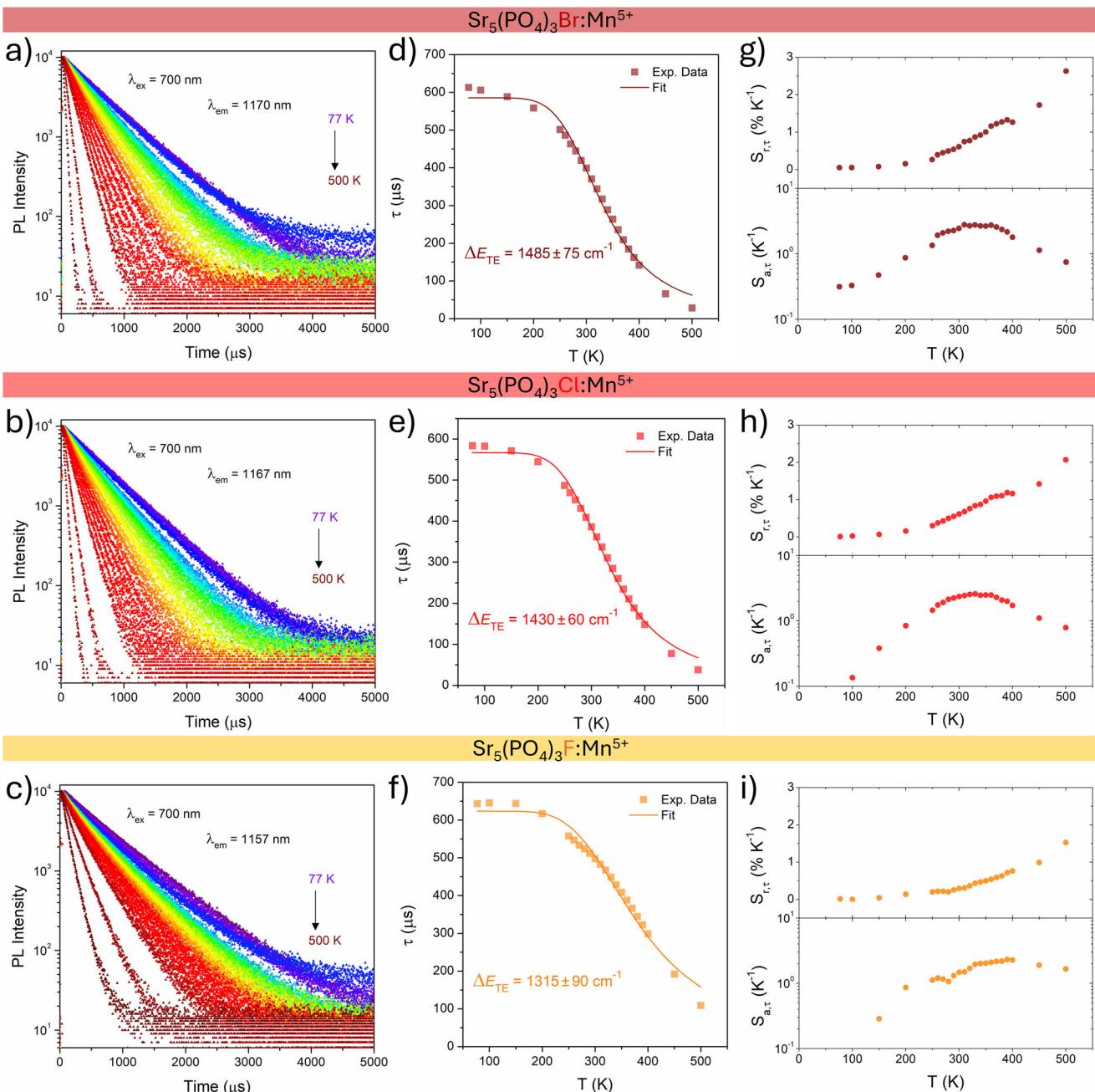
Among the  $\text{Mn}^{5+}$ -activated phosphors reported so far in literature (Table S7, Supporting Information),  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$  is one of the most promising, combining high quantum yield with one of the highest relative sensitivities for the thermometers built by using the  $^3T_1$ - $^1E$  ratio ( $2.05\% \cdot \text{K}^{-1}$  at 300 K) and the  $E_2/E_1$  ratio ( $0.33\% \cdot \text{K}^{-1}$  at 300 K) and the highest among the PL lifetime-based thermometers in the physiological range ( $0.61\% \cdot \text{K}^{-1}$  at 300 K). Moreover,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Mn}^{5+}$  can also be considered a suitable candidate for real applications by using the  $\tau$ -based technique, characterized by a relative sensitivity comparable to the bromide sample.

The obtained results show how to expand the working temperature range of  $\text{Mn}^{5+}$ -based thermometers by taking advantage of the  $^1E$  splitting. They also make it possible to predict the energy gap and, therefore, the sensitivity of the Boltzmann thermometer based on these thermally coupled excited states, by considering a geometric parameter (distortion index  $D$ ), predictable from structural information and existing databases. Overall, this work lays the foundation for future research directions in this field.

### 3. Conclusion

In conclusion, the structure-optical properties relationship in the NIR emitting  $\text{Sr}_5(\text{PO}_4)_3\text{X}:\text{Mn}^{5+}$  ( $\text{X} = \text{Br}, \text{Cl}$ , and  $\text{F}$ ) apatite phosphors was investigated by combining an experimental and theoretical approach. The effect of the local tetrahedral oxygen shell on the  $3d2$  electrons of  $\text{Mn}^{5+}$  ions was studied by means of the Tanabe-Sugano theory and the exchange charge model of the crystal field theory, showing the strong effect of the tetrahedral distortion. Temperature-dependent PL measurements were carried out in the 77–500 K range to address the potential of the phosphors as ratiometric luminescent thermometers. The use of two Boltzmann thermometers based on the ratio between the  $^3T_2$  and  $^1E$  PL emissions ( $LIR_{TE}$ ) and the split components of  $^1E$ ,  $E_1$  and  $E_2$  ( $LIR_E$ ) ensures a high reliability in a wide temperature range, overcoming the limit of the  $LIR_{TE}$ -based  $\text{Mn}^{5+}$  thermometers around the physiological range due to the weak  $^3T_2 \rightarrow ^3A_2$  transition expanding the temperature range.

Based on the NIR emission and excitation,  $\text{Mn}^{5+}$ -doped phosphors are considered particularly suitable for biological applications. The most reliable lifetime-based thermometry technique was employed, showing the highest relative sensitivity reported so far ( $0.61\% \cdot \text{K}^{-1}$  at 300 K) for both  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Mn}^{5+}$  apatite. Moreover, considering the high quantum yield (66%), the highest relative sensitivity among the apatites for the  $LIR_E$ -based thermometers ( $4\% \cdot \text{K}^{-1}$  at 77 K), one of the highest value for  $LIR_{TE}$ -based ( $2.05\% \cdot \text{K}^{-1}$  at 300 K) and the lifetime-based thermometry,  $\text{Sr}_5(\text{PO}_4)_3\text{Br}:\text{Mn}^{5+}$  is considered a promising candidate for real applications. Finally, a correlation between the  $E_1$ - $E_2$  energy gap, and, therefore, the sensitivity of the  $LIR_E$ -based thermometers, and the distortion index  $D$  was



**Figure 7.** Temperature dependence of a-c) PL decay curves, d-f) lifetimes with single-barrier energy gap model fit (Equation 9), and g-i) absolute  $S_{a,\tau}$  and relative  $S_{r,\tau}$  sensitivities.

disclosed, allowing the prediction of suitable hosts based on structural information.

#### 4. Experimental Section

**Synthetic Procedure:** The synthesis of  $\text{Mn}^{5+}$ -doped  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) was performed by a two-step procedure. In the first step,  $\text{Sr}_3(\text{PO}_4)_2$  powder was synthesized by the wet precipitation method, followed by high-temperature annealing (the purity was verified by XRD analysis, Figure S4, Supporting Information). During the second step, three series of  $\text{Mn}^{5+}$ -

doped  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) powders were synthesized by the molten salt method. In a typical procedure, 1 g of  $\text{Sr}_3(\text{PO}_4)_2$  was thoroughly mixed with a certain amount of  $\text{Mn}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$  ( $\geq 98\%$ , Roth) and an appropriate metal halide salt. The mass ratio between precursors and flux was chosen as 1:2 (calculated with respect to anhydrous salt).  $\text{SrCl}_2$  ( $\geq 95\%$ , Thermo Scientific) and  $\text{SrBr}_2 \bullet 6\text{H}_2\text{O}$ , ( $\geq 99\%$ , Thermo Scientific) were used for the synthesis of  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{Br}$ , respectively. For the synthesis of  $\text{Sr}_5(\text{PO}_4)_3\text{F}$ , a mixture of  $\text{SrF}_2$  ( $\geq 99\%$ , Thermo Scientific) and  $\text{NaF}$  ( $\geq 99\%$ , Scharlau) with a molar ratio of 0.025:0.975 was used. Manganese precursor was added according to a nominal Mn substitution level from 1 to 5 mol% with respect to  $\text{P}^{5+}$  ions. The obtained mixture

was transferred into the corundum crucible, covered with a lid, and annealed at an appropriate temperature for 5 h in air with a heating rate of 5 °C/min. The annealing temperature was 1050 °C, 1050 °C and 700 °C for  $\text{Sr}_5(\text{PO}_4)_3\text{F}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{Br}$ , respectively. After the annealing procedure, the furnace was allowed to cool down naturally. The obtained products were washed with hot deionized water to dissolve residual metal halides. All powders were then dried in an oven at 80 °C and ground in an agate mortar.

**Structural and Optical Characterizations:** X-ray diffraction patterns (XRD) were collected at room temperature using an Empyrean diffractometer (Malvern Panalytical) with Bragg-Brentano para focusing geometry equipped with a PIXcel3D-Medipix3 1×1 area detector and Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), with a scan rate of 1°/80 sec at 40 kV and 40 mA with continuous acquisition lasting 300 seconds. In order to consider the preferred orientation of the materials prepared, the March-Dollase function was employed:<sup>[54,55]</sup>

$$W(\alpha) = (r_n^2 \cos^2 \alpha_{n,h} + r_n^{-1} \sin^2 \alpha_{n,h})^{-3/2} \quad (10)$$

where  $\alpha_{n,h}$  is the angle between the orientation vector and diffraction plane vector, and  $r_n$  is the March number determining the preferred orientation strength. When  $r_n = 1$ , no preferred orientation is present, while  $r_n < 1$  and  $r_n > 1$  are characteristic of a preferred orientation by plate crystallites and needle crystallites, respectively.

The room temperature and temperature-dependent (77–500 K range) excitation and emission spectra and PL decay curves were recorded using an Edinburgh Instruments FLS980 spectrometer (Edinburgh Instruments, Livingston, UK) equipped with double-grating Czerny-Turner excitation and emission monochromators. For steady-state measurements, a 450 W ozone-free xenon arc lamp (Osram, Germany) was used as the excitation source. For the kinetic measurements, a micro flash lamp ( $\mu\text{F}2$ ) was used as the excitation source. The emission in the UV-Vis spectrum was detected using a Hamamatsu R928P photomultiplier (cooled to  $-20^\circ\text{C}$ ). Emission in the NIR range was detected using a Hamamatsu R5509-42 photomultiplier (cooled to  $-80^\circ\text{C}$ ). Emission spectra were corrected for the spectral response of the instrument. The excitation spectra were corrected using a reference detector. A MicrostatN cryostat (Oxford Instruments) was used for temperature-dependent measurements. The samples were cooled with liquid nitrogen.

Quantum efficiencies (QE) were measured by a direct method employing Teflon coated integrating sphere and using barium sulfate as a white standard ( $\text{BaSO}_4$  for white standard DIN 5033, Merck). QE was calculated using the following equation:<sup>[67]</sup>

$$QE = \frac{\int I_{\text{em, sample}} - \int I_{\text{em, BaSO}_4}}{\int I_{\text{refl, BaSO}_4} - \int I_{\text{refl, sample}}} \times 100\% = \frac{N_{\text{em}}}{N_{\text{abs}}} \times 100\% \quad (11)$$

where  $\int I_{\text{em, sample}}$  and  $\int I_{\text{refl, sample}}$  are integrated emission and reflectance of the sample, respectively.  $\int I_{\text{em, BaSO}_4}$  and  $\int I_{\text{refl, BaSO}_4}$  are integrated emission and reflectance of the barium sulfate standard.  $N_{\text{em}}$  and  $N_{\text{abs}}$  stand for emitted and absorbed photons, respectively.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

apatite, distortion index, Mn5+, near-infrared, phosphors, thermometry

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