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Structurally induced tuning of the relative sensitivity of $\text{LaScO}_3\text{:Cr}^{3+}$ luminescent thermometers by co-doping lanthanide ions

by Karolina Elzbieciak-Piecka,^{*,a} Markus Suta,^{b,c} and Lukasz Marciniak,^{*,a}

a. Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland.

b. Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Department of Chemistry, Utrecht University, Princetonplein 1, 3584 CC Utrecht, Netherlands.

c. Inorganic Photoactive Materials, Department of Inorganic Chemistry, Heinrich Heine University Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany.

*E-mail: k.elzbieciak@intibs.pl, l.marciniak@intibs.pl

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Abstract

Ratiometric luminescence thermometry for remote temperature sensing has been constantly gaining an increasing popularity due to its simplicity with yet high precision. Transition metal ions still have an underestimated potential in that area as their luminescence properties can be tuned by targeted modification of the host compound. In this work, we demonstrate that concept in the phosphor $\text{LaScO}_3\text{:Cr}^{3+}$ by co-doping with various lanthanide ions that partially substitute the La^{3+} ions of the host. It is demonstrated that the incorporated lanthanide ions affect the bond lengths of the $[\text{CrO}_6]^{9-}$ octahedra in the structure and thus, have a subtle impact on the local crystal field around the Cr^{3+} ions. The changes in the crystal field strength lead to a variation in the energy gap between the thermally coupled ${}^2\text{E}_{(g)}$ and ${}^4\text{T}_{2(g)}$ states of Cr^{3+} . This has an immediate consequence for the potential use of Cr^{3+} as a luminescent thermometer and allows to selectively tune the relative thermal sensitivity and performance of this ion by a suitable choice of the co-doped lanthanide ions.

Introduction

Luminescence thermometry has recently gained considerable attention and become a rapidly growing field of nanotechnology especially in the case of remote temperature sensors[1–8]. The uniqueness of this technique results from the fact that it exploits the temperature-dependent luminescent properties of the phosphor, such as the spectral shape, intensity of the emission bands or the kinetics of the excited states of incorporated dopants to determine temperature changes. Hence, it provides fast and in-real-time exact information about the temperature of the phosphor with down to submicrometer spatial and millikelvin thermal resolution[9–11]. It thus complements thermographic cameras which only allow thermal imaging of the surface of an object. Moreover, they are only sufficiently sensitive in case of high emissivity of thermal radiation by the object or at high temperatures due to the fourth power dependence of the intensity of black body radiation with local temperature [12–14]. This opens up opportunities for many, previously unexplored, areas of temperature monitoring especially in nanomedicine for precise mapping of the temperature of living cells or tissues and feedback therapies like hyperthermia treatment as well as in microelectronics and microfluidics which are inaccessible field for conventional temperature probes [3,15,16]. The uncertainty in temperature determination using LT depends on both the emission intensity of the phosphor and its relative sensitivity to temperature changes [6,17–19]. This imposes the need for the research devoted to optimization of the thermometric properties of the phosphor to meet these requirements. The great majority of the currently investigated LT exploits the emission of the lanthanide ions (Ln^{3+}). Although their application potential for non-contact temperature sensing has been already proved[20], their main limitation is the relatively low emission intensity and narrow absorption bands resulting from the forbidden by the selection rules character of the $4f\text{--}4f$ transitions. Transition metal (TM) ions have significantly higher absorption cross sections due to a stronger coupling to local vibrational odd-parity modes and are investigated to a much lower extent in the context of LT. In contrast to the $4f\text{--}4f$ transitions of the Ln^{3+} ions, the spectroscopic properties of the TM ions such as emission and absorption wavelength are influenced by the locally surrounding ligand field of the ions. This allows to optimize the thermometric performance of these luminescent ions and tailor it with respect to the practical requirements[14,21–32]. This is especially well manifested in the case of Cr^{3+} ions[22,27,28,30–33]. The emission spectra of these ions can significantly differ in their appearance dependent on the crystal field strength. In strong crystal fields, a narrow and sharp emission band based on the spin-forbidden ${}^2\text{E}_{(g)} \rightarrow {}^4\text{A}_{2(g)}$ transition (in cubically symmetric crystal fields) dominates the spectrum, while a broad emission band due to a spin-allowed ${}^4\text{T}_{2(g)} \rightarrow {}^4\text{A}_{2(g)}$ transition is more prominent in intermediate to weak crystal fields. In contrast to

the ${}^2E_{(g)}$ state stemming from to the same $(t_{2g})^3$ ground configuration, the harmonic potential of the ${}^4T_{2(g)}$ state is usually characterized by higher equilibrium metal-ligand distances with respect to the ground state ${}^4A_{2(g)}$ since an electron was then excited into the more antibonding e_g orbital. The energy of the ${}^4T_{2(g)}$ state is directly proportional to the crystal field strength. Consequently, the crossing point of the two potentials representing the ${}^2E_{(g)}$ and ${}^4T_{2(g)}$ states, respectively, can critically controlled by the local chemical environment of the Cr^{3+} ions [27,31,32,34–36]. This does not only affect the appearance of the luminescence spectra of Cr^{3+} (either narrow R lines or broad band emission), but also has an impact on the thermal quenching of the luminescence at elevated temperatures. Currently, a number of works are performed aiming the optimization of the host material composition to alter the thermometric performance of the solely Cr^{3+} -based LT [6,31,32,37]. Up till now, several approaches for lowering the crystal field strength, involving modification of the host material stoichiometry and the concentration of Cr^{3+} dopant ions were described in detail [27,28,38]. It was shown that by gradual substitution of small ions such as Al^{3+} by larger ions like Ga^{3+} in octahedral sites of the host crystal matrix, the metal-oxygen bond distance gradually increased and should result in a decrease of the crystal field strength acting on incorporated Cr^{3+} ions occupying these sites ($Dq \propto R_{Cr-O}^{-5}$) [39,40]. Subsequently, the influence of the Cr^{3+} doping concentration was examined. It was reported that an increase in concentration of Cr^{3+} ions (30% Cr^{3+} in $Y_3Al_2Ga_3O_{12}$, 50% in $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$, respectively) caused a statistical elongation of the metal-oxygen distances, which led to a decrease in the crystal field strength [28]. This unique feature of the Cr^{3+} ions has been used by many authors to develop highly sensitive ratiometric luminescent thermometers using two operating strategies: (i) based on the intensity ratio of the narrow ${}^2E_{(g)} \rightarrow {}^4A_{2(g)}$ and broad ${}^4T_{2(g)} \rightarrow {}^4A_{2(g)}$ bands [14,22,30–32] and (ii) based on the change in that respective intensity ratio with respect to an internal luminescent reference like Ln^{3+} ion, whose luminescence is not affected within the regarded temperature range [25,27,28,41,42]. It is usually found that the relative sensitivities are higher upon comparison of the temperature evolution of the general Cr^{3+} -based luminescence compared to the lanthanide-based luminescence than upon simple exploitation of thermal coupling between the ${}^2E_{(g)}$ and ${}^4T_{2(g)}$ states of Cr^{3+} alone.

Although the introduction of the Ln^{3+} ions as a co-dopant ion appears beneficial from a thermometric performance perspective, they may yet induce changes in the spectroscopic properties of the Cr^{3+} itself not only by energy transfer processes but also by modification the local crystal field. In this work, we investigated the impact of the Ln^{3+} ions on a distortion in the $[CrO_6]^{9-}$ octahedra in $LaScO_3:Cr^{3+}$, Ln^{3+} and how this affects the thermometric performance of Cr^{3+} . For that purpose, all lanthanide ions from Ce^{3+} to Lu^{3+} has been co-doped into $LaScO_3:Cr^{3+}$ and the spectroscopic properties of the resulting phosphors were analyzed. We observed that for the Ln^{3+} co-doped nanocrystals the emission intensity of Cr^{3+} increased at low temperatures in contrast to the solely Cr^{3+} doped nanocrystals. Usually, such an increase in intensity of the Cr^{3+} -related emission is ascribed to vibrationally induced mixing between the ${}^2E_{(g)}$ and ${}^4T_{2(g)}$ states that leads to an increase of the radiative decay rate. Such an effect has been already reported in literature before [43–45], which is, however related to vibronically induced mixing between the ${}^2E_{(g)}$ and ${}^4T_{2(g)}$ state that increases the radiative decay rate of the narrow ${}^2E_{(g)} \rightarrow {}^4A_{2(g)}$ emission. Similar effects are known from the isoelectronic ion Mn^{4+} [46]. The authors observed that while the same temperature range is being maintained, in which the probability of non-radiative transitions is constant and the probability of radiative transitions increases due to symmetry changes, the integral intensity also increases.

Experimental

Synthesis

The series of LaScO₃ nanocrystals doped with Cr³⁺ and co-doped with Cr³⁺ and Ln³⁺ have been synthesized by means of a modified Pechini method [47]. The following starting materials were used for synthesis without further purification: La₂O₃ (99.995% purity, Stanford Materials Corporation), Sc₂O₃ (99.99% purity, Alfa Aesar), Nd₂O₃ (99.998% purity, Stanford Materials Corporation), Yb₂O₃ (Yb₂O₃ 99.995% purity, Stanford Materials Corporation), Eu₂O₃ (99.995% purity, Stanford Materials Corporation), Ho₂O₃ (99.99% purity, Alfa Aesar), Sm₂O₃ (99.99% purity, Alfa Aesar), Ce(NO₃)₃ · 6 H₂O (99.999% purity, Alfa Aesar), Tb₄O₉ (99.99% purity, Stanford Materials Corporation), Er₂O₃ (99.99% purity, Stanford Materials Corporation), Tm₂O₃ (99.99% purity, Stanford Materials Corporation), Dy₂O₃ (99.99% purity, Stanford Materials Corporation), Pr₆O₁₁ (99.99% purity, Stanford Materials Corporation), Y₂O₃ (99.99% purity, Stanford Materials Corporation), Lu₂O₃ (99.99% purity, Stanford Materials Corporation), Cr(NO₃)₃ · 9 H₂O (99.99% purity, Alfa Aesar), citric acid (C₆H₈O₇, 99.5+% purity, Sigma) and poly(ethylene glycol) (PEG 200, C₂H₆O₂, Sigma). The molar concentration of the Ln³⁺ was calculated with respect to the La³⁺ ions while the concentration of Cr³⁺ was referred to the Sc³⁺ ion content. If not stated otherwise, 1 mol% of Cr³⁺ and 1 mol% of Ln³⁺ ions were incorporated. The rare earth nitrates were prepared from the respective oxides upon dissolution in slightly diluted hot ultrapure nitric acid. The isolated nitrates were recrystallized three times. After that, the required amount of the rare earth nitrates and Cr(NO₃)₃ · 9 H₂O were dissolved in deionized H₂O. In a separate batch, the six-fold molar excess with respect to the metal ions of both citric acid and PEG 200 were mixed, respectively, and slowly added to the nitrate containing solution. The overall mixture was then stirred for 3h. In order to form resins, the resulting solutions were heated for one week at 90°C and finally annealed at 800 °C for 8h.

Characterization

The purity of the obtained powders was verified by X-ray powder diffraction (XRPD) measurements carried out on PANalytical X'Pert diffractometer, equipped with an Anton Paar TCU 1000 N temperature control unit, using Ni-filtered Cu-K_α radiation (V = 40 kV, I = 30 mA). Transmission electron microscope images were taken on a Philips CM-20 SuperTwin microscope using an accelerating voltage of 160 kV and a 0.25 nm spectral resolution. Excitation spectra and luminescence lifetimes were measured on a FLS1000 Fluorescence Spectrometer from Edinburgh Instruments equipped with a 450 W Xenon lamp. Both the excitation and emission 300 mm focal length monochromators were in Czerny-Turner configuration. The excitation arm was supplied with a holographic grating of 1800 lines/mm, blazed at 250 nm, while the emission compartment was supplied with ruled grating, 1800 lines/mm blazed at 500nm. The spectral resolution was 0.1 nm. The R928P side window photomultiplier tube from Hamamatsu was used as a detector.

Temperature dependent emission spectra were measured upon excitation with a 445 nm laser diode and detection with a Silver-Nova Super Range TEC CCD Spectrometer from Stellarnet affording 1 nm spectral resolution. Raman spectra were measured on an inVia confocal microscope from Renishaw equipped with an 830 nm laser as the excitation source and a Si CCD camera as the detector. The spectra were taken in a range of 100-1000 cm⁻¹ at room temperature under an objective with 100-fold enlargement. The spatial resolution was lower than 1 μm. The temperature during the measurement was externally controlled using a THMS 600 heating-cooling stage from Linkam Scientific (± 0.1°C stability and 0.1°C set point resolution).

Results and Discussion

The lanthanum scandates (LaScO₃) analyzed in this work, belong to the group of (distorted) perovskites characterized by the general formula AMO₃. Oxides crystallizing in perovskite-type structures constitute a large group of compounds with appealing properties such as ferroelectricity, pyroelectricity and piezoelectricity under phase transitions to lower symmetric structures [48]. The compounds LaScO₃ crystallize in an orthorhombically distorted GdFeO₃-type structure with the space group *Pnma* (no. 62). In the unit cell of LaScO₃, the Sc³⁺ ions are surrounded by six O²⁻ ions in the form of almost undistorted [ScO₆]⁹⁻ octahedra. The octahedra share corners along one crystallographic direction and are tilted towards one another in an angle smaller than 90° (which gives rise to the lower symmetry than the cubic one) [49–51]. As reported by Huang *et al.* an increase of the temperature causes the enlargement of the cell parameters manifested as a shift of the diffraction reflection toward smaller angles [52]. This can strongly affect the spectroscopic properties of the Cr³⁺ ions as the appearance of the emission spectra of this transition metal ion is sensitive to changes in the crystal field strength. In agreement with the abovementioned description, Cr³⁺ ions could substitute Sc³⁺ ions (green polyhedral representation in Fig. 1a), while the lanthanide ions will preferably substitute the La³⁺ ions (light yellow polyhedral representation in Fig. 1a), respectively. Additionally, in the case of perovskite materials, the assessment on the geometric stability and distortion of crystal structures can be evaluated by calculation of the Goldschmidt tolerance factor *t*, according to the following formula [53]:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_M + R_X)} \quad (1)$$

where *R_A*, *R_M* and *R_X* are ionic radii of particular cations of the AMO₃ structure. The ideal perovskite materials adopt a cubic structure with *t* = 1, lower values of *t* in the range of 0.71 - 0.90 favor the distorted GdFeO₃-type orthorhombic structure. The result of the calculations of the *t* parameter for La_{0.99}Ln_{0.01}Sc_{0.99}Cr_{0.01}O₃ nanocrystals (Ln = Ce – Lu) as a function of increasing atomic number of lanthanide dopant ions indicates a gradual decrease of *t* from 0.8452 for Ce³⁺ to 0.8446 for Lu³⁺ (see Fig. 1b). This could indicate a structurally imposed impact of the Ln³⁺ ions on the Cr³⁺ ions environment reciprocally proportional to the ionic size of the dopant. All The Bragg reflections in the XRD patterns (Fig. 1c, for more see Fig. S1) are in accordance with the reference pattern from ICSD Crystallographic Database (ICSD 99538) and confirms crystal phase purity of all doped LaScO₃ nanocrystals. A slight shift of the reflections toward higher angles with an increasing atomic number of the dopant lanthanide ions is explicable in terms of the lanthanide contraction and causes a lowering of the unit cell dimensions. The representative TEM image shown in Fig. 1d reveals that synthesized powders consist of well-crystallized agglomerated grains of relatively narrow distribution. The diameter of the LaScO₃:Cr³⁺, Ln³⁺ particles determined based on the TEM images was around (45 ± 11) nm and was not significantly affected by the Ln³⁺ dopants (Fig. 1e).

Figure 1. Structural and morphological characterization of synthesized materials: a) the visualization of simple polyhedral LaScO_3 structure. b) Dependence of Goldschmidt tolerance factor in respect to atomic number of lanthanide ion dopant in LaScO_3 : 1% Cr^{3+} , 1% Ln^{3+} . c) XRD patterns for LaScO_3 : 1% Cr^{3+} ; 1% Cr^{3+} , 1% Ce^{3+} and 1% Cr^{3+} , 1% Yb^{3+} . d) representative TEM image of LaScO_3 : 1% Cr^{3+} nanocrystals. e) Histogram of the nanoparticle size distribution calculated based on TEM image of LaScO_3 : 1% Cr^{3+} .

In order to understand the luminescence properties of the Cr^{3+} ions, a generalized configurational coordinate diagram is depicted in Fig. 2a. Throughout this work, we assumed an octahedral symmetry at the Sc^{3+} sites, which is a valid approximation given the very similar Sc-O bond lengths (standard deviation = 0.001678 nm) and almost undistorted O-Sc-O bond angles of around 90° . Since LaCrO_3 crystallizes isotypically to LaScO_3 , no significant structural changes upon doping with Cr^{3+} are expected [54]. In the case of the transition metal ions of the $3d^3$ electronic configuration, radiative emission arises from the ${}^2\text{E}_{\text{(g)}}$ and/or ${}^4\text{T}_{2\text{(g)}}$ state. Due to negligible change in bond length in the ${}^2\text{E}_{\text{(g)}}$ state parabola stemming from the same electron configuration as the ground state ${}^4\text{A}_{2\text{(g)}}$, the ${}^2\text{E}_{\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ electronic transition is represented as sharp emission lines. On the other hand, the shift of the ${}^4\text{T}_2$ state with respect to the ground state imposes two important consequences: a broad emission band associated with the ${}^4\text{T}_{2\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ electronic transition and a dependence of the energy of ${}^4\text{T}_{2\text{(g)}}$ state on the crystal field strength parametrized by $10Dq$. A weak crystal field lowers the energy of the ${}^4\text{T}_{2\text{(g)}}$ state and thus, the ${}^4\text{T}_{2\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ transition is expected to be dominant for low crystal field strengths while the ${}^2\text{E}_{\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ transition dominates in strong crystal fields. The energies of the intersection points between the ${}^2\text{E}_{\text{(g)}}$ and ${}^4\text{T}_{2\text{(g)}}$ as well as the ${}^4\text{T}_{2\text{(g)}}$ and ${}^4\text{A}_{2\text{(g)}}$ state potentials determine the thermal stability of the emission intensity. In the case of the excitation spectra of Cr^{3+} two broad absorption bands with maxima at around 475 nm and 660 nm are observed. These are associated with the ${}^4\text{A}_{2\text{(g)}} \rightarrow {}^4\text{T}_{1\text{(g)}}$ and ${}^4\text{A}_{2\text{(g)}} \rightarrow {}^4\text{T}_{2\text{(g)}}$ electronic transitions of Cr^{3+} , respectively. Based on the energy of the two absorption bands, the crystal field strength parameter Dq/B was determined with 2.67 (see SI Eqs. 1-3) [55]. This value indicates that the Sc^{3+} sites in LaScO_3 give rise to an intermediately strong crystal field and hence, both ${}^2\text{E}_{\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ - and ${}^4\text{T}_{2\text{(g)}} \rightarrow {}^4\text{A}_{2\text{(g)}}$ -based emission are expected (see Fig 2c). The introduction of Ln^{3+} ions as co-dopants may modify both emission and excitation spectra of LaScO_3 : Cr^{3+} , Ln^{3+} .

nanocrystals by the occurrence of the characteristic narrow $4f-4f$ intraconfigurational electronic transitions. Figure 2a schematically depicts simplified energy diagrams of Nd^{3+} , Pr^{3+} , Tm^{3+} and Yb^{3+} as representative examples emitting in a similar range as Cr^{3+} . Dependent on the energy level scheme of the respective Ln^{3+} ions and spectral overlap of the absorption bands of the Ln^{3+} ions with those of the Cr^{3+} ions can be found (e.g. Nd^{3+} , Pr^{3+} , Ho^{3+}). In particular, the rich energy level configuration of Nd^{3+} prevents a selective excitation of the Cr^{3+} ions without exciting Nd^{3+} as well. Notably, the energy level diagram of Nd^{3+} facilitates the $\text{Cr}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer, which has been reported by many authors [52]. It is noteworthy that the excitation of Ln^{3+} ions in co-doped materials could occur in two ways. Upon excitation with 445 nm excitation line in the case of co-doped materials either both Cr^{3+} and Ln^{3+} ions are excited independently or a $\text{Cr}^{3+} \rightarrow \text{Ln}^{3+}$ energy transfer may populate the excited states of Ln^{3+} ions non-radiatively (see also Figs. S2-S8). Therefore, the emission spectra of $\text{LaScO}_3:\text{Cr}^{3+}$, Ln^{3+} contain both the Cr^{3+} -based emission bands and the characteristically narrow $4f-4f$ transitions of the respective Ln^{3+} ions (Figure 2e, g, i, k).

Figure 2. a) Simplified energy level diagrams of Cr^{3+} and lanthanide dopant ions with possible energy transfer models. b), d), f), h), j) Representative excitation spectra upon monitoring the emission at x nm. c), e), g), i), k) Representative emission spectra upon excitation at 445 nm. All spectra were recorded at $T = -196^\circ\text{C}$.

In order to understand the influence of the temperature on the appearance of the luminescence spectra of $\text{LaScO}_3:\text{Cr}^{3+}$ and $\text{LaScO}_3:\text{Cr}^{3+}$, Ln^{3+} nanocrystals, their emission spectra were measured in the temperature range between $-190 - 300^\circ\text{C}$ (Figure 3, see also Fig S9-S19). In the case of the $\text{LaScO}_3:\text{Cr}^{3+}$ nanocrystals, the intensity of the $^2E_{(g)} \rightarrow ^4A_{2(g)}$ emission band was quenched at elevated temperatures above -50°C for the sake of stronger $^4T_{2(g)} \rightarrow ^4A_{2(g)}$ -based emission. This effect can be explained in terms of thermalization of the $^4T_{2(g)}$ state with respect to the $^2E_{(g)}$ state. Further increase of the temperature results in a gradual reduction of the $^4T_{2(g)} \rightarrow ^4A_{2(g)}$ emission of the Cr^{3+} ions up to 290°C , above which the emission intensity is completely quenched. This thermal quenching results from a direct non-radiative depopulation of the $^4T_{2(g)}$ state to the $^4A_{2(g)}$ ground state. In contrast, the temperature-dependent

luminescence intensity of Cr^{3+} in the $\text{LaScO}_3:\text{Cr}^{3+}$, Yb^{3+} nanocrystals shows a slightly different behavior at low temperatures. In that phosphor, the Cr^{3+} emission intensity increases up to around 80 °C followed by luminescence quenching. The intensity of the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ -based emission of the Yb^{3+} ions shows a similar behavior, which is understandable based on the $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer that populates the ${}^2\text{F}_{5/2}$ state of Yb^{3+} . A similar temperature dependence with initial increase in emission intensity of the Cr^{3+} -based emission at low temperatures has been observed in the case of the nanocrystals with other Ln^{3+} co-dopants. The comparison of the integral emission intensity of Cr^{3+} ions (integrated in the 700-750 nm spectral range) as a function of temperature for different co-dopants is depicted in Figure 3c (see also Fig. S 20). In the case of the Ce^{3+} , Pr^{3+} , Nd^{3+} ions an increase of the temperature results in luminescence thermal quenching at even lower temperatures (already in the range between -190 °C - 100 °C) compared to the singly Cr^{3+} doped counterpart. In the case of $\text{LaScO}_3:\text{Cr}^{3+}$, Sm^{3+} nanocrystals, the intensity of the Cr^{3+} -related emission shows a similar temperature dependence to the solely Cr^{3+} -activated LaScO_3 nanocrystals. However, with additional increase in the atomic number of the Ln^{3+} ions a gradual enhancement of the Cr^{3+} -based emission at low temperatures is observed. The magnitude of the enhancement depends on the Ln^{3+} ion and reached a maximum in $\text{LaScO}_3:\text{Cr}^{3+}$, Yb^{3+} , for which 140% of the initial emission intensity was recorded at 80 °C. The integral emission intensity for different Ln^{3+} ions with respect to the one recorded for singly Cr^{3+} doped LaScO_3 nanocrystals has been analyzed in a function of the Ln^{3+} ion to provide comparative analysis (Figure 3d). A monotonic correlation can be found between the atomic number of the Ln^{3+} ion and the magnitude of enhancement of the Cr^{3+} -based luminescence. Thus, the lanthanide contraction appears to intensify the Cr^{3+} -related luminescence at low temperatures. Notably the emission intensity of $\text{LaScO}_3:\text{Cr}^{3+}, \text{Nd}^{3+}$ nanocrystals does not fit into this tendency (Fig. S 20). A possible reason could be an effective spectral overlap of the Cr^{3+} -based emission and the Nd^{3+} -related absorption from the ${}^4\text{I}_{9/2}$ ground level into the excited ${}^4\text{F}_{5/2}$ level and an efficient $\text{Cr}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer. More detailed studies on this particular ion couple would be necessary to fully elucidate the excited state dynamics there. Overall, the monotonic tendency of the enhancement as a function of the atomic number of the Ln^{3+} ions generally excludes energy transfer as a potential explanation as this would imply a specific dependence on the electronic energy level structure of the lanthanide ions. The strongest observed enhancement in the Yb^{3+} co-doped nanocrystals additionally confirms this idea. Yb^{3+} only has one excited level (${}^2\text{F}_{5/2}$) at around 10,000 cm^{-1} above the ground level, which only weakly overlaps with the ${}^4\text{T}_{2(g)} \rightarrow {}^4\text{A}_{2(g)}$ emission of Cr^{3+} .

The observed enhancement of the Cr^{3+} emission intensity is unusual and reveals an opposite thermal tendency with respect to the one expected for transition metal ions. Under continuous excitation and steady-state conditions, an increase of the emission intensity is not expected unless the absorption cross section is modified by changes in the local temperature. In order to verify the hypothesis that the absorption cross section increases by thermally induced broadening of the absorption band, the excitation spectra of $\text{LaScO}_3:\text{Cr}^{3+}$ and $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ were measured as a function of temperature (Fig. S 21). Only a small red shift of the absorption band associated with the thermalization of higher vibrational states can be observed, which is typical for TM ions. An increase of the emission intensity at elevated temperatures for the d^3 ions Mn^{4+} and Cr^{3+} has been previously reported and discussed in terms of vibronically induced mixing of the ${}^2\text{E}_{(g)}$ and ${}^4\text{T}_{2(g)}$ states by odd-parity vibrational modes [44][43][46]. Therefore, we interpret the results by means of a structural argument. The incorporation of the successively smaller Ln^{3+} ions can induce an elongation (based on the more available space) of the bond lengths of the $[\text{CrO}_6]^{9-}$ octahedra associated with and thus, a decrease of the energy gap between the ${}^2\text{E}_{(g)}$ and ${}^4\text{T}_{2(g)}$ states of Cr^{3+} (given the sensitive

R_{ML}^{-5} dependence of Dq). At smaller energy gaps between these two states, the perturbative vibronic coupling mechanism is more pronounced (strength proportional to $1/\Delta E$ in first order) given a negligible variation of the frequency of the respective odd-parity vibrational mode. Consequently, the increase in intensity and the related decrease in average decay time (see Fig. S22) is expectedly higher in the scandates doped with smaller lanthanide ions. It is important to realize that potential energy transfer processes between Cr^{3+} and the lanthanide ions can severely complicate this analysis. However, given the very small doping concentrations of 1 mol% of both Cr^{3+} and the Ln^{3+} ions, respectively, energy transfer probabilities are minimized.

In fact, in all co-doped nanocrystals, the Cr^{3+} luminescence decays slightly faster (and not singly exponential) than in singly doped $LaScO_3:Cr^{3+}$, which are typical signatures of energy transfer processes. On the other hand, Grinberg showed that the luminescence decay time of Cr^{3+} scales linearly with the energy gap ΔE between the $^2E_{(g)}$ and $^4T_{2(g)}$ level, respectively[44]. A separation of both effects is difficult in this complete series. Only for the non-luminescent lanthanide ions such as Y^{3+} and Lu^{3+} , the effect can be clearly correlated to the structural impact. In fact, a decrease in the average luminescence decay time from singly Cr^{3+} -doped over Cr^{3+} , Y^{3+} to Cr^{3+} , Lu^{3+} co-doped $LaScO_3$ is observed (see Fig. S22), in line with the expected decrease in the energy gap ΔE between the $^2E_{(g)}$ and $^4T_{2(g)}$ level (see above).

The luminescence decay times for $LaScO_3:Cr^{3+}$ and $LaScO_3:Cr^{3+},Yb^{3+}$ were additionally measured as a function of temperature (Figs. S23-S24). For a more detailed analysis, the average lifetimes were estimated according to the following formula:

$$\langle \tau \rangle = \frac{\int I(t) \cdot t dt}{\int I(t) dt} \quad (2)$$

where $I(t)$ is the luminescence intensity at delay time t after the excitation pulse. It could be noticed that the average lifetimes for the co-doped material are slightly shorter than for singly doped nanocrystals. Additionally, at temperatures above 200 °C for $LaScO_3:Cr^{3+},Yb^{3+}$, constant values of average lifetimes can be observed, which may mean that the $Cr^{3+} \rightarrow Yb^{3+}$ energy transfer accelerated the depopulation of the Cr^{3+} excited state.

The significant change of the thermal dependence of the Cr^{3+} emission intensity induced by the Ln^{3+} co-dopant may be utilized as a design strategy as a luminescent thermometer. In a ratiometric approach, in which the luminescence of the Cr^{3+} ions is used as a temperature probe while the Ln^{3+} luminescence is treated as an internal reference. The most important aspect that determines the thermometric performance of the luminescent thermometer is the optimization of the host material in order to reach the high thermal variability of the TM luminescence. Thus, several thermometric parameters of the presented intensity-based luminescent thermometer were analyzed to elucidate the impact of the structural modification by co-doping with the Ln^{3+} ions (see Figure 4). The relative sensitivities (S_R) were calculated using the following formula:

$$S_R = \frac{1}{X} \frac{\Delta X}{\Delta T} \cdot 100\% \quad (3)$$

where X is the Cr^{3+} -related integral emission intensity while ΔX denotes the change of the response signal X in a temperature interval ΔT . It is important to note that both relative sensitivity and a high signal-to-noise ratio contribute to an overall desirable low temperature uncertainty. Since the absolute intensity of both the Cr^{3+} - and Ln^{3+} -related emission are well above the noise level at lower temperatures, the main relevant control parameter is the relative sensitivity. As depicted in Fig 4a), the S_R calculated for $LaScO_3:Cr^{3+}$ nanocrystals is relatively low up to 130 °C, followed by the increase of its value to $S_{RMAX} = 1.23\% / ^\circ C$ at 220°C.

Figure 3. Thermal evolution of the emission spectra of a) $\text{LaScO}_3:\text{Cr}^{3+}$ and b) $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ (excitation at 445 nm). c) Representative thermal evolution of the integral emission intensity of Cr^{3+} ions in $\text{LaScO}_3:\text{Cr}^{3+}$, Ln^{3+} nanocrystals. d) Thermal map of the maximal intensity of Cr^{3+} emission in Ln^{3+} co-doped nanocrystals. e) Maximum intensity of Cr^{3+} emission in Ln^{3+} co-doped LaScO_3 nanocrystals as a function of the Goldschmidt tolerance factor t . f) Average decay times for $\text{LaScO}_3:\text{Cr}^{3+}$ and $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ nanocrystals as a function of temperature ($\lambda_{\text{exc}} = 445$ nm, $\lambda_{\text{em}} = 720$ nm).

However, the introduction of the Ln^{3+} causes two important effects: (i) change of the monotonicity of Cr^{3+} intensity is reflected in negative values of S_R and (ii) an increase in the S_R values observed in the high temperature range (above 80 °C). The maximal $S_R = 1.7\% \text{ } ^\circ\text{C}^{-1}$ was reached in the case of the $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ at 220 °C. This significant enhancement of the S_R by almost 40% with respect to the singly Cr^{3+} -doped counterpart indicates high applicative potential of the proposed approach. The maximum relative sensitivities, $S_{R\text{MAX}}$, obtained for the other Ln^{3+} ions are depicted in Figure 4b. Generally, a gradual enhancement of the relative sensitivity with decrease in the ionic radius of the Ln^{3+} ions is observed. This clearly suggests a correlation between the structurally induced elongation of the $[\text{CrO}_6]^{9-}$ octahedra and the achievable maximum relative sensitivity (see Figure 4c). However, the change of the monotonicity of the S_R also makes the usable temperature range (UTR) much narrower. Dependent on the trend of the intensity variation of the Cr^{3+} -related emission with temperature (either increase at low temperatures or decrease at high temperatures) two usable temperature ranges (UTR) can be determined (Figure 4 d). Although the UTR in the case of the $\text{LaScO}_3:\text{Cr}^{3+}$ has the widest range from 10 °C to 250 °C, the constantly low S_R values exclude this phosphor from real applications. This changes in the Ln^{3+} co-doped scandates. To verify the reliability and repeatability of the temperature readout using $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ nanocrystals, the respective LIR between the Cr^{3+} - and Yb^{3+} -based emission has been analyzed within several heating-cooling cycles and confirms that the conceptual thermometer can be used reproducibly. Finally, the theoretically expected minimum temperature uncertainty was assessed as follows

$$\delta T = \frac{1}{S_R} \frac{\delta X}{X} \quad (4)$$

where $\delta X/X$ is the (relative) uncertainty of the thermometric parameter. It was determined as the statistical relative standard deviation based on the 30 measurements of the LIR value at a

given temperature. It becomes evident from Figure 4.f) that an introduction of Yb^{3+} ions significantly reduces the temperature uncertainty from $\delta T = \pm 4.8\text{ }^{\circ}\text{C}$ for $\text{LaScO}_3:\text{Cr}^{3+}$ to $\delta T = \pm 0.08^{\circ}\text{C}$ for $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ at $90\text{ }^{\circ}\text{C}$. These obtained results suggest that the structural variation of the bond lengths at the octahedral sites of Cr^{3+} ions by means of additional incorporation of the Ln^{3+} ions in the distorted perovskite LaScO_3 can have a beneficial effect on the thermometric properties of this TM ion.

Figure 4. a) The relative sensitivity, S_R , as a function of temperature for different Ln^{3+} ions. b) $S_{R\text{MAX}}$ for different Ln^{3+} ions, and c) as a function of the Goldschmidt tolerance factor, t . d) The UTR of the proposed $\text{LaScO}_3:\text{Cr}^{3+}, \text{Ln}^{3+}$ nanocrystals for different Ln^{3+} ions. e) Reproducibility of the LIR measured for $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ nanocrystals within several heating-cooling cycles. f) Theoretically expected minimum temperature uncertainties for $\text{LaScO}_3:\text{Cr}^{3+}$ and $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ nanocrystals.

Conclusions

The nanocrystalline $\text{LaScO}_3:\text{Cr}^{3+}$ and $\text{LaScO}_3:\text{Cr}^{3+}, \text{Ln}^{3+}$ powders were synthesized using the modified Pechini method. Their potential as luminescent thermometers was studied in the temperature range between $-150\text{ }^{\circ}\text{C}$ and $300\text{ }^{\circ}\text{C}$. At higher temperatures, the luminescence of the Cr^{3+} ions is thermally quenched based on a thermally activated non-radiative crossover between the ${}^4\text{T}_{2(g)}$ and ${}^4\text{A}_{2(g)}$ state. Additional incorporation of small fractions (1 mol%) of Ln^{3+} ($\text{Ln} = \text{Ce} - \text{Lu}$) ions leads to an observable increase in luminescence intensity of the Cr^{3+} -related emission band at low temperatures before thermal quenching takes over. The magnitude of the low temperature enhancement in intensity is inversely proportional to the atomic number of the Ln^{3+} ions. A linear correlation between the enhancement of the Cr^{3+} -related emission intensity and the Goldschmidt tolerance factor indicates a structural origin of the observed phenomenon. The incorporation of gradually smaller Ln^{3+} ions was interpreted to induce an elongation of the Cr-O bond lengths in the $[\text{CrO}_6]^{9-}$ octahedra thus leading to a weaker crystal field. Consequently, the energy gap between the ${}^2\text{E}_{(g)}$ and ${}^4\text{T}_{2(g)}$ states of Cr^{3+} decreases, which favors a perturbative vibrational mixing between these states via an odd-parity phonon mode. This additional temperature-induced change of the intensity of the Cr^{3+} -based emission was investigated for a potential in luminescence thermometry. It was found that the incorporation of the Ln^{3+} ions leads to an increase of the relative sensitivity of the Cr^{3+} -based emission as a temperature measure. While the relative sensitivity is $1.23\text{ }^{\circ}\text{C}^{-1}$ at $220\text{ }^{\circ}\text{C}$ for $\text{LaScO}_3:\text{Cr}^{3+}$, it increases up to $S_R = 1.70\text{ }^{\circ}\text{C}^{-1}$ at the same temperature for $\text{LaScO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$. The linear correlation between the tolerance factor and the relative

sensitivity may suggest that host modification is a valuable tool to specifically design and modify the thermometric performance of Cr³⁺ or more generally, transition metal ions with luminescent properties that are sensitive to the local chemical surrounding.

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