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Mn⁵⁺-activated Ca₆Ba(PO₄)₄O near-infrared phosphor and its application in luminescence thermometry

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Abstract

The near-infrared luminescence of $Ca_6Ba(PO_4)_4O:Mn^{5+}$ is demonstrated and explained. When excited into the broad and strong absorption band that spans the 500–1000 nm spectral range, this phosphor provides an ultranarrow (FWHM = 5 nm) emission centered at 1140 nm that originates from a spin-forbidden ${}^{1}E \rightarrow {}^{3}A_{2}$ transition with a 37.5% internal quantum efficiency and an excited-state lifetime of about 350 µs. We derived the crystal field and Racah parameters and calculated the appropriate Tanabe–Sugano diagram for this phosphor. We found that ¹E emission guenches due to the thermally-assisted cross-over with the ${}^{3}T_{2}$ state and that the relatively high Debye temperature of 783 K of $Ca_6Ba(PO_4)_4O$ facilitates efficient emission. Since $Ca_6Ba(PO_4)_4O$ also provides efficient yellow emission of the Eu²⁺ dopant, we calculated and explained its electronic band structure, the partial and total density of states, effective Mulliken charges of all ions, elastic constants, Debye temperature, and vibrational spectra. Finally, we demonstrated the application of phosphor in a luminescence intensity ratio thermometry and obtained a relative sensitivity of 1.92% K^{-1} and a temperature resolution of 0.2 K in the range of physiological temperatures.

Introduction

 Mn^{5+} optical centers have the [Ar] $3d^2$ electron configuration and always encounter a strong crystal field when tetrahedrally coordinated in crystals. Their lower electronic states have the ${}^{3}A_{2}\,{<}\,{}^{1}E\,{<}\,{}^{1}A_{1}\,{<}\,{}^{3}T_{2}\,{<}\,{}^{3}T_{1}$ progression in energy. The ground state $({}^{3}A_{2})$ is orbitally non-degenerate and the first excited state ¹E has almost no nuclear displacement with respect to the ³A₂ state and can be split by the low-symmetry ligand field¹. The ¹E energy of approximately $8000-9000 \text{ cm}^{-1}$ is strongly affected by a nephelauxetic effect. At low temperatures, emission occurs

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solely from the spin-forbidden ${}^{1}E \rightarrow {}^{3}A_{2}$ electronic transition of a genuine electric dipole origin. At these temperatures, the emission from the spin-allowed ${}^{3}T_{2} \rightarrow {}^{3}A_{2}$ transition is almost negligible since the low energy orbital of the ${}^{3}T_{2}$ state is localized more than 1000 cm⁻¹ above the ¹E state, which results in its low population. Therefore, Mn^{5+} emissions appearing in the near infrared (NIR) spectral range at wavelengths longer than 1100 nm and have a narrow spectral band (FWHM < 10 nm) that can be split into two bands with an energy difference of up to 300 cm^{-1} . These emission bands are usually accompanied by vibronic sidebands and have decay times of a few tens to a few hundred microseconds.

The ultranarrow-band NIR luminescence of Mn5+ is especially favorable for NIR lasers $^{2-4}$ and the development of narrow-band NIR light sources for the selective identification of chemical analytes⁵. Recent research suggests that Mn⁵⁺ activated nanoparticles are excellent probes for deep-tissue luminescence imaging and luminescence

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thermometry in the second biological transparency window (1000-1350 nm) and that they show high photo- and chemical stabilities^{6,7}. One of their features, especially favorable from the biomedical application perspective, is that they exhibit broad and strong absorption bands from the spin-allowed electronic transitions that span the 500-1000 nm range⁸⁻¹³, which facilitates their excitation by the wavelength of the first optical biological window. They have a higher quantum efficiency (QE) than Ag₂S or Ag₂Se quantum dots, and do not contain toxic heavy metals like InAs or PbS quantum dots, nor suffer from photobleaching and photoblinking. In comparison to the lanthanide activated NIR bioimaging nanoprobes, Mn⁵⁺ nanoparticles are brighter due to higher values of the d-d absorption cross-section compared to the spin-forbidden f-f absorptions in the NIR-excited lanthanides. All these advantages of Mn^{5+} indicate that it is an ion with a very important and, so far, unexplored application potential worth large-scale intensive research.

Emissions from Mn⁵⁺ centers have been demonstrated in a considerably smaller number of host materials compared to Mn²⁺ and Mn⁴⁺ optical centers¹⁴. To facilitate Mn^{5+} emission, the material needs to provide both the tetrahedral environment for Mn⁵⁺ and a sufficiently large energy bandgap compared to the Mn⁵⁺ transitions' energies. More importantly, the host material must provide the stabilization of the Mn 5+ valence state, which imposes more constraints on the materials' structure and composition than the 2+ and 4+ valance states. For these reasons, the majority of Mn⁵⁺ emitting host materials contain electropositive ions such as alkaline earth metals and PO4³⁻ and VO_4^{3-} groups (or SiO₄⁴⁻ group with a charge compensation). The typical examples of such materials are Mn^{5+} activated $Li_3PO_4^{15}$, $Sr_5(VO_4)_3F^{4,16}$, $Ba_5(PO_4)_3Cl^{17}$, Sr₅(PO₄)₃Cl^{1,17,18}, Ca₂PO₄Cl^{1,17}, Ca₂VO₄Cl^{1,17}, Sr₂VO₄Cl^{1,17}, $Y_2SiO_5^{19}$, and M_2SiO_4 (M = Ba, Sr, Ca)²⁰.

Recently, Kim et al.²¹ have introduced the $\rm Ca_6Ba(\rm PO_4)_4O:\rm Mn^{5+}$ as a new blue pigment that shows coloration due to intense Mn⁵⁺ absorption, but its luminescent properties have not been analyzed. Also recently, the efficient yellow emission from Eu²⁺ activated Ca₆Ba(- $PO_4)_4O$ has been demonstrated^{22–24}, implying that Ca₆Ba(PO₄)₄O is an interesting host material for luminescent ions. Considering Ca₆Ba(PO₄)₄O structure and composition, one can observe seven electropositive ions (six Ca and one Ba) surrounding the rigidly connected PO₄ tetrahedra. Thus, one may assume that the Mn^{5+} emission, in this new host-activator combination, would be efficient and of high energy due to the nephelauxetic effect. For this reason, we prepared the $Ca_6Ba(PO_4)_4O:Mn^{5+}$ powder for this research and observed the intense NIR emission under the 650 nm excitation. The emission energy of 8772 cm^{-1} is among the highest energies detected for Mn⁵⁺ activated phosphors. Considering the potential use of Ca₆Ba(PO₄)₄O

for both yellow and NIR phosphors and the absence of data on its electronic and vibrational properties, we calculated and explained its electronic band structure, the partial and total density of states (DOS), effective Mulliken charges of all constituent ions, elastic constants, Debye temperature, and vibrational spectra of undoped and Mn⁵⁺ doped material. Then, we proceeded with the detailed characterization and analysis of Ca₆Ba(PO₄)₄O:Mn⁵⁺ luminescence that includes the measurements of material absorption, excitation and emission spectra, emission decays, concentration quenching, quantum yield, the temperature dependence of emission band shift, bandwidth and decay, and the calculation of the crystal field parameters. This versatile characterization and analysis of Ca₆Ba(PO₄)₄O:Mn⁵⁺ undoubtedly confirm the high potential of this material in NIR applications.

Experimental

The conventional solid-state reaction was employed for the preparation of Ca₆BaP_{4-4x}Mn_{4x}O₁₇ (x = 0.005, 0.0075, 0.0125, 0.01, 0.015, 0.02) powder samples. Stoichiometric amounts of CaCO₃ (Alfa Aesar, 98%), BaCO₃ (Alfa Aesar, 99.8%), (NH₄)H₂PO₄ (Alfa Aesar, 98%), and MnO (Aldrich, 99.99%) were thoroughly mixed in an agate mortar for 1 h with an appropriate amount of ethanol. Mixtures of the raw materials were placed in alumina crucibles and heated in an air atmosphere at 600 °C for 6 h, ground in an agate mortar, and further calcinated at 1280 °C for 10 h.

The crystal structure of powders was examined by powder X-ray diffraction (PXRD) using the Rigaku SmartLab instrument (Cu-K $\alpha_{1,2}$ radiation; $\lambda = 0.1540$ nm) at room temperature. Data were recorded over the 6° -130° 20 range, with a 0.01° step size and 1 min/° counting time. All PXRD data were analyzed by the Rietveld method implemented in TOPAS Academic software^{25,26}. Raman scattering measurements were performed using micro - Raman system TriVista 557 equipped with a triple monochromator and CCD detector (monochromator configuration 900/900/1800 points per millimeter) with 1.5 cm^{-1} resolution. For excitation, Ar laser line at 514.5 nm has an incident power of less than 60 mW to minimize the heating effect. Laser beam was focused on the samples by means of microscopic lenses with 100× magnification. Spectra were recorded in the range of 100–1200 cm⁻¹. Measurements of diffuse reflectance were performed on the Thermo Evolution 600 spectrometer equipped with an integrated sphere, using BaSO₄ as a reference over the 220-1350 nm wavelength range. The photoluminescence emission and emission decays were measured using the FLS1000 Fluorescence spectrometer (Edinburgh Instruments; 0.1 nm spectral resolution) supplied with R5509-72 photomultiplier tube from Hamamatsu in nitrogen-flow

cooled housing for near-infrared range detection. For measurements of the emission spectra and decays, the 668 nm laser diode excitation is used in the continuous and pulsed mode, respectively. The temperature of the sample was controlled using a THMS 600 heatingcooling stage from Linkam (0.1 K temperature stability and 0.1 K set point resolution). Emission decays at low temperatures were recorded at 1136 nm for all samples. The luminescence quantum efficiencies were measured using FLS980 Fluorescence Spectrometer from Edinburgh Instruments equipped with 450 W Xenon lamp, R5509-72 photomultiplier tube from Hamamatsu in nitrogen-flow cooled housing for near-infrared range detection, and calibrated integrating sphere for the direct absolute efficiency reading. The Al₂O₃ powder was used as a scattering reference. Thermometry was performed using a custom-made Peltier-based heating stage in the 20-100 °C range (0.02 °C precision). An Ocean Insight LSM-635A LED was used as the excitation source and is controlled by the Ocean Insight LDC-1 single channel driver and controller. The bifurcation optical Y cable was used for measuring PL emission spectra by Ocean Insight NIRQuest+ Spectrometers.

Results and discussion

The structure of Ca₆Ba(PO₄)₄O and Ca₆Ba(PO₄)₄O:Mn⁵⁺

The starting model used for Rietveld refinement and detailed structural analysis of the two key materials the $Ca_6Ba(PO_4)_4O$ host and the sample containing 0.5% Mn – was the previously published crystal structure of Ca₆Ba(PO₄)₄O determined from synchrotron powder diffraction data²². Refined parameters included the zeropoint error, background polynomial terms, peak shape function terms, unit cell parameters, an isotropic atomic displacement parameter per atom type and atomic fractional coordinates, using bond valence sum restraints on the two P atoms. The key crystallographic parameters are summarized in Table 1. Ca₆Ba(PO₄)₄O and Ca₆Ba(PO₄)₄O:0.5%Mn adopt monoclinic space group C2/m, with one Ba, two Ca, two P and seven O atoms in the asymmetric unit. Ba atoms are 12-coordinate, the two crystallographically unique Ca atoms are 7- and 8-coordinate, while both unique P atoms adopt tetrahedral coordination environments. Dopant Mn⁵⁺ ions replace P^{5+} on these two sites, which lie on a mirror plane (Wyckoff site 4 m in space group C2/m). In $Ca_6Ba(PO_4)_4O_4$, the average cation-oxygen bond lengths in the two tetrahedra are 1.534(13) and 1.529(15) Å, while bond angles range from 105.1(8) to 112.9(7)° and 105.3(7) to $112.8(9)^{\circ}$, with bond valence sums of 5.0(1)for both P atoms. In $Ca_6Ba(PO_4)_4O:0.5\%Mn$, the coordination environments remain similar, as expected given a low doping level. Average bond lengths are 1.534(22) and 1.504(27) Å, while bond angles range from 103.4(16) to 112.8(12)° and from 105.5(13) to 112.5(11)°, with bond valence sums of 5.0(2) and 5.4(2) for P1 and P2 sites, (see Tables 2 and 3), respectively. The final Rietveld fits obtained are shown in Fig. 1a, b, while the unit cell and the P atom environments are given in Fig. 1c, d, respectively.

Electronic properties

A detailed calculation of the electronic properties of the $Ca_6Ba(PO_4)_4O$ was performed to verify if its electronic structure is suitable to facilitate the Mn^{5+} emission. The electronic configurations for all chemical elements in $Ca_6Ba(PO_4)_4O$ were as follows: $O - 2s^22p^4$, $P - 3s^23p^3$, $Ca - 3s^23p^64s^2$, $Ba - 5s^25p^66s^2$. The following parameters were used for the calculations: energy 10^{-5} eV per atom; maximal force $0.03 \text{ eV}\text{Å}^{-1}$; maximal stress 0.05 GPa; maximal displacement 0.001 Å. K-points set was $2 \times 2 \times 2$ for geometry optimization and $3 \times 3 \times 3$ for the DOS calculations; the energy cut-off was 340 eV.

The structures obtained by geometry optimizations using the generalized gradient approximation (GGA) and the local density approximation (LDA) calculations are shown in Table 1 and are in excellent agreement, LDA especially, with the data obtained by Rietveld analysis of PXRD.

The band gaps in both GGA and LDA calculations, Fig. 2a, are direct, equal to 4.365 eV (GGA) and 4.475 eV (LDA) and have similar values to the reported bandgaps of 4.75 eV for the Ca₄(PO₄)₂O and 5.0 eV for the Ba₂Ca(PO₄)₂^{27,28}. Since the density-functional theory-based calculations (DFT) always tend to underestimate the true band gaps, the calculated values should be considered as lower band gap estimates.

The conduction band is due to the Ca 4s, 3d and Ba 6s states, Fig. 2b. The top of the valence band is remarkably flat, thus indicating extremely high effective masses of holes. The valence band consists of two sub-bands, which are separated by a narrow gap of about 0.5 eV. The upper one - from about -4.2 eV to 0 eV is made predominantly by the oxygen 2p states. The lower one (from -4.7 eV to about -7 eV) consists of the O 2p states and P 3p states, highly hybridized with each other. The P 3s states make another narrow band between -7.5 eV and -8.5 eV. The O 2s and P 3s states are spread between -22 eV and -17.5 eV, making several clearly seen maxima. The Ba 5s and 5p states are peaked at about -26 eV and -11 eV, respectively, whereas the Ca 3s and 3p states are localized deep in energy at about $-38 \, \text{eV}$ and $-20 \, \text{eV}$, respectively.

The considered crystal has a high degree of covalency of chemical bonds, which can be assessed by calculating effective Mulliken charges. Since there are two crystal-lographically inequivalent P^{5+} ions, two Ca^{2+} ions and seven O^{2-} ions and since two types of calculations

Exp. Ca ₆ Ba(PO ₄) ₄ O				Exp. C				
<i>a</i> , Å	12.300	06 (1)		12.2973 (2)				
b, Å	7.1047	72 (7)		7.10258	3 (1)			
<i>c</i> , Å	11.715	540 (9)		11.712	5 (1)			
β, °	134.46	519 (4)		134.455	52 (8)			
<i>V</i> , Å ³	730.73	3 (1)		730.22	(2)			
Fractional	atomic coordinates							
	x	у	z	x	у	z		
Ba	0	0	0	0	0	0		
Ca1	0.7196 (6)	0	0.3117 (8)	0.719 (1)	0	0.311 (1)		
Ca2	0.0505 (4)	0.7665 (5)	0.6929 (4)	0.0505 (8)	0.766 (1)	0.6930 (7)		
0	0	0	0.5	0	0	0.5		
011	0.399 (1)	0	0.5822 (5)	0.39 4 (2)	0	0.5822 (8)		
012	0.281 (1)	-0.175 (1)	0.3367 (6)	0.281 (2)	-0.175 (2)	0.336 (1)		
O13	0.120 (1)	0	0.366 (1)	0.120 (2)	0	0.365 (2)		
O21	0.289 (1)	0	0.106 (2)	0.290 (3)	0	0.104 (3)		
022	0.242 (1)	0	-0.1373 (5)	0.241 (3)	0	-0.1368 (7)		
O23	0.462 (1)	-0.179 (1)	0.114 (1)	0.461 (2)	-0.174 (2)	0.114 (1)		
P1	0.2673 (6)	0	0.3999 (2)	0.266 (1)	0	0.3998 (2)		
P2	0.3659 (8)	0	0.0469 (2)	0.365 (1)	0	0.0469 (3)		
	Calcu	lated						
	GGA			LDA				
<i>a</i> , Å	12.41	30		12.07	55			
b, Å	7.14	193		6.965	58			
<i>c</i> , Å	11.83	311		11.4881				
β, °	134.3735		134.4363					
<i>V</i> , Å ³	750.48	39		689.983				
Fractional	atomic coordinates							
	x	У	z	x	у	z		
Ba	X	У	Ζ	X	У	Ζ		
Ca1	0	0	0	0	0	0		
Ca2	0.71621	0	0.30969	0.71770	0	0.31126		
0	0.05261	0.76649	0.69427	0.05232	0.76734	0.69366		
011	0	0	0.5	0	0	0.5		
012	0.39056	0	0.58173	0.39300	0	0.58450		
O13	0.28457	-0.17593	0.34032	0.28484	-0.17824	0.33934		
O21	0.11338	0	0.34744	0.11195	0	0.34779		
O22	0.29114	0	0.11117	0.29072	0	0.11278		
O23	0.24386	0	-0.13571	0.24374	0	-0.13726		
P1	0.46648	-0.17433	0.11348	0.46930	-0.17679	0.11594		
P2	0.26593	0	0.39888	0.26621	0	0.39890		

Table 1 Summary of structural data for $Ca_6Ba(PO_4)_4O$ and $Ca_6Ba(PO_4)_4O:Mn^{5+}$ (space group C2/m)

(GGA/LDA) were run, we give the ranges, in which these charges fall for all ions. They are -1.07-1.09 (in units of proton charge) for the oxygen ions, +2.25 + 2.34 for the phosphorus ions, +1.25 + 1.31 for the calcium ions, and +1.39 + 1.47 for the barium ions. The deviation from the formal charges is especially large

for the P and O ions, whereas the Ca and Ba effective charges are closer to their formal ones. This is consistent with the P-O bonds being more covalent than the Ca-O and Ba-O ones.

With the calculated elastic constants, it is possible to estimate the Debye temperature using the following equations:

$$\theta_D = \frac{h}{k} \left(\frac{3n}{4\pi} \frac{N_A \rho}{M}\right)^{1/3} \nu_m \tag{1}$$

$$\nu_m = \left[\frac{1}{3}\left(\frac{2}{\nu_t^3} + \frac{1}{\nu_l^3}\right)\right]^{-1/3}$$
(2)

$$\nu_l = \sqrt{\frac{3B + 4G}{3\rho}}, \ \nu_t = \sqrt{\frac{G}{\rho}} \tag{3}$$

where $h = 6.626 \times 10^{-34}$ J·s is the Planck's constant; $k_B = 1.381 \times 10^{-23}$ JK⁻¹ is the Boltzmann constant; $N_A = 6.022 \times 10^{23}$ mol⁻¹ is the Avogadro's number; ρ is the crystal's density; n is the number of atoms per one formula unit (twenty eight in the case of Ca₆Ba(PO₄)₄O), and M is the formula weight. The average, transverse and longitudinal sound velocities are denoted by v_m , v_v , v_h , correspondingly. The B (bulk modulus) and G (shear modulus) values are calculated as the average values of the corresponding Voigt and Reuss (denoted with the V and R

Table 2 P–O bond lengths (Å)

	Undoped Ca	₆ Ba(PO ₄) ₄ O	Mn ⁵⁺ doped Ca ₆ Ba(PO₄)₄O		
	P1	P2	P1	P2	
	1.530 (5)	1.52 (3)	1.527 (8)	1.48 (6)	
	1.523 (13)	1.542 (5)	1.53 (2)	1.537 (7)	
	1.523 (13)	1.527 (12)	1.53 (2)	1.50 (2)	
	1.56 (2)	1.527 (12)	1.55 (4)	1.50 (2)	
Avg:	1.534 (13)	1.529 (15)	1.534 (22)	1.504 (27)	

subscripts, respectively) values from Table 4. With these equations and calculated elastic parameters, the Debye temperature for $Ca_6Ba(PO_4)_4O$ was estimated to be 496 K (GGA) and 551 K (LDA).

Vibrational spectra

For an undistorted tetrahedron (T_d symmetry), the four fundamental vibrational modes (all Raman active) are $a_1 + e + 2t_2^{1,29,30}$. The $v_1(a_1)$ is the totally symmetric stretching mode, $v_2(e)$ is bending deformation, and $v_3(t_2)$ and $v_4(t_2)$ vibrations are the two stretching t_2 modes. With symmetry lowered from T_d to C_s , several bands appear for each vibrational mode. Raman scattering spectra of the Ca₆Ba(PO₄)₄O and Ca₆Ba(PO₄)₄O:Mn⁵⁺ powders are shown in Fig. 3a, b, respectively. The following assignment is made for the $Ca_6Ba(PO_4)_4O: v_L$ $(cm^{-1}) = 123, 153, 183, 215.4, 262.5, and 294.7$ are the lattice modes; $v_1(a_1)$ (cm⁻¹) = 944 and 985.3; $v_2(e) = 434.5 \text{ (cm}^{-1}); v_3(t_2) \text{ (cm}^{-1}) = 1040.1, \text{ and } 1074.2;$ $v_4(t_2)$ (cm⁻¹) = 584.3 and 608.3. In Raman scattering spectra of the $Ca_6Ba(PO_4)_4O:Mn^{5+}$ powder, Fig. 3b, additional vibrations from the MnO_4^{3-} ion are clearly visible: $v_1(a_1)$ (cm⁻¹) = 807; $v_2(e)$ (cm⁻¹) = 314.4; $v_3(t_2)$ $(cm^{-1}) = 851.4; v_4(t_2) (cm^{-1}) = 343.9, 356.2, and 368.5;$ $v_{1+} v_L / v_{3+} v_L$ (cm⁻¹) = 1128.5 and >1128.5. They agree with the data reported by Gonzalez-Vilchez and Griffith²⁹ for vibrational modes of the MnO_4^{3-} molecular ion.

Photoluminescence properties

Figure 4a, b displays the absorption, color (inset in Fig. 4a), and emission spectra of $Ca_6Ba(PO_4)_4O:0.5\%Mn^{5+}$ powder. The observed absorption and emission, the blue coloration of the Mn^{5+} doped powder, and the characteristic vibrational modes of MnO_4^{3-} in the Raman scattering spectrum of $Ca_6Ba(PO_4)_4O:Mn^{5+}$ (Fig. 3b) all unambiguously demonstrate the presence of Mn^{5+} in the sample.

Table 3 O–P–O angles and their difference, δ , to regular tetrahedron angle of 109.5°

Undoped Ca ₆ Ba(PO ₄) ₄ O				Mn ⁵⁺ doped Ca ₆ Ba(PO ₄) ₄ O			
P1	δ [°]	P2	δ [°]	Mn1	δ [°]	Mn2	δ [°]
109.8 (12)	0.3	112.8 (9)	3.3	110 (2)	0.5	111.9 (17)	2.4
107.9 (4)	-1.6	105.3 (7)	-4.2	108.8 (8)	-0.7	105.5 (13)	-4.0
107.9 (4)	-1.6	105.3 (7)	-4.2	108.8 (8)	-0.7	105.5 (13)	-4.0
105.1 (8)	-4.4	109.1 (11)	-0.4	103.4 (16)	-6.1	10 9 (2)	-0.5
112.9 (7)	3.4	111.9 (6)	2.4	112.8 (12)	3.3	112.5 (11)	3.0
112.9 (7)	3.4	111.9 (6)	2.4	112.8 (12)	3.3	112.5 (11)	3.0
Avg (δ)	-0.08		-0.12	Avg (δ)	-0.07		-0.42
Avg (abs(δ))	2.4		2.8	Avg (abs(δ))	2.4		2.8



Fig. 1 The structure of Ca₆Ba(PO₄)₄O:Mn⁵⁺. a Rietveld fits for Ca₆Ba(PO₄)₄O, R_{wp} = 5.31%. b Rietveld fit for Ca₆Ba(PO₄)₄O:Mn⁵⁺, R_{wp} = 8.59%. In each case the blue curve represents the observed pattern, the red curve is the calculated pattern and the difference curves are shown in grey, while blue tick marks represent the positions of the Bragg peaks. c The crystal structure of Ca₆Ba(PO₄)₄O, with the unit cell viewed along the b-axis; d Geometries of two PO₄ tetrahedra with average P–O bond lengths in Ca₆Ba(PO₄)₄O:Mn⁵⁺.



Table 4 Calculated elastic constants (in GPa) for $Ca_6Ba(PO_4)_4O$

	GGA	LDA
C ₁₁	127.8	162.1
C ₂₂	141.2	180.3
C ₃₃	149.1	186.3
C ₄₄	29.7	42.4
C ₅₅	48.0	60.7
C ₆₆	55.5	67.3
C ₁₂	62.7	81.8
C ₁₃	45.5	62.8
C ₁₅	4.0	-2.0
C ₂₃	38.9	56.4
C ₂₅	-4.7	-11.7
C ₃₅	-5.2	-7.7
C ₄₆	3.5	-3.8
B _V	79.2	103.4
B _R	79.0	102.5
G _V	44.7	55.9
G _R	41.6	53.3

Figure 4a depicts the Kubelka-Munk transformation of the Ca₆Ba(PO₄)₄O:Mn⁵⁺ powder diffuse reflection measured between 220 and 1350 nm. The $O^{2-} \rightarrow Mn^{5+}$ charge-transfer band appears at around 301 nm $(33,222 \text{ cm}^{-1})$ as expected for the tetraoxo-coordinated Mn^{5+31} and the peak at the lower wavelength (225 nm) is associated with the intrinsic host absorption. The strong absorption around $639 \text{ nm} (15,649.5 \text{ cm}^{-1})$ is associated with the ${}^{3}A_{2} \rightarrow {}^{3}T_{1}({}^{3}F)$ electronic transition, which is electric dipole-allowed in an undistorted tetrahedral symmetry and is composed of three overlapping components due to the removal of the orbital degeneracy of the ${}^{3}T_{1}({}^{3}F)$ state with the site symmetry lowering from T_d to C_s . The weak shoulder at about 943 nm $(10,604.5 \text{ cm}^{-1})$ corresponds to the symmetry forbidden ${}^{3}A_{2} \rightarrow {}^{3}T_{2}({}^{3}F)$ transition (in T_{d} site symmetry) and becomes partially allowed with a symmetry lowering. The electric dipole-allowed ${}^{3}A_{2} \rightarrow {}^{3}T_{1}({}^{3}P)$ transition that corresponds to a two-electron jump is located at approximately 369 nm $(27,100 \text{ cm}^{-1})$ and is barely visible due to the much more intense charge transfer band. The spin-forbidden transitions to the singlet states ${}^{1}A_{1}({}^{1}G)$ at 740 nm $(13,513.5 \text{ cm}^{-1})$ and ${}^{1}E({}^{1}D)$ at 1140 nm (8772 cm^{-1}) are weak, sharp, and only weakly depend on the host materials properties. The transitions to ${}^{1}T_{1,2}$ singlet states are difficult to observe in the spectrum



since they are very weak and superimposed on the main and stronger bands.

Emission spectra of $Ca_6Ba(PO_4)_4O:Mn^{5+}$ powder measured at -190 °C and 10 °C are shown in Fig. 4b with blue and red lines, respectively, and are typical for emissions from transitions of $3d^2$ electronic configuration in a tetrahedral environment as described by the Tanabe–Sugano diagram, Fig. 4c. The spectra show ultranarrow emission bands (FWHM = 3 nm (20 cm⁻¹) at -190 °C; FWHM = 5 nm (35 cm⁻¹) at 10 °C) from the $^{1}E \rightarrow ^{3}A_2$ intraconfigurational transition (1140 nm), followed by vibrational sidebands with progressions of $\approx 320 \text{ cm}^{-1}$ (($v_2(e)$) and $\approx 800 \text{ cm}^{-1}$ (($v_1(a_1)$). This indicates the coupling of the ^{1}E excited state and the nontotally symmetric $v_2(e)$ mode of MnO₄³⁻, i.e., a dynamic Jahn–Teller effect.

The very small splitting of ¹E emission band is due to only weakly distorted MnO_4 tetrahedra (see Table 3) and it is barely visible with our instrument resolution at the emission spectrum measured at low temperatures (-190 °C). The low-intensity broad emission band from the ${}^{3}T_2({}^{3}F) \rightarrow {}^{3}A_2$ transition is centered at 1062 nm (9416 cm⁻¹) and can be resolved only spectral deconvolution, Fig. 4d.

Temperature dependence of the ¹E lifetime and emission peak spectral position are shown in Fig. 4e, f, respectively. The ¹E level emission decays show lifetime values of about 350 μ s at room temperature and 560 μ s at low temperatures. The temperature dependence of



10 °C. **c** Tanabe–Sugano diagram for $3d^2$ electron configuration in tetrahedral coordination. **d** Emission spectrum of the Ca₆Ba(PO₄)₄O:Mn⁵⁺ measured at room temperature (black line) and the fit to the Gaussian of the ${}^{3}T_{2} \rightarrow {}^{3}A_{2}$ emission peak (red line) showing its maximum 1062 nm/ 9416 cm⁻¹. Spectra shown in logarithmic scale. **e** Temperature dependence of the excited state lifetime (symbols – experimental data, solid line – the fit to Eq. (4)). The inset shows emission decay measured at 208 K. **f** Temperature dependence of the ${}^{1}E$ emission peak spectral position (symbols – experimental data, solid line – the fit to Eq. (4)). The inset shows emission decay measured at 208 K. **f** Temperature dependence of the ${}^{1}E$ emission peak spectral position (symbols – experimental data, solid line – the fit to Eq. (5)). **g** The estimate of configurational diagram based on the spectroscopic data with calculated Stokes shift (E_{stokes}) and Huang–Rhys parameter (S). **h** Photoluminescence internal quantum efficiency (QE) of Ca₆Ba(PO₄)₄O:Mn⁵⁺ powders for different concentrations of Mn. The inset shows linear dependence of the ${}^{1}O_{0}CE/concentration$) vs ${}^{1}O_{10}(concentration)$ for data equal and above critical concentration (0.75%) with a slope of -1.97 indicating that a multipolar dipole-dipole mechanism is responsible for the concentration quenching of emission. **i** The linear dependence of Ca₆Ba(PO₄)₄O:Mn⁵⁺ emission intensity on excitation power

lifetime, Fig. 4e, shows that a low-temperature lifetime value is approximately the value of a radiative lifetime. Considering that the excited state is separated in energy from the ground state by 8772 cm^{-1} , almost eight quanta of the highest vibrational frequencies of the phosphor ($\approx 1100 \text{ cm}^{-1}$) are needed to bridge the gap. Thus, a multiphonon non-radiative relaxation is not probable as the emission quenching mechanism.

The ¹E emission deactivation through the crossing with a charge transfer band is also not probable due to very high energy difference. Therefore, we assume that the thermal quenching of the ¹E state population takes place by a thermally activated cross-over via ³T₂ state, see Fig. 4g, similarly to Mn^{4+} activated phosphors. The temperature dependence of the emission lifetime, shown in Fig. 4e, can be described by the following equation^{32–35}:

$$\tau(T) = \frac{\tau_{R0} \cdot \tanh(h\nu/2k_BT)}{1 + (\tau_{R0} \cdot \tanh(h\nu/2k_BT)/\tau_{NR}) \cdot \exp(-\Delta E/k_BT)}$$
(4)

where $\tau_{R0} = 560 \pm 19 \,\mu s$ is the radiative lifetime at $T = 0 \,\text{K}$, $k_B = 0.69503476 \,\text{cm}^{-1}\text{K}^{-1}$ is the Boltzmann constant, $h\nu = 448 \pm 90 \,\text{cm}^{-1}$ is the average energy of phonon coupled to the ${}^{1}\text{E} \rightarrow {}^{3}\text{A}_{2}$ transition, $1/\tau_{NR} = 1527 \pm 120 \,\text{ms}^{-1}$ is the nonradiative decay rate, $\Delta E = 1631 \pm 200 \,\text{cm}^{-1}$ is the activation energy of the process (the cross-over via the ${}^{3}\text{T}_{2}$ state), and T represents the temperature. The smaller the configuration coordinate parabola offset between the ground state (${}^{3}\text{A}_{2}$) and the ${}^{3}\text{T}_{2}$ state, the larger the cross-over energy ΔE (activation energy of the process) needed to activate the non-radiative de-excitation process. Thus, the ${}^{1}\text{E} \rightarrow {}^{3}\text{A}_{2}$ emission of Mn⁵⁺ activated phosphors, which have large ${}^{3}\text{T}_{2}$ energies and smaller Stokes shifts, will start to quench at higher temperatures.

The shift of ${}^{1}E$ emission band with energy is shown in Fig. 4f. It can be described by the following equation: 36,37

$$\delta E\left[\mathrm{cm}^{-1}\right] = \alpha \cdot \left(\frac{T}{\theta_D}\right)^4 \cdot \int_0^{T/\theta_D} \frac{x^3}{e^x - 1} dx \tag{5}$$

where $\theta_D = 783 \pm 12$ K is the Debye temperature of the host material, $x = \hbar \omega_D / k_B T = \theta_D / T$, ω_D is Debye cut-off frequency, and $\alpha = -650 \pm 17$ cm⁻¹ represents the electron-phonon coupling coefficient. The relatively high Debye temperature indicates a rigid structure which favors efficient emissions from optical centers³⁸.

The concentration dependence of an internal quantum efficiency (QE) is given in Fig. 4h. The largest value of $37.5 \pm 2.0\%$ is recorded for the 0.5% Mn⁵⁺ doped sample, after which the concentration quenching of emission occurs. This is a relatively high value for an NIR-emitting phosphor, and comparable to one obtained in Ba₃(PO₄)₂⁷. The log₁₀(QE/concentration) vs log₁₀(concentration) plot has a -1.97 slope, which is close to -2, which undoubtedly indicates that a multipolar electric dipole-dipole mechanism is responsible for the concentration quenching of emission. The linear dependence of Ca₆Ba(PO₄)₄O:Mn⁵⁺ emission intensity on excitation power, Fig. 4i, is expected for the typical downshifting photoluminescence emission process.

The 3d² electronic configuration of Mn⁵⁺ in a tetrahedral environment is described by the Tanabe–Sugano model for 3d⁸ electronic configuration in octahedral symmetry³⁹, see Fig. 4c. The crystal field and Racah parameters are calculated from the following equations using data from diffuse

reflection and emission spectra^{40,41}:

$$Dq = \frac{E({}^{3}A_{2} \to {}^{3}T_{2})}{10} = \frac{10604.5}{10} \text{ cm}^{-1} = 1060 \text{ cm}^{-1}$$
(6)

$$\begin{aligned} x &= \frac{E({}^{3}A_{2} \rightarrow {}^{3}T_{1}) - E({}^{3}A_{2} \rightarrow {}^{3}T_{2})}{Dq} \\ &= \frac{15649.5 - 10604.5}{1060.45} = 4.757 \end{aligned}$$
(7)

$$B = \frac{x^2 - 10x}{15 \cdot (x - 8)} \cdot Dq = 544 \text{ cm}^{-1} \to \frac{10Dq}{B} = 19.5$$
(8)

$$C = \frac{1}{2} \cdot \left(E \left({}^{3}A_{2} \rightarrow {}^{1}E \right) - 10Dq - 8.5B + \frac{1}{2}\sqrt{400Dq^{2} + 40DqB + 49B^{2}} \right)$$
$$= 2292 \text{ cm}^{-1}$$

$$C/B = 4.21$$
 (10)

By comparing the obtained Dq, B and C parameters with literature data, Table 5, one can observe that $Ca_6Ba(PO_4)_4O$ provides the smallest Dq and the largest B parameters amongst all phosphate hosts, and that Li_3VO_4 is the only host with a smaller Dq (considering available data).

By considering the obtained parameters and the configuration coordinate diagram, Fig. 4g, the relatively small value of Huang–Rhys parameter S = 0.53 is found for the assumed coupling to the v_{1+} v_L / v_{3+} v_L vibrational mode with energy $\hbar\omega = 1128.5$ cm⁻¹.

The Slater parameters are calculated from Racah parameters by the simple relations^{42,43}:

$$F^{(2)} = 49F_2 = 7(7B + C) = 42271 \text{cm}^{-1}$$
(11)

$$F^{(4)} = 441F_4 = 441\frac{C}{35} = 28877 \text{ cm}^{-1}$$
 (12)

Table 5 Comparison of the *Dq*, *B* and *C* parameters (all in cm^{-1}) for the tetrahedrally coordinated Mn^{5+} ions in different crystalline solids

Host material	Dq	В	с	Reference
Li ₃ PO ₄	1208	475	2556	49
Ca ₂ PO ₄ Cl	1162	455	2657	49
Y ₂ SiO ₅	1133	550	2255	50
Sr ₅ (PO ₄) ₃ Cl	1100	500	2320	3
YAIO ₃	1100	485	2256	51
Sr ₁₀ (VO ₄) ₆ F ₂	1088	518	2321	52
Ca ₆ Ba(PO ₄) ₄ O	1060	544	2292	This work
Li ₃ VO ₄	1049	646	2006	53



represents the value at 303.15 K ($30 ^{\circ}\text{C}$)

Both values are considerably reduced from the free-ion values of $F^{(2)} = 91427$ cm⁻¹ and $F^{(4)} = 56625$ cm⁻¹¹⁸.

As it follows from the Tanabe–Sugano diagram for the $3d^2$ configuration in the tetrahedral crystal field (Fig. 4c), the energy separation between the ground state ${}^{3}A_{2}$ and the first excited state ${}^{1}E$ (in the strong crystal field) is practically independent on the crystal field strength (both states are parallel to each other). At the same time, this energy interval is very close to the energy interval between the ${}^{3}F$ and ${}^{1}D$ states of the free ion, which is determined by the Racah parameters *B* and *C*, which vary from host to host because of the covalent effects. As a result, the nephelauxetic effect is dominating in this case.

Application in luminescence thermometry

We have tested the performance of Mn^{5+} activated $Ca_6Ba(PO_4)_4O$ (the sample containing 0. 5% Mn since it showed the best quantum efficiency) as a NIR luminescent thermometer operating in the second biological window and in the physiological temperature range.

As can be seen from Fig. 5a, when temperature increases, the broad emission peak from the ${}^{3}T_{2}$ level in the 950 nm to 1030 nm range also increases in intensity, while the intensity of the narrow emission peak from the ${}^{1}E$ level around 1140 nm decreases with temperature. This occurs due to thermalization between ${}^{1}E$ and ${}^{3}T_{2}$ levels where the energy difference between these two levels (ΔE_{T}) is bridged by thermally exited electrons. Consequently, a simple Boltzmann-type relation for the luminescence intensity ratio (LIR) between the two abovementioned emission intensities applies^{44,45}:

$$LIR(T) = \frac{I({}^{3}T_{2})}{I({}^{1}E)} = B \cdot \exp\left(-\frac{\Delta E_{T}}{k_{B}T}\right)$$
(13)

where *B* is a temperature-invariant constant and *T* represents temperature. The fit of Eq. (13) (full line, Fig. 5b) to experimental LIR data (diamond markers, Fig. 5b) is almost perfect ($R^2 = 0.997$) and provides an energy difference ΔE_T of 1216 cm⁻¹ that agrees with the energy difference obtained from spectroscopy (Fig. 4g).

To experimentally determine the uncertainty in the LIR (error budget), 50 emission spectra were acquired at each temperature. Then, the measurement distribution mean was used as the LIR value while a standard deviation (σ_{LIR}) was used as an uncertainty in LIR as shown in the insert of Fig. 5b on the LIR value distribution measured at 30 °C).

The absolute (S_a) and relative (S_r) sensitivities of the thermometer were then calculated from the following equations:

$$S_{a}[\mathbf{K}^{-1}] = \left| \frac{\partial LIR}{\partial T} \right|, \ S_{r}[\%\mathbf{K}^{-1}] = 100\% \cdot \left| \frac{\partial LIR}{\partial T} \frac{1}{LIR} \right|$$
(14)

and presented in Fig. 5c (blue dots represent values obtained at a temperature of 30 °C). The relative sensitivity value varies from 2.35%K⁻¹ to 1.26%K⁻¹ over the measurement range, being 1.92%K⁻¹ at 30 °C. These are relatively high values⁴⁶, especially for luminescence thermometers operating in the second biological transparency window (>1000 nm). For example, Gschwend et al.⁴⁷ achieved a relative sensitivity of 0.43%K⁻¹ for an LIR thermometer based on Mn⁵⁺-activated Ba₃(PO₄)₂, while Shen et al.⁴⁸ achieved a relative sensitivity of 1.3%K⁻¹ for an LIR thermometer based on Ag₂S quantum dots.

The temperature resolution (uncertainty in measured temperature, δT) is determined as a ratio between experimentally obtained LIR uncertainty (σ_{LIR}) and absolute sensitivity (S_a) for a given temperature, Fig. 5d:

$$\delta T = \frac{\sigma_{LIR}(T)}{S_a(T)} \tag{15}$$

and it has an average value of 0.21 K. Finally, repeatability of measurement (R_M) is quantified as⁴⁶:

$$R_M = 1 - \frac{max \left| \overline{LIR} - LIR_i \right|}{\overline{LIR}} \tag{16}$$

where \overline{LIR} is the average LIR measured at a certain temperature over all LIR_i acquired. Based on experimental data, an R_M value of 0.97 (97%) is obtained.

Conclusion

Because of its rigid structure, appropriate crystal sites for doping, and sufficiently large energy band gap to accommodate the energy levels of dopant ions, $Ca_6Ba(PO_4)_4O$ is an excellent host for Eu^{2+} , Sm^{2+} and Mn^{5+} luminescence centers. In this host, Mn^{5+} provides ultranarrow emission in the near-infrared spectral range at 1140 nm that can be easily excited over the broad spectral range that spans 500–1000 nm covering the entirety of the first biological transparency window and making this material an excellent near-infrared phosphor and non-toxic blue/turquoise pigment. The phosphor has an internal guantum efficiency of 37.5%, which is a high value considering the quantum efficiencies of inorganic NIR phosphors. The thermal quenching of the ¹E emission takes place by a thermally activated cross-over via the ${}^{3}T_{2}$ state with an activation energy of 1631 cm⁻¹. The optimal Mn^{5+} doping concentration is 0.5%. For higher doping concentrations, quantum efficiency decreases due to non-radiative deexcitation caused by a dipoledipole electric interaction. Based on the available literature data, the $Ca_6Ba(PO_4)_4O:Mn^{5+}$ phosphor provides the smallest Dq and the largest B parameters amongst all phosphate hosts. This material is one of the best singledoped ratiometric luminescence thermometry sensors for use in a second biological transparency window due to the opposite temperature dependence of the ¹E and ${}^{3}T_{2}$ emission intensities. It provides a relative sensitivity of 1.92%K⁻¹ and a temperature resolution of 0.2 K in the range of physiological temperatures, with a measurement repeatability of 97%. These findings, particularly the high value of quantum efficiency and strong absorption, tuneability of emission wavelength by changing the Mn⁵⁺ environment, long emission decay times that allow for time-gated measurements, and strong temperature susceptibility of emission, demonstrate the great potential of Mn⁵⁺-activated phosphors for NIR applications. When reduced to nano dimension, $Ca_6Ba(PO_4)_4O:Mn^{5+}$ has great potential for bioimaging and biothermal imaging applications in the second biological transparency window. Future research will concentrate on the synthesis and applications of $Ca_6Ba(PO_4)_4O:Mn^{5+}$ nanoparticles.

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Data availability

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

Conflict of interest

The authors declare no competing interests.

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References

- Capobianco, J. A. et al. Near-infrared intraconfigurational luminescence spectroscopy of the Mn⁵⁺ (3*d*²) ion in Ca₂PO₄Cl, Sr₅(PO₄)₃Cl, Ca₂VO₄Cl and Sr₂VO₄Cl. *J. Lumin.* **54**, 1–11, https://doi.org/10.1016/0022-2313(92) 90043-9 (1992).
- Merkle, L. D. et al. Laser action from Mn⁵⁺ in Ba₃(VO₄)₂. Appl. Phys. Lett. 61, 2386–2388, https://doi.org/10.1063/1.108172 (1992).
- Moncorgé, R., Manaa, H. & Boulon, G. Cr⁴⁺ and Mn⁵⁺ active centers for new solid state laser materials. *Optical Mater.* 4, 139–151, https://doi.org/10.1016/ 0925-3467(94)90071-X (1994).
- Merkle, L. D., Guyot, Y. & Chai, B. H. T. Spectroscopic and laser investigations of Mn⁵⁺:Sr₅(VO₄)₃F. *J. Appl. Phys.* **77**, 474–480, https://doi.org/10.1063/1.359585 (1995).
- Ma, L. J. et al. Systematic discovery about NIR spectral assignment from chemical structural property to natural chemical compounds. *Sci. Rep.* 9, 9503, https://doi.org/10.1038/s41598-019-45945-y (2019).
- Gschwend, P. M. et al. Bi₂O₃ boosts brightness, biocompatibility and stability of Mn-doped Ba₃(VO₄)₂ as NIR-II contrast agent. J. Mater. Chem. B 9, 3038–3046, https://doi.org/10.1039/d0tb02792h (2021).
- Cao, R. P. et al. Near-infrared emission Ba₃(PO₄)₂:Mn⁵⁺ phosphor and potential application in vivo fluorescence imaging. *Spectrochimica Acta Part A* **128**, 671–673, https://doi.org/10.1016/j.saa.2014.02.081 (2014).
- Medina, E. A. et al. Intense turquoise colors of apatite-type compounds with Mn⁵⁺ in tetrahedral coordination. *Solid State Sci.* 52, 97–105, https://doi.org/ 10.1016/j.solidstatesciences.2015.12.001 (2016).
- Laha, S. et al. Stabilization of a tetrahedral (Mn⁵⁺O₄) chromophore in ternary barium oxides as a strategy toward development of new turquoise/greencolored pigments. *Inorg. Chem.* 55, 3508–3514, https://doi.org/10.1021/ acs.inorgchem.5b02957 (2016).
- Wang, Y. Q. et al. Synthesis and optical properties of intense blue colors oxides based on Mn⁵⁺ in tetrahedral sites in Ba₇A_{12,x}Mn_xO_{10+y}. *Ceram. Int.* 47, 686–691, https://doi.org/10.1016/j.ceramint.2020.08.177 (2021).
- Cui, K. Y. et al. Synthesis and properties of novel inorganic green chromophore based on Bi₂₄Al_{2-x}Mn_xO₃₉. *Ceram. Int.* **47**, 8944–8948, https://doi.org/10.1016/ j.ceramint.2020.12.016 (2021).
- Zhou, Y. C. et al. Synthesis and properties of novel turquoise-green pigments based on BaAl_{2-x}/Mn_xO_{4+y}. *Dyes Pigments* **155**, 212–217, https://doi.org/ 10.1016/j.dyepig.2018.03.042 (2018).
- Dardenne, K, Vivien, D. & Huguenin, D. Color of Mn(V)-substituted apatites *A*₁₀((β, Mn)O₄)₆F₂, A = Ba, Sr, Ca; B = P, V. J. Solid State Chem. **146**, 464–472, https://doi.org/10.1006/jssc.1999.8394 (1999).
- Zhou, Q. et al. Mn²⁺ and Mn⁴⁺ red phosphors: synthesis, luminescence and applications in WLEDs. A review. J. Mater. Chem. C 6, 2652–2671, https:// doi.org/10.1039/C8TC00251G (2018).
- Hazenkamp, M. F. et al. Excited state absorption and laser potential of Mn⁵⁺doped Li₃PO₄. *Chem. Phys. Lett.* **265**, 264–270, https://doi.org/10.1016/S0009-2614(96)01434-0 (1997).
- Kück, S., Schepler, K. L. & Chai, B. H. T. Evaluation of Mn⁵⁺-doped Sr₅(VO₄)₃F as a laser material based on excited-state absorption and stimulated-emission measurements. *J. Optical Soc. Am. B* **14**, 957–963, https://doi.org/10.1364/ JOSAB.14.000957 (1997).

- Herren, M. et al. Near-infrared luminescence of manganate(V)-doped phosphates and vanadates. J. Luminescence 53, 452–456, https://doi.org/10.1016/ 0022-2313(92)90196-G (1992).
- Capobianco, J. A. et al. Crystal-field analyis of Mn⁵⁺ (3d²) in Sr₅(PO₄)₃Cl. *Optical Mater.* 1, 209–216, https://doi.org/10.1016/0925-3467(92)90029-M (1992).
- Hömmerich, U. et al. The optical center M_nO₄³⁻ in Y₂SiO₅Mn, X (X=Al, Ca). *Chem. Phys. Lett.* **213**, 163–167, https://doi.org/10.1016/0009-2614(93)85435-Q (1993).
- Zhang, X. W. et al. Structural variation and near infrared luminescence in Mn⁵⁺-doped M₂SiO₄ (M = Ba, Sr, Ca) phosphors by cation substitution. *J. Mater. Sci. Mater. Electron.* 29, 6419–6427, https://doi.org/10.1007/s10854-018-8622-2 (2018).
- Kim, S. W. et al. Discovery of novel inorganic Mn⁵⁺-doped sky-blue pigments based on Ca₆BaP₄O₁₇: crystal structure, optical and color properties, and color durability. *Dyes Pigments* **139**, 344–348, https:// doi.org/10.1016/j.dyepig.2016.12.038 (2017).
- Komuro, N. et al. Synthesis, structure and optical properties of europium doped calcium barium phosphate – a novel phosphor for solidstate lighting. *J. Mater. Chem. C* 2, 6084–6089, https://doi.org/10.1039/ c4tc00732h (2014).
- Ji, H. P. et al. Facile solution-precipitation assisted synthesis and luminescence property of greenish-yellow emitting Ca₆Ba(PO₄)₄O:Eu²⁺ phosphor. *Mater. Res. Bull.* **75**, 233–238, https://doi.org/10.1016/j.materresbull.2015.11.055 (2016).
- Meng, Y. J. et al. Thermal stability of the luminescence of Ca₆Ba(PO₄)₄O₅Eu²⁺ yellow phosphor for white light-emitting diodes. *Appl. Phys. A* **122**, 636, https://doi.org/10.1007/s00339-016-0141-5 (2016).
- Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 2, 65–71, https://doi.org/10.1107/ S0021889869006558 (1969).
- Coelho, A. A. et al. The TOPAS symbolic computation system. *Powder Diffr.* 26, S22–S25, https://doi.org/10.1154/1.3661087 (2011).
- Deng, D. G. et al. Ca₄(PO₄)₂O:Eu²⁺ red-emitting phosphor for solid-state lighting: structure, luminescent properties and white light emitting diode application. J. Mater. Chem. C 1, 3194–3199, https://doi.org/10.1039/ C3TC30148F (2013).
- Yu, H. et al. Ba₂Ca(PO₄)₂:Eu²⁺ emission-tunable phosphor for solid-state lighting: luminescent properties and application as white light emitting diodes. J. Mater. Chem. C 1, 5577–5582, https://doi.org/10.1039/C3TC30998C (2013).
- Gonzalez-Vilchez, F. & Griffith, W. P. Transition-metal tetra-oxo-complexes and their vibrational spectra. J. Chem. Soc. Dalton Trans. 1416–1421, https://doi.org/ 10.1039/DT9720001416 (1972).
- Griffith, W. P. Raman studies on rock-forming minerals. Part II. Minerals containing MO₃, MO₄, and MO₆ groups. J. Chem. Soc. A 286-291, https://doi.org/ 10.1039/J1970000286 (1970).
- Lachwa, H. & Reinen, D. Color and electronic structure of manganese(V) and manganese(VI) in tetrahedral oxo coordination. A spectroscopic investigation. *Inorg. Chem.* 28, 1044–1053, https://doi.org/10.1021/ic00305a011 (1989).
- Ristić, Z. et al. Near-infrared luminescent lifetime-based thermometry with Mn⁵⁺-activated Sr₃(PO₄)₂ and Ba₃(PO₄)₂ phosphors. ACS Appl. Electron. Mater. 4, 1057–1062, https://doi.org/10.1021/acsaelm.1c01207 (2022).
- Senden, T., van Dijk-Moes, R. J. A. & Meijerink, A. Quenching of the red Mn⁴⁺ luminescence in Mn⁴⁺-doped fluoride LED phosphors. *Light Sci. Appl.* 7, 8, https://doi.org/10.1038/s41377-018-0013-1 (2018).
- Dramićanin, M. D. et al. Li₂TiO₃:Mn⁴⁺ deep-red phosphor for the lifetimebased luminescence thermometry. *Chem. Select* 4, 7067–7075, https://doi.org/ 10.1002/slct.201901590 (2019).
- 35. Srivastava, A. M. et al. Unusual luminescence of octahedrally coordinated divalent europium ion in Cs₂M²⁺P₂O₇ (M²⁺=Ca, Sr). J. Luminescence **129**, 919–925, https://doi.org/10.1016/j.jlumin.2009.03.018 (2009).
- McCumber, D. E. & Sturge, M. D. Linewidth and temperature shift of the *R* lines in ruby. *J. Appl. Phys.* 34, 1682–1684, https://doi.org/10.1063/1.1702657 (1963).
- Yen, W. M., Scott, W. C. & Schawlow, A. L. Phonon-induced relaxation in excited optical states of trivalent praseodymium in LaF₃. *Phys. Rev. J. Archive* 136, A271–A283, https://doi.org/10.1103/PhysRev.136.A271 (1964).
- Pust, P. et al. Narrow-band red-emitting Sr[LiAl₃N₄]:Eu²⁺ as a next-generation LED-phosphor material. *Nat. Mater.* **13**, 891–896, https://doi.org/10.1038/ nmat4012 (2014).
- Tanabe, Y. & Sugano, S. On the absorption spectra of complex ions. I. J. Phys. Soc. Jpn 9, 753–766, https://doi.org/10.1143/JPSJ.9.753 (1954).

- Brik, M. G. et al. Spin-forbidden transitions in the spectra of transition metal ions and nephelauxetic effect. *ECS J. Solid State Sci. Technol.* 5, R3067–R3077, https://doi.org/10.1149/2.0091601jss (2016).
- Schmidtke, H. H. The variation of slater-condon parameters F^k and racah parameters B and C with chemical bonding in transition group complexes. In: *Optical spectra and chemical bonding in inorganic compounds* (eds Mingos, D. M. P. & Schönherr, T.) 19–35 (Springer, Berlin, Heidelberg, 2004) https://doi.org/ 10.1007/b11303.
- Racah, G. Theory of complex spectra. III. Phys. Rev. J. Arch. 63, 367–382, https:// doi.org/10.1103/PhysRev.63.367 (1943).
- Dramićanin, M. Lanthanide and transition metal ion doped materials for luminescence temperature sensing. In: *Luminescence thermometry: methods, materials, and applications* (ed. Dramićanin, M.) (Elsevier, Amsterdam, 2018), https://doi.org/10.1016/B978-0-08-102029-6.00006-3.
- Marciniak, L. et al. Luminescence thermometry with transition metal ions. A review. *Coordination Chem. Rev.* 469, 214671, https://doi.org/10.1016/ j.ccr.2022.214671 (2022).
- Dramićanin, M. D. Trends in luminescence thermometry. J. Appl. Phys. 128, 040902, https://doi.org/10.1063/5.0014825 (2020).

- Gschwend, P. M. et al. Simultaneous nanothermometry and deep-tissue imaging. *Adv. Sci.* 7, 2000370, https://doi.org/10.1002/advs.202000370 (2020).
- Shen, Y. L. et al. Ag₂S nanoheaters with multiparameter sensing for reliable thermal feedback during in vivo tumor therapy. *Adv. Funct. Mater.* **30**, 2002730, https://doi.org/10.1002/adfm.202002730 (2020).
- Brik, M. G. et al. Crystal field parameters and energy level structure of the MnO₄³⁻ tetroxo anion in Li₃PO₄, Ca₂PO₄Cl and Sr₅(PO₄)₃Cl crystals. *J. Luminescence* **129**, 801–806, https://doi.org/10.1016/j.jlumin.2009.02.018 (2009).
- Shen, Y. R., Riedener, T. & Bray, K. L. Effect of pressure on site-symmetry distortions of Mn⁵⁺ and C⁴⁺ in Y₂SiO₅. *Phys. Rev. B* 61, 9277–9286, https:// doi.org/10.1103/PhysRevB.61.9277 (2000).
- Brik, M. G. et al. Spectroscopic and crystal field studies of YAIO₃ single crystals doped with Mn ions. J. Phys. Condensed Matter 21, 025404, https://doi.org/ 10.1088/0953-8984/21/2/025404 (2009).
- Scott, M. A. et al. Optical spectroscopy of (MnO₄)³⁻ and (VO₄)⁵⁻ in Sr₁₀(VO₄)₆F₂. J. *Phys. Condensed Matter* 9, 9893–9908, https://doi.org/10.1088/0953-8984/9/45/ 017 (1997).
- Andreici, E. L. Modeling of crystal field and spin-hamiltonian parameters for tetrahedral coordinated Mn⁵⁺ doped In Li₃VO₄. *AIP Conf. Proc.* 1472, 101–107, https://doi.org/10.1063/1.4748075 (2012).