






RESEARCH ARTICLE

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Revisiting the reported emission spectrum of Cs₂NaBiCl₆

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In this study, we revisit Cs₂NaBiCl₆ and focus upon several assignments previously given for emission bands. A broad emission band spanning from 1200 nm to 1550 nm (centered at ~1350 nm) is observed for Fe³⁺ when excited at 450 nm or shorter wavelengths into its electron transfer bands in chloride double perovskites. This band was previously assigned to a color center (A. Huang, M. Liu, C.-K. Duan, K.-L. Wong and P. A. Tanner, Understanding the Ultraviolet, Green, Red, Near Infrared and Infrared Emission Properties of Bismuth Halide Double Perovskite, *Inorg. Chem. Front.*, 2022, 9, 6379–6390) because it was observed as an unintended impurity in pristine chloride double perovskites. The undoped material also exhibits Cr³⁺ emission which overlaps the 1 μm Bi³⁺ emission. We are unaware of previous reports of Fe³⁺ emission in chloride hosts at an octahedral site. The ms lifetime is typical of 3dⁿ–3dⁿ transitions. This work demonstrates the requirement to check for unintended impurity emission bands from cations at ppm or lower levels.

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Introduction

We recently published an understanding of the ultraviolet, green, red, near-infrared and infrared emission properties of a bismuth halide double perovskite (bismuth chloro-elpasolite).¹ With the surge in publications concerning halide double perovskites, we have noticed that many papers have wrongly attributed spectral features because of the presence of unintended impurities. This partly arises from the use of only 99.99% purity rare earth oxides in synthesis, the imperfect synthesis methods which easily produce impurities, and the ease of attack of the final product by moisture. In particular, we have confirmed that the presence of Sb³⁺ impurity has gone unnoticed in many cases.² A small amount of metal ion impurity, even at the ppb level, can lead to unwanted emission. It is clear to us that the pristine elpasolites Cs₂NaMCl₆ (M = Y, Lu, La, Sc) do not emit in the visible or infrared spectral regions. For this reason, these transparent compounds have been employed in many studies as hosts for luminescent ions, such as M = Sc for Pr³⁺,³ Mo³⁺,⁴ Cr³⁺,^{5–7} V³⁺,^{8,9} Er³⁺,¹⁰ and As³⁺.¹¹ However, in some other studies, the Cs₂NaScCl₆ host is clearly contaminated with Sb³⁺.^{12–14} It was therefore a surprise to read about “dual-band STE emissions encompassing blue and NIR

regions” from the Cs₂NaScCl₆ host.¹⁵ These are not self-trapped exciton emissions, but rather emissions from the unintentional impurity ions Sb³⁺² and Cr^{3+5–7}. It was good news for us to read this paper because it provoked us to re-scrutinize our own assignments in the Cs₂NaBiCl₆ study¹ and in this report we revisit some of them.

The optical spectra of Fe³⁺ have been extensively studied in oxide host lattices.^{16–18} In particular, the distinction between the spectra of Fe³⁺ at octahedral and tetrahedral sites in oxide systems has been made clear.^{19–21} The data are much sparser for halide host lattices. Emission of Fe³⁺ has been assigned in γ-AlF₃ to a broad band at 735 nm.²² There are broad emission bands at 820 nm in Na₃FeF₆,²³ and at 826 nm in Na₃AlF₆:Fe³⁺.²⁴ However, Poirier and Walsh have assigned sharp features near 700 nm in the 2 K and 30 K emission spectra of KMgF₃ doped with iron to Fe³⁺ emission.²⁵

Due to the position in the nephelauxetic series, the emission of Fe³⁺ in chloride systems is expected to be at longer wavelengths than for fluoride hosts. The broad emission band reported at 566 nm for CsCdCl₃:Fe³⁺²⁶ is not due to Fe³⁺ and results from Mn²⁺ or other impurities. We are unaware of other reports of the emission spectra of Fe³⁺ in chloride systems. Perhaps such bands may be beyond the normal range of ultraviolet–visible detectors, or alternatively, nonradiative processes dominate in such cases.

The charge transfer bands of halide systems lie at lower energy than those of oxide systems. Taking advantage of this fact, Neuenschwander *et al.* made a careful study of the electron transfer bands in the absorption spectrum of Fe³⁺ doped in the Cs₂NaYCl₆ system, where this ion occupies an octahedral symmetry site with FeCl₆^{3–} coordination (Fig. 1a).²⁷

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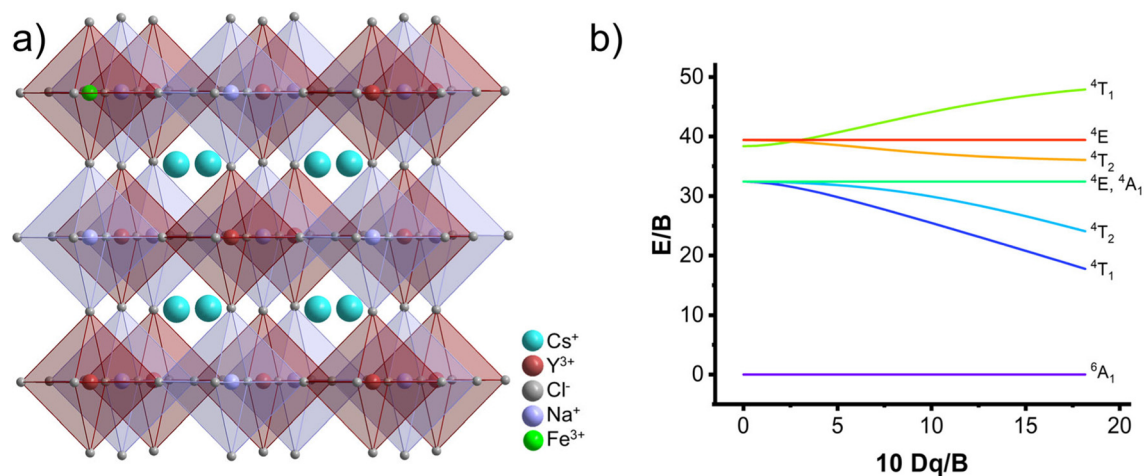


Fig. 1 (a) Structure of Fe^{3+} in $\text{Cs}_2\text{NaYCl}_6$. The ionic radii of $\text{Y}^{3+}(\text{VI})$ and $\text{Fe}^{3+}(\text{VI})$ are 0.9 Å and 0.645 Å, respectively. (b) Schematic Tanabe–Sugano diagram for d^5 ions in octahedral symmetry.

These bands are particularly intense – much more so than the electric dipole and spin forbidden $3d^5-3d^5$ intraconfigurational transitions of Fe^{3+} . Hence, they can serve as a fingerprint in the excitation spectra to identify Fe^{3+} in halide double perovskites (elpasolites).

The semiconductor compound $\text{Cs}_2\text{NaFeCl}_6$ has been well investigated, and it shows strong dependence of the bandgap energy on temperature, giving rise to novel and reversible thermochromic properties. The crystal color changes gradually from light yellow to black in the range of 10–423 K.²⁸ Armer *et al.* have reported an emission band with a maximum at 517 nm.²⁹ This band is asymmetric and unusual in that it has a big ‘dip’ at 534 nm.

Yamatera and Kato³⁰ published the diffuse reflectance spectra of some FeCl_6^{3-} complexes, with bands at 781 nm and 1124 nm. Xian *et al.*³¹ reported a broad band at 750 nm. From these wavelengths, Neuenschwander *et al.*²⁷ concluded from the Tanabe–Sugano diagram for the d^5 configuration, Fig. 1b, that the Dq/B ratio is near 1.4.

Chen *et al.*²⁰ attributed the smaller value of the ligand field parameter of Fe^{3+} in octahedral coordination, compared to that of Cr^{3+} , to the reduced effective radius of the $3d$ orbital in the former. These authors have noted that nonradiative quenching of ${}^4\text{T}_1$ $\text{Fe}^{3+}(\text{oct})$ luminescence can occur in oxide hosts with $Dq/B \sim 2$ due to crossover with ${}^2\text{T}_2$.

An absorption band at a long wavelength of 1124 nm for the lowest excited state implies that infrared emission is possible. We have therefore investigated the emission spectra for Fe^{3+} in the pristine system $\text{Cs}_2\text{NaFeCl}_6$ and also for this ion doped into other elpasolite systems. We did not observe infrared emission for $\text{Cs}_2\text{NaFeCl}_6$ but did observe it for Fe^{3+} doped into other elpasolites. In the course of this work, we discovered that our previous assignment of the infrared emission of $\text{Cs}_2\text{NaBiCl}_6$ to a color center¹ was incorrect, and it was in fact due to Fe^{3+} .

As mentioned above,^{5–7,32} the spectra of Cr^{3+} doped into elpasolite lattices have been thoroughly investigated at low

temperatures and high resolution. In contrast to oxide hosts, where the sharp line spin-forbidden ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission bands often appear from unintentional Cr^{3+} impurity, the weaker ligand field choro-elpasolite hosts exhibit broad spin-allowed ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ emission bands around 1 μm . We detected a weak NIR emission band with several peaks and maximum intensity at ~ 965 nm for our $\text{Cs}_2\text{NaBiCl}_6$ samples at room temperature (RT), with the excitation band at 381 nm.¹ This feature was associated with Bi^{3+} at the Cs^+ site. The emission lifetime at 77 K in the region of 900–1000 nm was fitted by biexponential decay with lifetimes of 1 μs and 8 μs . Although the emission is at a similar wavelength to that of Bi^+ doped into various chloride hosts, the moderately intense excitation bands near 600 nm normally associated with Bi^+ are absent and the above lifetimes are much shorter than the 270–765 μs for the chloride hosts.³³ We therefore present alternative evidence that the emission band in $\text{Cs}_2\text{NaBiCl}_6$ could be due in part to Cr^{3+} impurity.

Luminescence data from recent RT studies of Cr^{3+} doped into elpasolite lattices are summarized in Table 1. The broad emission band around 1 μm is characterized by weak excitation bands near 550 nm and 800 nm, and a stronger band around 300 nm. Interestingly, it was found in the study of $\text{Cs}_2(\text{Na,Ag})\text{InCl}_6:\text{Cr,Bi}$ ³⁴ that Cr^{3+} emission can be excited by 365 nm radiation, which populates the Bi^{3+} level. The Cr^{3+} emission lifetime varies considerably in the μs range as shown in Table 1, and it has been discussed and fitted in the study of $\text{Cs}_2\text{NaMCl}_6:\text{Cr}$ ($M = \text{Y, In}$) by Knockenmuss *et al.*³²

Experimental section

Materials

Cesium chloride (CsCl , 99.999%), bismuth(III) oxide (Bi_2O_3 , 99.999%) and yttrium(III) oxide (Y_2O_3 , 99.9999%) were purchased from Alfa Aesar. Sodium chloride (NaCl , 99.999%) and mineral oil (nujol oil) were purchased from Sigma Aldrich.

Table 1 Spectroscopic details of Cr³⁺ RT emission in elpasolite lattices

System	λ_{exc} (nm)	λ_{em} (max) (nm)	FWHM (nm)	τ	Ref.
Cs ₂ NaYCl ₆ :Cr	310, 553, 770	980	185	18 μs	35
Cs ₂ NaScCl ₆ :Cr	~300, 550, 790	950	—	μs range	36
Cs ₂ (Na,Ag)InCl ₆ :Cr,Bi	330, 564, 814	1000	—	—	34
Cs ₂ AgInCl ₆ :Cr,Er	300–400, 500–650, 730–900	1010	—	12 μs	37
Cs ₂ NaScCl ₆ :Cr	290, 550, 790	970	153	45–62 μs	38
Cs ₂ AgInCl ₆ :Cr	353, 565, 800	1010	—	13–18 μs	39
Cs ₂ NaScCl ₆ :Cr	300, 550, 800	950	162	61 μs	40
Cs ₂ NaBiCl ₆	550, 765	971	—	—	1
Cs ₂ NaBiCl ₆ :Cr	568, 793	979 \pm 14	—	101 μs^a	This work
Cs ₂ NaScCl ₆ :Cr	285, 569	951	189	59 μs	This work

λ_{em} , λ_{exc} are wavelengths of emission and excitation Cr³⁺ bands; FWHM = full width at half maximum of Cr³⁺ emission band; τ = lifetime of the Cr³⁺ emission band. ^aMeasured at 77 K.

Hydrochloric acid (HCl, 37%) was purchased from RCI Labscan. None of the above chemicals were further purified.

Synthesis method

Samples were prepared by the evaporation of solutions of the respective halides and also by the hydrothermal method. For Cs₂NaYCl₆ doped with Fe³⁺, using the latter method, 2 mmol of CsCl, 0.5 mmol of Y₂O₃, 2 mmol NaCl, and 0.01 mmol of FeCl₃ (or 0.005 mol Fe₂O₃) were weighed and dissolved in 10 mL of concentrated hydrochloric acid in a 25 mL Teflon vessel. The vessel was sealed in a steel cup and heated at 180 °C in an oven for 12 h, and then slowly cooled to RT at a rate of 3 °C h⁻¹. Crystals at the bottom of the vessel were washed several times with isopropanol before drying on filter paper at RT. Some crystals were coated with nujol oil for storage. Other hexachloroelpasolite systems were prepared analogously.

Instrumental methods

The X-ray diffraction (XRD) patterns of samples were collected using a Rigaku SmartLab 9 kW – Advance instrument with CuK α radiation (λ = 1.5418 Å). The emission, excitation spectra and lifetime measurements at room temperature were recorded using an Edinburgh FLS1000 spectrometer, with a 450 W xenon lamp as the light source and PMT-900 and PMT-1700 detectors for the visible and NIR regions, respectively. A Fluorolog FL3 instrument was also alternatively employed. The absorption spectra were recorded using an Edinburgh LP980 transient absorption spectrometer at RT using the steady state mode. ICP-MS analysis was performed using an Agilent Technologies 7900 series ICP-MS instrument. The materials for ICP-MS measurements were prepared by dissolving 0.2 g of neat sample in 5 mL of concentrated nitric acid (70%, trace metal basis) or 0.001 g of doped samples in 10 mL of Milli-Q water. 100 μL or 1 mL of the resulting solution was diluted with Milli-Q water to reach the total volume of 10 mL for measurements.

The stated temperatures of 77 K herein and other low temperatures in ref. 1 are very approximate due to the use of powder samples in the copper block. The actual sample temperatures

are often much higher due to heating by the excitation source. The near infrared spectra were recorded using an Edinburgh FLS1000 Instrument and a Horiba FL3 Instrument. A calibration check of the instruments using the Nd-YAG laser at 575 nm excitation wavelength gave the same emission at 1054 nm as for a phosphate glass reference sample. The instruments were located in different buildings about 500 m apart. We noticed deviations in some cases of ± 25 nm for wavelengths measured around 1 μm using the two instruments at different times which can only be caused by environmental conditions and/or faulty alignment. We have accordingly labeled spectra based on the instrument employed.

Results and discussion

Characterization

The XRD patterns of different host elpasolites are shown in Fig. S1. The patterns agree with the pure cubic phase of elpasolite while small diffraction peaks detected in the sample correspond to CsCl and/or NaCl impurities. ICP-MS analysis was carried out for pristine (Table S1) and Cr/Fe doped elpasolites (Table S2). The concentration of Fe and Cr in pristine Cs₂NaBiCl₆ were found to be 169 and 683 ppb, respectively.

Fe³⁺ emission in elpasolites

The low temperature ~ 1350 nm emission band observed under ~ 320 – 460 nm excitation in Cs₂NaBiCl₆ (Fig. 2a)¹ is also observed in pristine Cs₂NaLuCl₆¹ and in Fe-doped Cs₂NaYbCl₆ (Fig. 2a). The long wavelength side of the emission band is decorated by water absorption. This does not occur for the RT Cs₂NaY_{0.99}Fe_{0.01}Cl₆ spectrum (Fig. 2b) and the 77 K spectrum of Cs₂NaY_{0.99}Fe_{0.1}Cl₆ (Fig. 2c). The emission band has the maximum wavelength of 1360 ± 40 nm with the full width at half maximum (FWHM) of 330 ± 30 nm at RT and 215 nm at 77 K. The excitation spectrum of this emission does not display bands in the visible spectral region but several bands are observed around 300–450 nm (Fig. 2d(i) and (ii)). The charge transfer absorption bands of Fe³⁺ doped into Cs₂NaYCl₆ in the study of Neuenschwander *et al.*²⁷ are displayed in Fig. 2d(iii) and show a characteristic fingerprint

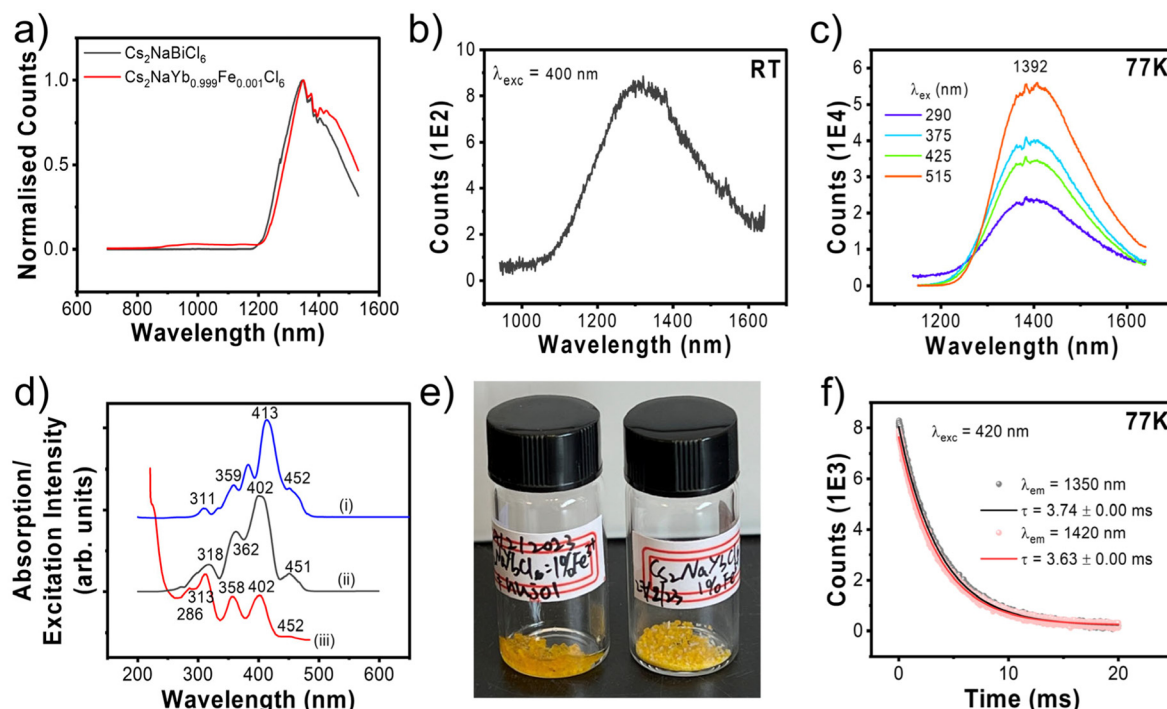


Fig. 2 (a) (black) 400 nm excitation emission spectrum of $\text{Cs}_2\text{NaYb}_{0.999}\text{Fe}_{0.001}\text{Cl}_6:\text{Fe}^{3+}$ at 13 K; (red) 410 nm excitation emission spectrum of $\text{Cs}_2\text{NaBiCl}_6$ at 10 K. (b) RT $\text{Cs}_2\text{NaY}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$ emission spectrum; (c) 77 K emission spectrum of $\text{Cs}_2\text{NaY}_{0.9}\text{Fe}_{0.1}\text{Cl}_6$. (d) (i) 10 K excitation spectrum of 1400 nm emission of $\text{Cs}_2\text{NaBiCl}_6$. (ii) 13 K excitation spectrum of 1346 nm emission of $\text{Cs}_2\text{NaYb}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$; (iii) 8 K absorption spectrum of $\text{Cs}_2\text{NaY}_{0.99}\text{Fe}_{0.001}\text{Cl}_6$ adapted from ref. 27; the spectra in (a) were recorded using a Horiba FL3 instrument, while the spectra in (b) and (c) were measured using an FLS1000 instrument. (e) Photograph of $\text{Cs}_2\text{NaYb}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$ crystals prepared by hydrothermal synthesis with (left) and without (right) nujol. (f) Luminescence decay of Fe^{3+} emission in $\text{Cs}_2\text{NaY}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$ at 77 K.

which matches the bands in the excitation spectra of the infrared emission spectra of $\text{Cs}_2\text{NaYbCl}_6:\text{Fe}^{3+}$ in Fig. 2d(ii) and pristine $\text{Cs}_2\text{NaBiCl}_6$ in Fig. 2d(i). The absorption spectra in Fig. S2 exhibit similar features in the region 500–260 nm and show total absorption when the doping concentration of Fe^{3+} is 10%. We consider that this is sufficient proof to show that the infrared emission is due to Fe^{3+} . No other excitation bands are observed because the intensity of the charge transfer transitions is much greater than for $3d^5-3d^5$ transitions. The doped $\text{Cs}_2\text{NaYbCl}_6$ crystals exhibit a yellow color, which is a more pronounced brown in the 1 at% doped material (Fig. 2e). The 77 K luminescence lifetime of the Fe emission in $\text{Cs}_2\text{NaY}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$ exhibits monoexponential decay with a lifetime of 3.69(6) ms (Fig. 2f), which increases to 6.0 ms at 40 K. In each case above, the Fe^{3+} ion is envisaged to replace the metal M octahedral symmetry site in $\text{Cs}_2\text{NaMCl}_6$ and the $3d^5 \rightarrow 3d^5$ emission corresponds to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition.

Cr^{3+} emission in elpasolite lattices

Fig. 3a displays the infrared emission spectra of $\text{Cs}_2\text{NaBiCl}_6$ published in Fig. 7a of ref. 1. We have assigned the broad feature labeled at 1356 nm to Fe^{3+} emission. The structured band around 1 μm was previously associated with Bi^{3+} at the Cs^+ site. While the latter assignment may be valid, we now recognize that the unusual shape of the band is due in part to

the superposition of the spin-allowed ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition of Cr^{3+} . Fig. 3b demonstrates the effect on the emission band of intentionally doping Cr^{3+} into $\text{Cs}_2\text{NaBiCl}_6$ and using different excitation lines. The 296 nm and 556 nm excitation lines are known, from Table 1, to populate Cr^{3+} energy levels and in these cases the emission band is less structured. Saikia *et al.*³⁴ have shown that excitation into Bi^{3+} energy levels gives rise to Cr^{3+} emission in addition to that from Bi^{3+} in a Cr^{3+} , Bi^{3+} double-doped elpasolite. This is the case for the other excitation wavelengths in Fig. 3b. In our original report, the excitation spectrum of 1000 nm emission of $\text{Cs}_2\text{NaBiCl}_6$ (Fig. 7g in ref. 1) exhibited an intense feature at 380 nm, and this band is also present in the excitation spectra of the red emission of $\text{Cs}_2\text{NaBiCl}_6$, indicating host-guest energy transfer. Notably, when the ordinate scale of Fig. 7g in ref. 1 is expanded, as in Fig. 3c herein, the two characteristic Cr^{3+} absorption bands are observed. Fig. 3d and e clearly demonstrate the distinction in band shape between Cr^{3+} emission and both Bi^{3+} and Cr^{3+} emission near 1 μm .

The RT excitation spectrum of 0.1 at% Cr^{3+} doped into $\text{Cs}_2\text{NaScCl}_6$ (Fig. 3g) demonstrates that the visible absorption bands are very weak. However, for 5 at% doping of Cr^{3+} into $\text{Cs}_2\text{NaBiCl}_6$ at 77 K, the bands are clearly observed in the excitation spectrum (Fig. 3f).

The RT Cr^{3+} emission in $\text{Cs}_2\text{NaSc}_{0.999}\text{Cr}_{0.001}\text{Cl}_6$ is monoexponential with a lifetime of 59 μs (Fig. 3i). On cooling to 77 K,

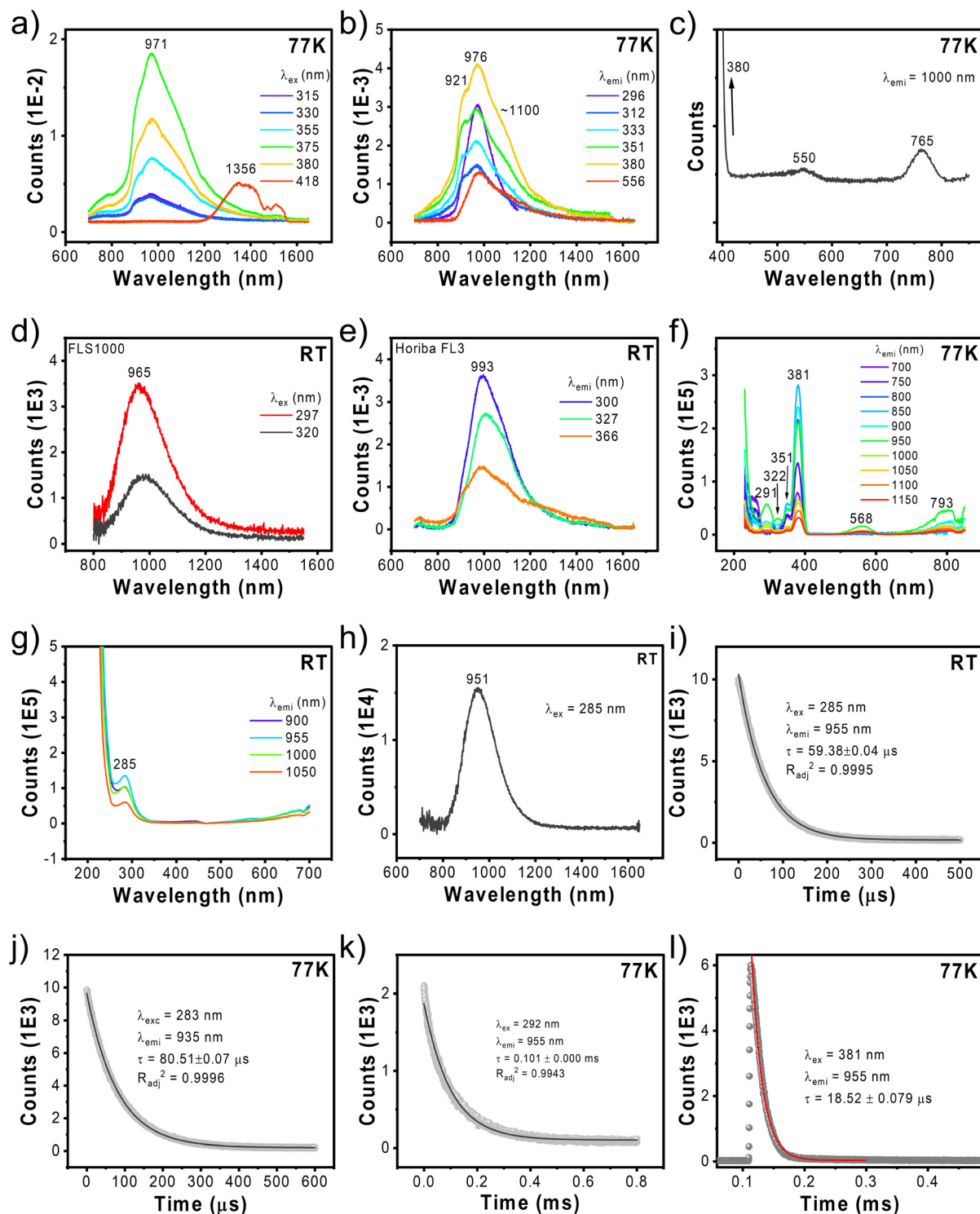


Fig. 3 (a) Reproduced Fig. 7a from ref. 1, showing the 77 K emission spectra of $\text{Cs}_2\text{NaBiCl}_6$ when using different excitation lines. (b) Nominal 77 K emission spectrum of $\text{Cs}_2\text{NaBi}_{0.95}\text{Cr}_{0.05}\text{Cl}_6$ using different excitation lines. (c) Enlarged Fig. 7g from ref. 1 showing part of the 77 K excitation spectrum of the 1000 nm emission of $\text{Cs}_2\text{NaBiCl}_6$. The weak 550 nm band was not evident in the excitation spectra of 1010 nm or 980 nm emission. Emission spectra of $\text{Cs}_2\text{NaBi}_{0.95}\text{Cr}_{0.05}\text{Cl}_6$ recorded using (d) FLS1000 and (e) Horiba FL3, respectively. (f) Excitation spectra of $\text{Cs}_2\text{NaBi}_{0.95}\text{Cr}_{0.05}\text{Cl}_6$. (g) Excitation and (h) emission spectra of $\text{Cs}_2\text{NaSc}_{0.999}\text{Cr}_{0.001}\text{Cl}_6$. Decay measurements of $\text{Cs}_2\text{NaSc}_{0.999}\text{Cr}_{0.001}\text{Cl}_6$ at (i) RT and (j) 77 K, respectively. Lifetimes of $\text{Cs}_2\text{NaBi}_{0.95}\text{Cr}_{0.05}\text{Cl}_6$ using (k) 292 nm and (l) 381 nm excitation, respectively.

it increases to 80 μs (Fig. 3j). A value of 101 μs was recorded at 77 K for the Cr^{3+} emission in $\text{Cs}_2\text{NaBi}_{0.95}\text{Cr}_{0.05}\text{Cl}_6$ using 292 nm excitation into Cr^{3+} energy levels (Fig. 3k), but a rather lower lifetime of 18 μs is observed when exciting at 381 nm into the Bi^{3+} absorption band (Fig. 3l), which is still longer than in our previous report using 355 nm excitation. The measured lifetime is therefore very sensitive to the excitation wavelength.

Conclusions

The presence of trace impurities at ppm or lower levels can lead to spurious emission bands for elpasolites. We have previously demonstrated this for Sb^{3+} and herein we observe unintended emission from Fe^{3+} and Cr^{3+} in the pristine elpasolite $\text{Cs}_2\text{NaBiCl}_6$. The previous assignment¹ given for the 1 μm Bi^{3+} emission is deemed valid, but the broad band is overlapped by another from Cr^{3+} . The previous assignment of the 1350 nm infrared emission has been changed to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Fe^{3+} . The infrared emission of Fe^{3+} complements that known for Cr^{3+} and Ni^{2+} in halide systems.⁴¹

Conflicts of interest

There are no conflicts to declare.

Data availability

The data in this manuscript will be made available upon reasonable request to the authors.

Supplementary information available: analytical results; X-ray diffractograms; room temperature absorption spectra. See DOI: <https://doi.org/10.1039/d5qi01285f>.

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