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Authors
Moses, W.W.
Derenzo, S.E.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

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W.W. Moses and S.E. Derenzo

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The Scintillation Properties of Cerium-Doped Lanthanum Fluoride

W.W. Moses and S.E. Derenzo,
Donner Laboratory and Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720

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Abstract

We report on the scintillation properties of cerium-doped lanthanum fluoride (LaF_3), a newly discovered dense (5.9 g/cm^3) heavy atom scintillator. We have investigated four dopant concentrations (0.01%, 1%, 10% and 50% mole fraction of CeF_3), measuring the emission spectrum, light output, and decay time distribution. The light output increases with increasing cerium concentration until a maximum of 2200 photons/MeV is reached at 10% CeF_3, then decreases to 1900 photons/MeV at 50% CeF_3. The emission spectrum depends on concentration, but consists of a pair of peaks centered at approximately 300 nm and 350 nm, with the lower cerium concentrations having a greater fraction of 300 nm emissions. The decay time distribution is well described by the sum of 3 exponential components: 3.0 ns, 26.5 ns, and a dopant dependent long component that varies between 185 ns and 275 ns. The fraction of the 3.0 ns fast component increases from 10% at 50% cerium to 15% at 1% cerium and the fraction of the long component increases from 3% at 50% cerium to 21% at 1% cerium. There is hope that a different cerium doping fraction or different host crystal would increase the intensity of these 3 ns emissions.

1 Introduction

This paper describes the scintillation properties of cerium-doped lanthanum fluoride (LaF_3), a newly discovered inorganic scintillator. The physical characteristics of LaF_3 doped with CeF_3 are well suited for use as a radiation detector. The samples are colorless, not hygroscopic [1], cut and polish easily, and can be grown with the vertical Bridgeman method.

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They have an index of refraction between 1.6 and 1.7 [2,3], and while the density was not measured explicitly, it should lie between the density of LaF_3 (5.9 g/cm^3) and CeF_3 (6.2 g/cm^3) [1]. All measurements described in this paper were made at room temperature (24° C) with crystals provided by Optovac, Inc. of N. Brookfield, MA.

This study is motivated by observations made on undoped cerium fluoride (CeF_3), an inorganic scintillator that was discovered recently [4,5,6]. The CeF_3 emission spectrum when excited with 511 keV gamma rays shows a double peak structure, with one of the peaks adjacent to the transmission cutoff at 300 nm (fig. 1). This suggests that this emission peak is partially occluded by the transmission cutoff, and as this occluded peak appears to have a decay time between 2 ns and 10 ns [5,6] (which is significantly faster than the main 27 ns decay component of CeF_3), we endeavored to enhance the scintillation properties of CeF_3 by making it more transparent to these faster emissions. We hypothesised that because of the extremely low transmission cutoff of LaF_3 (125 nm [3]), substituting some of the cerium ions with lanthanum ions might allow more of the shorter wavelength cerium emissions to be transmitted rather than be blocked by the 300 nm cutoff. This substitution should not alter the fluorescent properties significantly, as the lanthanum ion is crystallographically very similar to the cerium ion and so the cerium environment in the crystal would not change appreciably.

2 Undoped Cerium Fluoride

In order to determine that there is a fast emission component of CeF_3 that is self-absorbed, we investigated the surface fluorescence of CeF_3 by exciting a powdered sample with a pulsed (< 1 ns FWHM) 22.7 keV x-ray beam from beamline X23-A2 at the Brookhaven National Laboratory. By measuring the emissions from the surface of a powder, we observe the emission properties of CeF_3 unmodified by bulk transmission effects. The surface emission spectrum was measured by passing the resulting emissions through a 0.125 m Jarrell-Ash MonoSpec 18 monochromator with a 1200 line/mm grating blazed for 300 nm.

The entrance and exit slits of the monochromator were 25 μm wide, resulting in a spectral resolution of 0.6 nm. A quartz-windowed Hamamatsu R-2059 photomultiplier tube (spectral range 200 nm to 600 nm) was placed at the exit slit, and the single photoelectron count rate was measured as a function of monochromator wavelength. The resulting surface emission spectrum (fig. 2), which is not corrected for monochromator efficiency or photomultiplier tube response, shows large peaks centered at 284 nm and 300 nm, with much smaller peaks at 360 nm and possibly 420 nm. The abundance of emissions from the surface of the powder with wavelengths below the 300 nm transmission cutoff suggests that a large fraction of the CeF_3 scintillation light is self-absorbed when emitted from within a crystal.

The fluorescent decay lifetimes of the individual surface emission lines were measured by placing 500 μm entrance and exit slits in the monochromator, resulting in a 12 nm bandpass, and using the delayed-coincidence method of Bollinger and Thomas [7]. A single photoelectron pulse was used to start a time-to-amplitude converter (TAC), and the following x-ray burst (560 ns later) produced a trigger pulse from a plastic scintillator that stopped the TAC [8]. The resulting time spectra are shown in fig. 3 for monochromator wavelengths of 284 nm and 360 nm. The timing distribution at 300 nm is virtually identical to the 284 nm distribution and the 420 nm distribution is very similar to the 360 nm distribution.

The decay time distribution of the 284 nm emission line is well described (χ^2/D.O.F. = 1.2) by the sum of a 9.5 ns exponential, a 30.6 ns exponential, and a flat background. The majority (80%) of the counts result from the 9.5 ns fast decay component, and as is evident from fig. 2, the broad 360 nm emission line is wide enough to contaminate the data even at 284 nm and so is probably responsible for the small (20%) 30.6 ns slow emission component.

The decay time distribution of the 360 nm emission line cannot be well described by the sum of exponentials, as the count rate does not rise abruptly after excitation. It can,

however, be well fit (χ^2/D.O.F. = 0.9) by a cascade decay model in which the excited state associated with this emission is being pumped with a 9.5 ns time constant and depopulated with a 30.6 ns time constant. Mathematically, such a model is described by a flat background plus the difference of two exponential time constants, or

$$\frac{dN}{dt} \propto (e^{-t/30.6} - e^{-t/9.5}) \; . \tag{1}$$

Note that these are the same decay time constants used to fit the 284 nm line. These data confirm that the shorter wavelength emissions (284 and 300 nm) have a fast (< 10 ns) decay time, while the 350 nm emissions have a longer (roughly 30 ns) decay time.

3 Cerium-Doped Lanthanum Fluoride

Therefore, we obtained optical quality crystals of LaF_3 doped with 50%, 10%, 1%, and 0.01% mole fraction CeF_3 in order to test their scintillation properties. The crystals were cut and polished to form right circular cylinders approximately 1 cm in diameter and 3 mm high. The optical clarity of the crystals was excellent, with the exception of the 50% cerium sample, which had a slight yellow color. For all measurements except the transmission measurement, all but one face of these crystals were covered with a reflective coating of magnesium oxide.

3.1 Emission Spectrum

The emission spectra of these samples were obtained using the same apparatus used to measure the CeF_3 surface emission spectrum, except that the 500 μm slits (12 nm spectral resolution) were used and the samples were excited with the 511 keV photons from a 3.0 mCi ^{68}Ge source. The resulting spectra, shown in fig. 4, are not corrected for the spectral response of the photomultiplier tube or monochromator. The same method and equipment was used to obtain the CeF_3 spectrum in fig. 1.

The spectra for all four dopants tends to consist of a pair of peaks: a narrow (~40 nm FWHM) peak centered at approximately 300 nm and a broad (~80 nm FWHM) peak

centered at approximately 350 nm. The height of the 350 nm peak is approximately 20% of the 300 nm peak for the 50% and 10% CeF_3 samples, diminishing to about 10% of the 300 nm peak in the 1% CeF_3 sample, then climbing to 80% of the 300 nm peak in the 0.01% CeF_3 sample. The 0.01% CeF_3 sample also shows a large, narrow peak centered at 480 nm. This may be due to radiation induced defects in the LaF_3 crystal, as the low light output of this sample necessitated a long (24 hour) collection time and correspondingly high radiation exposure for the crystal. A pink color appeared in this crystal after the measurement was made – this has been seen before in radiation damaged LaF_3 and may be due to long lifetime, forbidden $4f$-$4f$ transitions [9]. In all cases, the presence of light below the 300 nm cutoff of borosilicate glass implies that fused silica or UV glass windowed photomultiplier tubes are necessary in order to avoid losing a significant fraction of the scintillation light.

Fig. 4 also shows the transmission spectrum of the samples, as measured with a Shimadzu Spectronic 200UV spectrophotometer. Again, the same method and equipment was used to obtain the CeF_3 spectrum in fig. 1. The transmission is relatively uniform in all four samples for wavelengths greater than 300 nm, although some structure near 375 nm and 445 nm is observed and the samples with the lowest (0.01%) and highest (50%) cerium concentrations show a gradual increase in the transmission between 300 nm and the structure at 445 nm. As expected, the transmission cutoff wavelength decreases with decreasing cerium concentration, from 295 nm for 100% CeF_3 down to 262 nm for 0.01% cerium. Some structure is also observed between 190 nm and 250 nm in the 0.01% cerium sample – these structures are consistent with the $4f\mathrm{Ce}^{3+} \rightarrow 5d\mathrm{Ce}^{3+}$ absorption bands observed by Elias, *et al.* [10].

3.2 Light Output

The light output of the four samples was measured by comparing their response to 511 keV photons to the response of a CeF_3 crystal with the same geometry. The light output of

CeF_3 is taken to be 4400 photons/MeV as reported earlier [4,5], which was measured by comparing to the Bismuth Germanate (BGO) photopeak position and normalizing to the BGO light output of 8200 photons/MeV reported by Holl, *et al.* [11]. The samples were optically coupled to a quartz-windowed Hamamatsu R-1306 photomultiplier tube operated at -1200 V with General Electric Viscasil 600M silicone fluid. The crystal was irradiated with 511 keV photons from a ^{68}Ge source, and the output of the photomultiplier tube amplified with a Tennelec TC-222 amplifier with 1.2 μsec shaping time and digitized with a LeCroy 3512 ADC. The resulting pulse height spectra are plotted (after pedestal subtraction) in Figure 5.

The photopeak corresponding to the 511 keV photon is clearly seen in the 100%, 50% and 10% cerium samples. The 511 keV photopeak in 100% CeF_3 sample is centered at a pulse height that is approximately twice of the 511 keV photopeak pulse height in 50% and 10% cerium samples. A 511 keV photopeak is not observed in the 1% or 0.01% cerium samples, but a 1.27 MeV photopeak can be observed when the 1% sample is irradiated with a ^{22}Na source, and this photopeak position is used to measure the light output of the 1% cerium sample. The results of these measurements are summarized in Table 1.

3.3 Fluorescent Decay Time

The fluorescent decay lifetime was measured using the delayed-coincidence method of Bollinger and Thomas [7], as modified by Moszyński and Bengtson [12]. A barium fluoride (BaF_2) scintillator coupled to a Hamamatsu R-2059 photomultiplier tube provided a start signal, and another quartz-windowed Hamamatsu R-2059 photomultiplier tube masked with a 5 mm diameter "pinhole" was placed 10 cm away from the sample to provide the stop signal. A 10 μCi ^{22}Na source provided the 511 keV photon pairs that excited both the BaF_2 trigger scintillator and the sample scintillator. Timing signals from both photomultiplier tubes were generated using two channels of a Tennelec TC-454 constant fraction discriminator, and the time difference between the start and stop signals was dig-

itized with an Ortec 457 time to amplitude converter and a LeCroy 3512 analog to digital converter (ADC).

The results of this measurement are shown in Figure 6. No timing measurements were made for the 0.01% cerium sample as its light output was too low. Good fits to the data (the chi-squared per degree of freedom is between 0.9 and 1.2) are obtained with a sum of three exponential decay lifetimes (3.0 ns, 26.5 ns, and long component ranging from 135 ns to 273 ns) plus a constant background. Although the data Figure 6 are displayed in 6.6 ns bins, the data was acquired and fit using 0.33 ns bins. The results of the fit are summarized in Table 1. In each sample, most of the light is emitted with a 26.5 ns decay time. The fraction of "fast" 3.0 ns light increases, as predicted, with decreasing cerium fraction, from 4% of the emitted photons at 100% CeF_3 to 16% of the emitted photons at 1% cerium. This is significantly smaller than the large (25%) fraction of "fast" light observed in 100% CeF_3 by Anderson [5,6]. A small amount (2% of the emitted photons) of previously unobserved "long" (135 ns) component is present in the 100% CeF_3 sample. Roughly the same fraction is present in the 50% and 10% cerium samples, rising to 15% in the 1% cerium sample, and the decay time of this long component increases with decreasing cerium fraction.

The optically excited fluorescent lifetime of 0.01% to 1% cerium-doped lanthanum fluoride has been measured by several authors [10,13] who have fit values between 18 ns and 20 ns, which appear to disagree with our measurements. We have found that if the data displayed in fig. 6 for these concentrations is rebinned with a bin width greater than 2 ns, a good fit can be obtained with a single, 18 ns exponential. However, a multi-exponential fit is necessary to achieve a good χ^2/D.O.F. when the data is fit using finer time bins.

4 Discussion and Conclusions

As hoped, replacing some of the cerium ions in CeF_3 with lanthanum ions (*i.e.* doping LaF_3 with CeF_3) causes the scintillation crystal to become more transparent to the fast

284 nm to 300 nm emissions observable with surface excitation. This reduces the effective scintillation decay time and causes the emission spectrum to peak at shorter wavelengths. However, this increase in shorter wavelength, "fast" scintillation light is not enough to offset the loss of cerium luminescence centers, and so the total light output decreases. The reduction in light output is not linear with cerium fraction, implying that the material is becoming progressively clearer to its own emanations as the cerium fraction is reduced.

Cerium-doped lanthanum fluoride is, however, a newly discovered, heavy, inorganic scintillator. Its properties, which are similar to those of CeF_3, are characterized by a density between 5.9 and 6.2 g/cm^3, which is between that of barium fluoride (4.9 g/cm^3) and BGO (7.1 g/cm^3). The scintillation light output depends on cerium concentration, ranging from approximately one quarter that of BGO for 50% and 10% cerium to 5% of BGO at 1% cerium. Its predominant decay time is 26.5 ns, but it also has a fast (3.0 ns) and a slow (185–273 ns) component, both of whose relative fraction increase with decreasing cerium concentration. While none of these components are as fast as the 0.8 ns "fast" component of BaF_2, the 3.0 ns component is among the fastest of heavy inorganic scintillators and all components are considerably faster than BGO (300 ns) or the "slow" component of BaF_2 (620 ns). A significant fraction of the emission spectrum is below 300 nm, implying that quartz or UV glass windowed photomultiplier tubes must be used.

The combination of high density, short fluorescence lifetime, and reasonable light output suggest that cerium-doped LaF_3 would be useful for applications where high counting rates, good stopping power, and nanosecond timing are important, such as medical imaging and nuclear science. The absence of a "slow" fluorescent decay component implies that they would be well suited for applications where counting rates as high as 10 Mhz are expected. The preponderance of "fast" emissions visible from surface excitation of CeF_3 give hope that a different cerium doping fraction or different host crystal would and result in an ultra-fast, luminous, high density scintillator.

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Cerium (CeF_3) Fraction	Light Output (photons/MeV)	3.0 ns Component	26.5 ns Component	"Long" Component
100%	4400	4%	94%	2% @ 135 ns
50%	1900	10%	87%	3% @ 185 ns
10%	2200	10%	86%	4% @ 185 ns
1%	440	15%	64%	21 @ 273 ns%
0.01%	<200	?	?	?

Table 1: Summary of the scintillation properties of cerium-doped lanthanum fluoride (LaF_3)

Figure 1: Emission and transmission spectra of crystalline CeF_3

Figure 2: Surface emission spectrum of powdered CeF_3

Figure 3: Wavelength resolved surface emission decay time spectrum of powdered CeF_3

Figure 4: Emission and transmission spectra of cerium-doped LaF_3

Figure 5: Scintillation light output of cerium-doped LaF_3

Figure 6: Decay time spectra of cerium-doped LaF_3

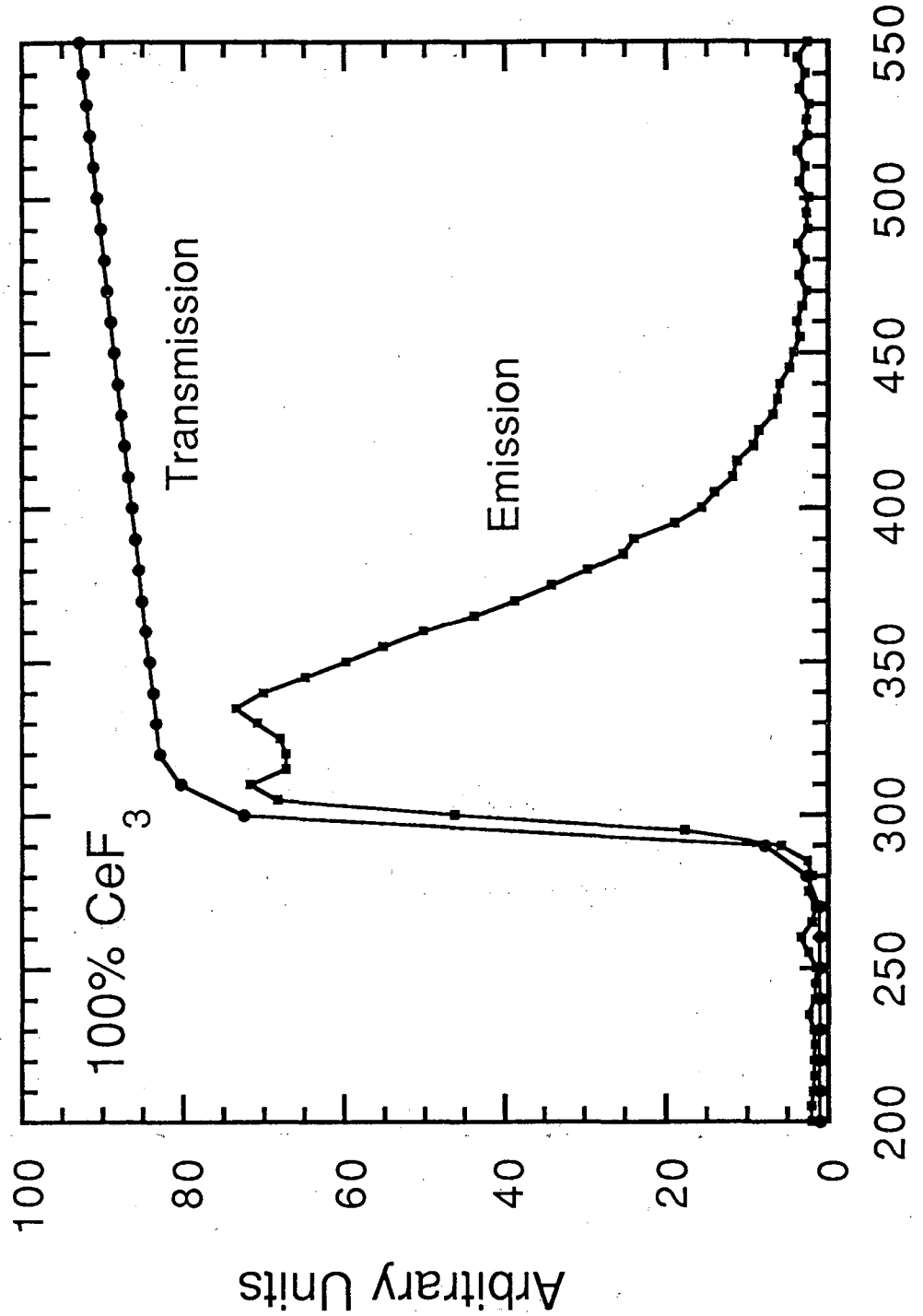
100% CeF3
Transmission
Emission
Arbitrary Units
Wavelength (nm)
0
20
40
60
80
100
200
250
300
350
400
450
500
550

Figure 1

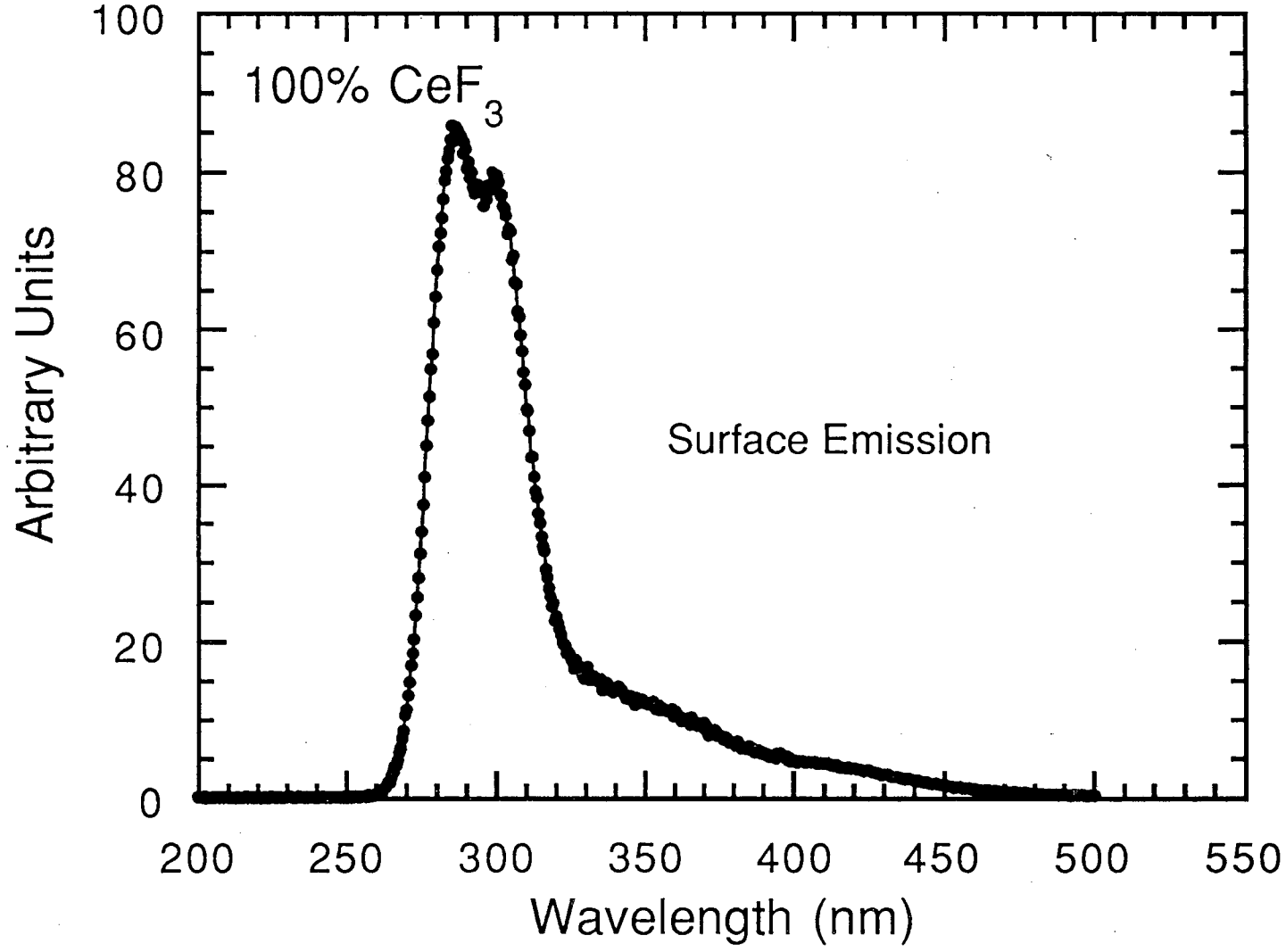
100% CeF_3
Surface Emission
Arbitrary Units
Wavelength (nm)
0
20
40
60
80
100
200
250
300
350
400
450
500
550

Figure 2

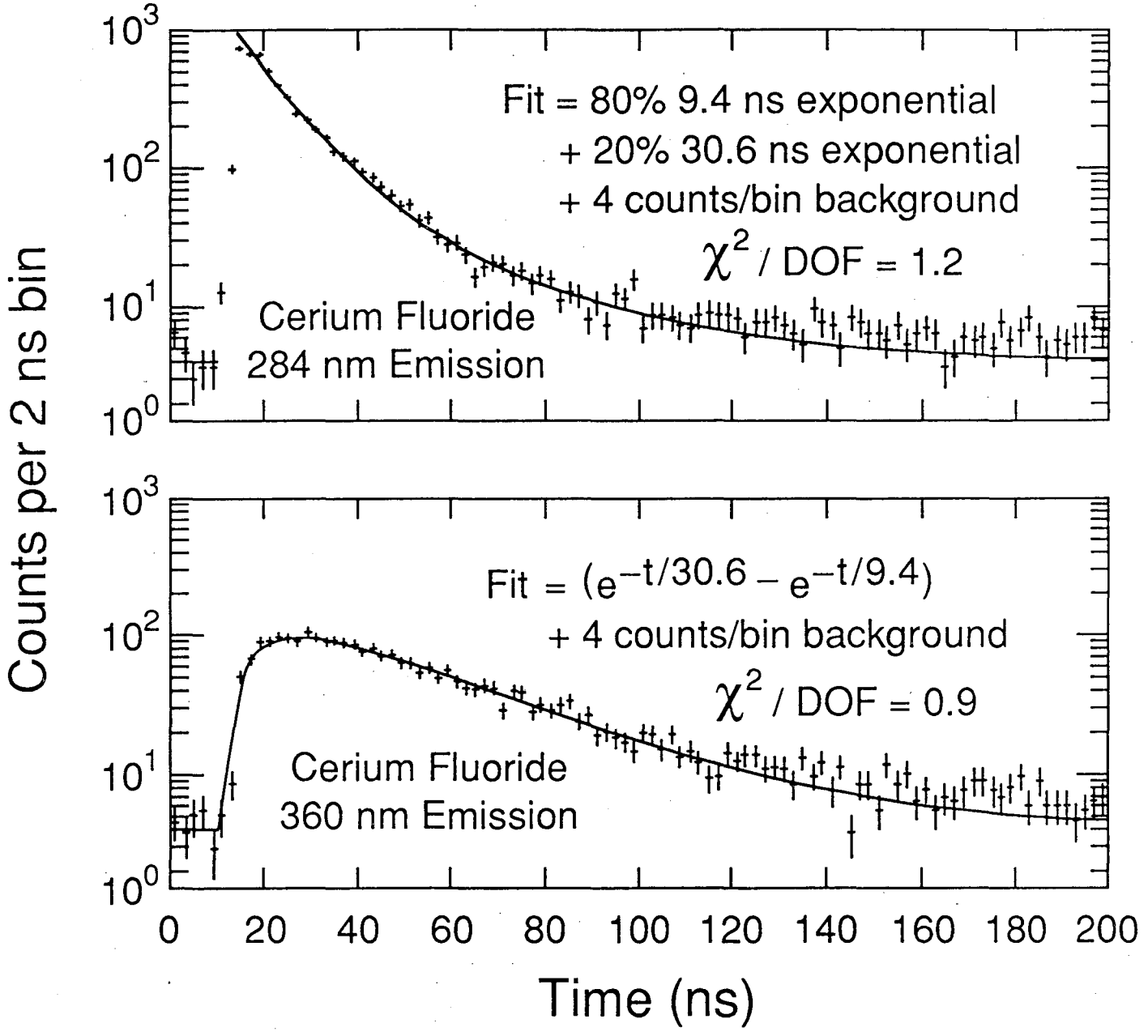
Counts per 2 ns bin
Time (ns)
Fit = 80% 9.4 ns exponential
+ 20% 30.6 ns exponential
+ 4 counts/bin background
χ² / DOF = 1.2
Cerium Fluoride
284 nm Emission
Fit = (e^−t/30.6 − e^−t/9.4)
+ 4 counts/bin background
χ² / DOF = 0.9
Cerium Fluoride
360 nm Emission

Figure 3

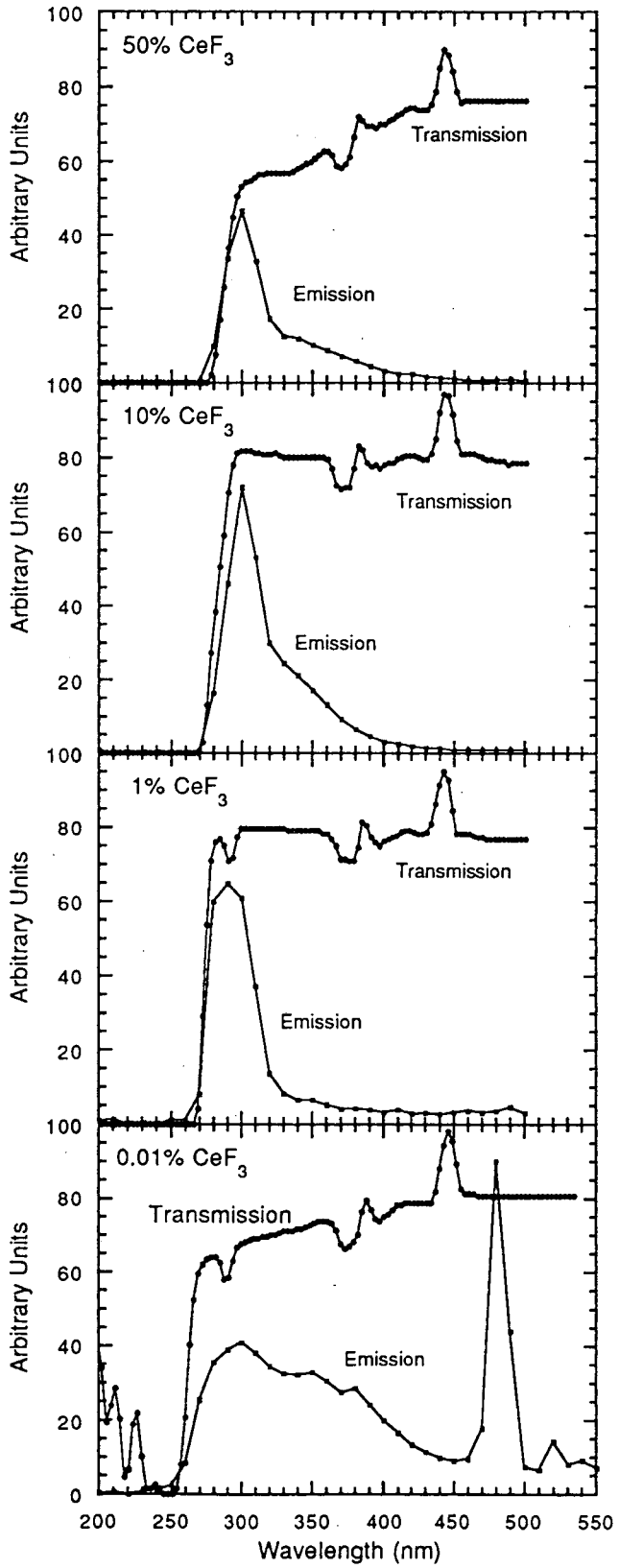
50% CeF3
Transmission
Emission
10% CeF3
Transmission
Emission
1% CeF3
Transmission
Emission
0.01% CeF3
Transmission
Emission
Arbitrary Units
Wavelength (nm)
0
20
40
60
80
100
200
250
300
350
400
450
500
550

Figure 4

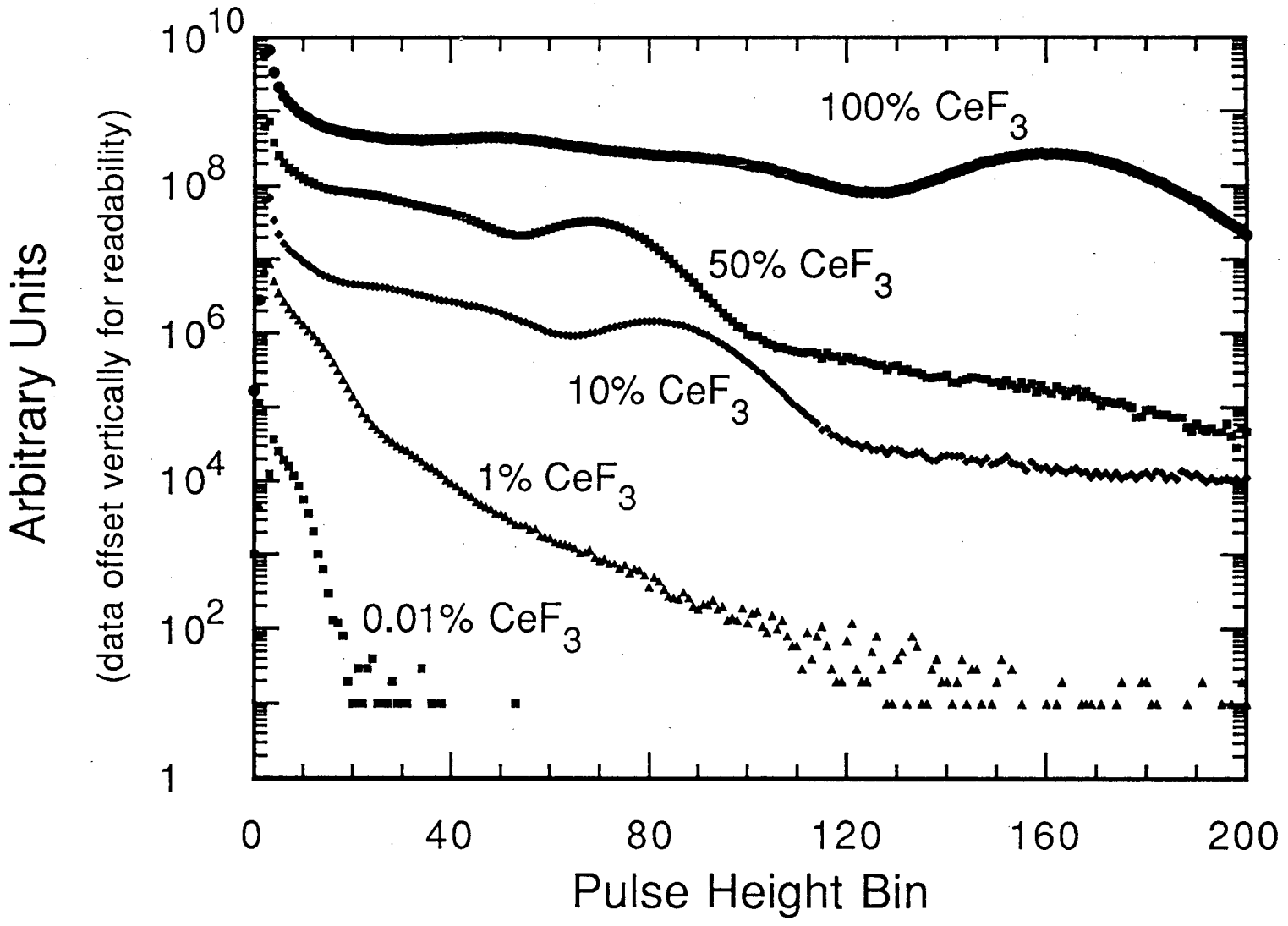
Arbitrary Units
(data offset vertically for readability)
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
1
100% CeF_3
50% CeF_3
10% CeF_3
1% CeF_3
0.01% CeF_3
0
40
80
120
160
200
Pulse Height Bin

Figure 5

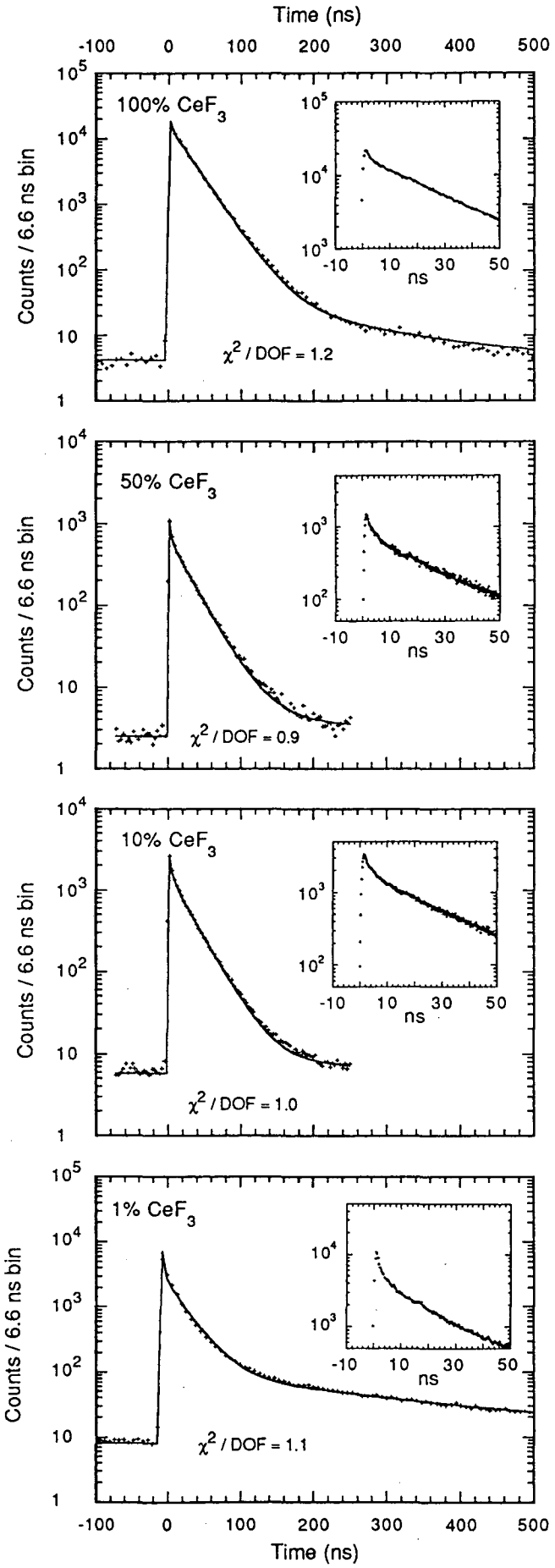
Time (ns)
-100 0 100 200 300 400 500
Counts / 6.6 ns bin
100% CeF3
χ2 / DOF = 1.2
50% CeF3
χ2 / DOF = 0.9
10% CeF3
χ2 / DOF = 1.0
1% CeF3
χ2 / DOF = 1.1
ns
-10 10 30 50
Time (ns)

Figure 6

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