INVESTIGATION OF THE INTERACTION OF Nd⁺ IONS IN CaF₂, SrF₂, AND BaF₂ CRYSTALS (TYPE I)

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The mechanism of the interaction of Nd⁺ ions and the nature of concentration quenching in CaF₂, SrF₂, and BaF₂ crystals were investigated. The concentration dependences of the absorption and luminescence spectra were obtained at 300, 77, and 4.2 K in a wide range of Nd⁺ concentrations (0.01-30 wt.%). The concentration dependences of the relative quantum yield were plotted and the lifetimes of the excited states of various Nd⁺ ion centers were measured. A scheme of crystal splitting of some Nd⁺ levels in SrF₂ was deduced for centers of the tetragonal symmetry.

INTRODUCTION

The optical properties of Nd⁺ ions in CaF₂, SrF₂, and BaF₂ crystals have already been investigated several times. These investigations are, to a considerable degree, related to the use of these materials in lasers. The fullest information on the optical and EPR spectra of the Nd⁺ ion is available for the CaF₂ lattice. In [1], the method of concentration series was used to distinguish, in the total optical spectrum, the spectra representing various types of tetragonal and two types of orthorhombic optical center, an energy level scheme for these types of center has been deduced taking into account their Stark splitting. In [2-4, 5], the results are given of an investigation of the nature of the concentration quenching in fluorite crystals with Nd⁺ impurities, as well as of measurements of the relative quantum yield and the radiative lifetime \( \tau_{\text{rad}} \) of the tetragonal centers and two types of orthorhombic centers as a function of the activator concentration in a crystal.

Karim, Tolstoi, and Feofilov [7] carried out spectroscopic investigations of MeF₃ (Me = Ca, Sr, Ba) crystals activated with Nd⁺; they obtained empirical schemes for the crystal splitting of the lower terms of the Nd⁺ ion in CaF₂ (type I and II spectra) and SrF₂ (type II spectra) [1]; the lifetime of the excited state of \( ^{4}F_{3/2} \) level of the Nd⁺ ion in CaF₂ was determined.

The EPR spectra of SrF₂: Nd⁺ crystals were investigated by Bleaney et al. [10] and by Kask and Korolienko. [11] They showed that, in these crystals, the Nd⁺ ion is in fields of the tetragonal and orthorhombic symmetries. Shekun [11] gave a table of the EPR data, which indicate that the tetragonal optical Nd⁺ centers exist in the lattices of CaF₂ and SrF₂. No Nd⁺ centers of any type have yet been observed in BaF₂.

It must be mentioned that all these investigations were carried out using relatively low activator concentrations. Only in one case [5] has the concentration of Nd⁺ in the investigated crystals reached 2 wt.%.

The purpose of our investigation was to study the absorption and luminescence spectra, as well as the concentration dependences of the lifetime of the excited state of the Nd⁺ ion in SrF₂ and BaF₂ crystals in a wide range of Nd⁺ concentrations (0.01-30 wt.%) in order to obtain information on the interaction of Nd⁺ ions and on the quenching processes.

APPARATUS AND EXPERIMENTAL METHOD

The absorption spectra were recorded at 300, 77, and 4.2 K using a DFS-12 diffraction spectrometer. At the spectrometer output, we used an FEU-22 photomultiplier in the measurement of the absorption in groups corresponding to transitions from the ground level \( ^{4}I_{5/2} \) to the Stark components of the levels \( ^{4}F_{3/2}, \ ^{4}F_{5/2}, ^{4}H_{9/2}, ^{4}G_{7/2}, ^{4}G_{9/2} \); an FEU-17 photomultiplier was used in the measurement of the absorption corresponding to \( ^{4}I_{5/2} \rightarrow ^{4}P_{1/2} \) transitions. The absorption spectra corresponding to transitions from the ground level \( ^{4}I_{5/2} \) to the Stark components of the \( ^{4}I_{15/2} \) level at room and liquid nitrogen temperatures were obtained using an SF-8 spectrophotometer and a DFS-12 diffraction spectrometer, adapted for recording spectra in the infrared region. A PGS-2 spectrograph was used for simultaneous photographic recording of the absorption spectra at liquid helium and nitrogen temperatures.

The luminescence of Nd⁺ at 77 and 4.2 K was investigated in the region of 1.05 \( \mu \) m corresponding to the \( ^{4}F_{3/2} \rightarrow ^{4}I_{15/2} \) transition. The luminescence was excited with an elliptical cylindrical light source fitted with a K-14 water-cooled tungsten incandescent lamp.

To calculate the dependence of the relative quantum yield of the luminescence from the concentration of Nd⁺, we used the luminescence and absorption spectra of SrF₂: Nd⁺ crystals containing 0.1-5 wt.% Nd⁺, and of BaF₂: Nd⁺ crystals containing 0.3-30 wt.% Nd⁺. To ensure that the absorption and luminescence results were comparable, our measurements were carried out on the same crystals, which all had the same length (30 mm). The luminescence was excited at one end of a crystal by the radiation of the incandescent lamp. This ensured that the geometrical conditions during the experiments were exactly reproducible. Two filters were placed between the lamp...
and the Dewar flask containing a crystal; water-cooled SZS-14 filter, which transmitted in the wavelength range 3000–10 000 Å, and an OS-12-filter, which transmitted wavelengths longer than 5200 Å. Thus, the luminescence was excited in the absorption bands of Nd³⁺ corresponding to the transitions ⁴I₉/₂ → ⁴F₅/₂, ⁴F₃/₂, ⁴H₉/₂, ⁴F₇/₂, ⁴S₁/₂, ⁴G₇/₂, ⁴G₉/₂. These transitions were the only ones whose contribution to the absorption was included in the calculation of the concentration dependence of the relative quantum yield because a control absorption spectrum, obtained using this control crystal, did not exceed 5%. After each measurement we recorded a control spectrum, allowing for the spectral distribution of the excitation source reduced the contribution of these two transitions even further. To check the reproducibility of the luminescence spectra, we were able to distinguish the lines of centers which were dominant at Nd³⁺ concentrations of 0.01–0.1 wt.% (Fig. 1a) and to plot for these centers a scheme of the energy levels of the Nd³⁺ ion in the lattice, modified to allow for the Stark splitting (Fig. 2). By analogy with the results reported in [7], we called these centers L type centers. We found that the splitting of the ⁴F₅/₂ level for L type centers was 82 cm⁻¹, which was in agreement with the results of Kariss, Tolstoi, and Feofilov.[7]

The position of the first excited component of the ⁴I₉/₂ level, obtained from analysis of the concentration and temperature dependences of the absorption corresponding to the transitions shown in the scheme of Fig. 2, was 60 cm⁻¹ (the accuracy of the determination of the level positions was ± 2 cm⁻¹).

Analysis of the luminescence spectra established the positions of all six split components of the ⁴I₉/₂ level. The positions of three components (2010, 2065, and 2369 cm⁻¹) coincided, within the limits of the experimental error, with the results of Kariss, Tolstoi, and Feofilov.[7] The component at 2283 cm⁻¹, reported in [7], was not observed by us.

The suggested scheme of the energy levels of the Nd³⁺ ion in the SrF₂ lattice, modified to allow for the luminescence, the photomultiplier signal was applied to an S-1-15 oscillograph. The measurements of τ_rad were carried out at 77°K.

**EXPERIMENTAL RESULTS**

Absorption and luminescence spectra of Nd³⁺ in the SrF₂ lattice. The absorption spectra of SrF₂ : Nd³⁺ crystals, like those of Nd³⁺-activated fluorite crystals, consisted of a series of narrow lines, whose number and relative intensities depended on the activator concentration. Using the method of concentration series, the temperature dependences of the absorption and luminescence, and the method of constant differences, we were able to distinguish the lines of centers which were dominant at Nd³⁺ concentrations of 0.01–0.1 wt.% (Fig. 1a) and to plot for these centers a scheme of the absorption and luminescence (Fig. 2).
When the activator concentration was increased above 0.1 wt.%, the absorption spectra of SrF$_2$:Nd$^{3+}$ exhibited, like the spectra of Nd$^{3+}$ in CaF$_2$, another series of lines (Fig. 1a). However, in contrast to fluorite, these lines appeared in the absorption spectra of SrF$_2$:Nd$^{3+}$ crystals at higher concentrations, they were wider, and weaker, all of which prevented us from carrying out a detailed analysis of the Stark structure.

When the concentration of Nd$^{3+}$ was increased further, the absorption spectra of SrF$_2$:Nd$^{3+}$ exhibited another family of lines. A characteristic feature of these spectra was a relatively small number of wide bands (Fig. 3). At high activator concentrations (5 wt.%), the absorption spectra were not affected by cooling from liquid nitrogen to liquid helium temperature, which indicated that the absorption involved transitions from the lower component of the ground level $^{4}I_{9/2}$. The group of centers responsible for the appearance of these lines was designated the P type centers.

An investigation of the luminescence spectra (Fig. 4a), using the methods already mentioned, also made possible the identification of the lines corresponding to the L type centers. At an Nd$^{3+}$ concentration of 0.3 wt.%, the luminescence spectra had a system of very weak lines which were evidently analogs of the M and N systems of lines in CaF$_2$:Nd$^{3+}$.[5] At activator concentrations from 1 wt.% upward, we observed broad lines of increasing intensity, which became dominant at 5 wt.% Nd$^{3+}$ (Fig. 4a); this was not observed in the luminescence spectra of fluorite.

Absorption and luminescence spectra of Nd$^{3+}$ in the BaF$_2$ lattice. The Nd$^{3+}$ absorption in BaF$_2$ at a concentration of 0.1 wt.% was much weaker than in CaF$_2$ and SrF$_2$ at the same concentration. Moreover, the absorption region corresponding to the $^{4}I_{9/2} ightarrow ^{4}F_{3/2}$ transition had about ten weak lines at liquid nitrogen temperature (Fig. 1b). When the activator concentration was increased to 0.3 wt.%, the number and intensities of the absorption lines corresponding to this transition increased considerably. When the Nd$^{3+}$ concentration was raised to 2 wt.%, the absorption spectra were found to consist only of three broad bands with a complex structure, which were observed also, with some modifications, at 30% concentration of the activator (Fig. 1b). We were unable to resolve the total spectra into their components.

Figure 4 shows the concentration dependences of the absorption in BaF$_2$:Nd$^{3+}$ corresponding to the transition $^{4}I_{9/2} ightarrow ^{4}P_{1/2}$. It is evident from this figure that, as in the case of SrF$_2$:Nd$^{3+}$, the absorption spectra in the case of high activator concentrations (5 wt.%) was not affected by cooling from liquid nitrogen to liquid helium temperature.

Figure 4b shows the luminescence spectra of BaF$_2$:Nd$^{3+}$. We could distinguish two groups of lines in these spectra. The first group consisted of two short-wavelength lines (they were observed at activator concentrations of 0.3–1 wt.% and disappeared completely from the luminescence spectrum at 5 wt.% Nd$^{3+}$); the second group consisted of long-wavelength lines, whose intensity was comparable with the short-wavelength lines at 0.3 wt.% Nd$^{3+}$, but at 5 wt.% the long-wavelength lines became dominant. Concentration dependences of the luminescence, relative quantum yield, and lifetime of the excited...
FIG. 5. Absorption spectra of BaF2: Nd3+ crystals for the 4I_{9/2} → 4F_{7/2} transition as a function of the Nd3+ concentration (in wt.%) and temperature (in °K): a) 5%, 4.2°; b) 5%, 77°; c) 10%, 77°; d) 5%, 77°; e) 2%, 77°; f) 1%, 77°.

states of the Nd3+ ion in the SrF2 and BaF2 lattices. Figure 6 shows the concentration dependence of the relative quantum yield of the luminescence of Nd3+ in the SrF2 and BaF2 lattices. This dependence was calculated as the ratio of the total luminescence to the total absorption. In the case of BaF2: Nd3+, we found a maximum at an activator concentration of about 2.5 wt.%. At this activator concentration, the absorption and luminescence spectra consisted mainly of lines corresponding to the P type centers. The relative quantum yield of Nd3+ in the SrF2 lattice did not exhibit such a maximum but the dependence became less strong at activator concentrations higher than 1 wt.%. Figure 7 shows the concentration dependences of the total Nd3+ luminescence in SrF2 (curve a) as well as the separate concentration dependences for different centers (curves b and c).

Figure 8 shows the corresponding dependences for BaF2: Nd3+. At Nd3+ concentrations higher than 2 wt.%, we observed in practice only the P-center luminescence and curves a and c merged.

Figure 9 shows the values of \( \tau_{\text{rad}} \) of the lifetime of the excited state of the \( ^{4}F_{3/2} \) level of the Nd3+ ion in the SrF2 lattice as a function of the activator concentration. The lifetime of the excited state of \( ^{4}F_{3/2} \) for the L type Nd3+ centers, amounting to 1.2 msec, remained constant up to a concentration of 0.8 wt.% Nd3+ (curve a). When the activator concentration was increased above this value, a considerable fall of the lifetime was observed for the L type centers. For the other types of center active in the luminescence, \( \tau_{\text{rad}} \) was considerably shorter and had a weak dependence on the concentration (curve b). At a concentration of 10 wt.% Nd3+, the values of \( \tau_{\text{rad}} \) for different centers became comparable.

The dependence of \( \tau_{\text{rad}} \) on the activator concentration for BaF2: Nd3+ is shown in Fig. 10. The lifetime of the excited state of the Nd3+ ion in optical centers, observed at low concentrations and corresponding to the luminescence lines at 10 406 and 10 434 Å, was 8 msec (curve a). When the concentration of Nd3+ exceeded 1.5 wt.%, we observed a rapid fall of \( \tau_{\text{rad}} \). Comparison of Figs. 9a and 10a indicated that the lifetime of the excited state of the centers observed in BaF2 at low Nd3+ concentrations was approximately seven times longer than that for the L centers in the SrF2 lattice.
DISCUSSION OF RESULTS

Analysis of the absorption and luminescence spectra and of the concentration dependences of the radiative quantum yield and the excited state lifetimes of Nd$^{3+}$ in SrF$_2$ and BaF$_2$ crystals shows that, as in fluorite, the optical properties are governed by several types of optical centers. In the first approximation, these centers can be divided into three groups, which we shall call the L, M, and P systems for all the investigated crystals. The absolute and relative numbers of centers in each group vary with the activator concentration and this is responsible for the changes observed in the optical spectra with the concentration and for the concentration dependences of the relative quantum yield and the excited state lifetimes of Nd$^{3+}$ in the investigated crystals. The L type centers are responsible for the absorption and luminescence spectra of crystals with low activator concentrations (0.3–0.5 wt.%). According to the EPR data for CaF$_2$:Nd$^{3+}$[12] and SrF$_2$:Nd$^{3+}$, the L type centers in these crystals are tetragonal[2]. We have been unable to determine the symmetry of the L system of centers in BaF$_2$:Nd$^{3+}$ crystals.

The M type centers are active in the absorption spectra at concentrations of 0.3–2 wt.%. As demonstrated in[5], in fluorite crystals of this type the M and P centers have the same orientation with respect to the lines of the tetragonal M and N centers in fluorite, or to determine the energy level scheme and the symmetry of these centers. This failure has been largely due to the considerable width of the spectral lines in the investigated crystals, which has prevented us from applying the method of concentration series[8] to the spectra of these crystals.

At still higher concentrations (>1 wt.%), the optical spectra of CaF$_2$, SrF$_2$, and BaF$_2$ crystals are governed by the P type centers. Strictly speaking the M and P type centers in SrF$_2$ and BaF$_2$ represent whole new systems of centers. Thus, Fig. 3 shows the concentration and temperature dependences of the absorption spectra of the $4\mathrm{I}_9/2\rightarrow 4\mathrm{F}_{9/2}$ transition in SrF$_2$:Nd$^{3+}$. We can see that, in the case of SrF$_2$, two lines belong to the P type centers, two lines to the M type centers, and one line to the L type centers; at high activator concentrations, the spectrum is not affected by cooling from liquid nitrogen to liquid helium temperature and therefore we cannot regard the long-wavelength components of the M and P series as excited. For the $4\mathrm{I}_9/2\rightarrow 4\mathrm{P}_{1/2}$ transition in BaF$_2$:Nd$^{3+}$ with high activator concentrations (5 wt.%), there are five lines of the P centers and one line of the M centers. Cooling from liquid nitrogen to liquid helium temperature again does not change the spectrum (Fig. 5).

However, since no appreciable redistribution of intensities is observed between the lines of the various P centers in the absorption and luminescence spectra, we are justified in combining these centers into one P group. Comparison of the luminescence spectra of the P centers in SrF$_2$ at liquid nitrogen and liquid helium temperatures makes it possible to determine the splitting of the initial luminescence level $4\mathrm{F}_{9/2}$, which is found to be 90 cm$^{-1}$ (Fig. 4a). The 10 473 Å line in the luminescence spectra of the P centers in BaF$_2$ is "frozen out" at liquid helium temperature. This line can represent an excited component of the 10 541 Å line (in this case, the splitting of the $4\mathrm{F}_{5/2}$ level should be 62 cm$^{-1}$) or of the 10 603 Å line (in this case, the splitting of the level should be 117 cm$^{-1}$) (cf. Fig. 4b).

Our investigations show that the intensity and the quantum yield of the luminescence of Nd$^{3+}$ vary from one matrix to another (CaF$_2$ → SrF$_2$ → BaF$_2$) and depend on the concentration of Nd$^{3+}$ in each of these matrices. Moreover, the concentration dependences of the Nd$^{3+}$ luminescence intensity and quantum yield in each of these matrices are different. In fact, the quenching of the Nd$^{3+}$ luminescence in CaF$_2$ begins at a concentration of 0.5 wt.% and at 5 wt.% the luminescence of the P centers is no longer observed at 300 or 77°K, i.e., it is quenched completely.

It is evident from Fig. 7 that in SrF$_2$ crystals the maximum of the intensity of the total Nd$^{3+}$ luminescence is observed at an activator concentration of 1 wt.%. This maximum is mainly due to the L type centers, although a small contribution to the total luminescence is made also by the P type centers. When the Nd$^{3+}$ concentration is increased from 1 to 5 wt.%, the total luminescence decreases smoothly. Such a concentration dependence is due to a redistribution of the intensity of the luminescence of the L and P centers. Thus, at activator concentrations higher than 1 wt.% Nd$^{3+}$, the intensity of the luminescence of the L centers becomes weaker, while the intensity of the luminescence of the P centers increases and passes through a maximum at an Nd$^{3+}$ concentration of 5 wt.%. However, the maximum intensity of the total luminescence is observed at 1 wt.% Nd$^{3+}$. This maximum is mainly due to the tetragonal centers.

Completely different behavior is observed in the BaF$_2$:Nd$^{3+}$ system (Fig. 8). In this case, the total luminescence intensity at high activator concentration is many times higher than the total luminescence intensity at low concentrations. In this system, the luminescence of the L centers is extremely weak (curve b) and at concentrations higher than 2.5 wt.% this luminescence is made also by the P type centers. An activator concentration higher than 1 wt.% Nd$^{3+}$, the intensity of the luminescence of the L centers increases and passes through a maximum at an Nd$^{3+}$ concentration of 5 wt.%. However, the maximum intensity of the total luminescence is observed at 1 wt.% Nd$^{3+}$. This maximum is mainly due to the tetragonal centers.

These experimental observations can be explained by the characteristic features of the energy level scheme of the Nd$^{3+}$ ion. It is known that the luminescence of the Nd$^{3+}$ ion starts from the $4\mathrm{I}_{5/2}$ level, which is separated by ~11 600 cm$^{-1}$ from the ground level $4\mathrm{I}_9/2$. Between these two levels, there are levels of the $4\mathrm{I}_{15/2}$ multiplet, which are the final levels in the luminescence, and one of these levels ($4\mathrm{I}_{15/2}$) is separated by
~5800 cm⁻¹ from the ground state. Thus, in principle, we can have a resonant energy transfer from the ⁴F₃/₂ level of one ion to the ¹I₉/₂ level of another ion, followed by nonradiative energy relaxation to the lattice (the ¹I₉/₂ level is nonradiative [10-11]). However, the positions of the ¹I₉/₂ and ⁴F₃/₂ levels of the Nd³⁺ ion depend on the crystal matrix and the nature of the center in which this ion is found. Very important contributions are also made by the broadening of the levels taking part in the cross relaxation, which is governed by the temperature and the vibration spectrum of the lattice. The conditions for the multipole energy transfer depend on these factors and thus they affect the magnitude and the nature of the luminescence quenching.

A detailed analysis of the energy level schemes of Nd³⁺ in CaF₂, SrF₂, and BaF₂ crystals yields the following results.

Figure 11 shows the scheme of the ⁴F₃/₂ and ¹I₉/₂ levels of Nd³⁺ in CaF₂ with allowance for their Stark splitting. It is evident from this figure that in the case of the tetragonal centers there is no resonance. However, there is a fairly considerable overlap of transitions in the orthorhombic M and N centers which, combined with the minimum distances between Nd³⁺ ions in paired centers, should result in effective quenching. In fact, experiments reported in [8] show that the quantum yield of the luminescence of the paired orthorhombic M and N centers is two orders of magnitude lower and the lifetime of the excited state is approximately an order of magnitude shorter than that for single tetragonal centers.

Figure 12a shows schematically the resonant overlap of the frequencies of the transition ¹I₉/₂ ← ⁴F₃/₂ with doubled frequency of the transition ¹I₉/₂ ← ¹I₉/₂ of the P centers in CaF₂ : Nd³⁺ crystals. The shaded rectangles in Fig. 12b show that part of the spectrum of the ¹I₉/₂ ← ¹I₉/₂ transition which takes part in the resonance. We can see that in the case of CaF₂ : Nd³⁺, an effective resonance is observed. In full agreement with this prediction, experiments show the absence of the Nd³⁺ luminescence in CaF₂ at high activator concentrations. The processes observed in SrF₂ : Nd³⁺ and BaF₂ : Nd³⁺ crystals at low activator concentrations are similar to the processes taking place in CaF₂ : Nd³⁺.

\[ \sum_{\nu} \frac{f_{1}(E)F_{1}(E)}{\nu^2} \, d\nu, \]

where \( n = 6 \) in the dipole-dipole interaction case and \( n = 8 \) for the dipole-quadrupole interaction. In our case, the function \( f_{1}(E) \) is understood to represent the luminescence corresponding to the ⁴F₃/₂ ← ¹I₉/₂ transition and the function \( F_{1}(E) \) represents the ab-
sorption corresponding to the $^4I_{9/2} \to ^4I_{15/2}$ transition. However, because the $^4F_{3/2} \to ^4I_{15/2}$ luminescence spectrum has not been investigated by us, we have considered resonance of the $^4I_{9/2} \to ^4F_{3/2}$ absorption and the doubled frequencies of the $^4I_{9/2} \to ^4I_{15/2}$ absorption. Such a change in the integrand is fully justified since there are practically no Stokes losses in our case.

The reported results allow one to explain completely the nature of the concentration dependences obtained for the optical spectra, the lifetimes, and the relative quantum yield of Nd$^{3+}$ in CaF$_2$, SrF$_2$, and BaF$_2$. At low Nd$^{3+}$ concentrations in the investigated crystals, single centers predominate and the absolute number of these centers is small, while the quantum yield of the luminescence is high. Centers of this type show practically no interaction with each other or with other centers because they are separated by considerable distances, which corresponds to the linear parts of the curves $\tau_{rad}(c)$. At intermediate activator concentrations (0.3–1.5 wt.%), the M centers begin to play an important role. These centers have a low quantum yield and a short lifetime. Strong quenching in the M centers is responsible for the fall of the relative quantum yield since the M centers make a considerable contribution to the absorption but practically no contribution to the luminescence. In CaF$_2$ crystals, the luminescence is completely quenched in the P centers. However, in SrF$_2$:Nd$^{3+}$ crystals the P-center luminescence is not completely quenched. The degree of quenching of the luminescence of the P centers in BaF$_2$ crystals is even less. The maximum in the $\eta(c)$ curve of BaF$_2$:Nd$^{3+}$ at an activator concentration of ~2.5 wt.% is due to a reduction in the relative concentration of the nonluminescent M centers and an increase in the number of the luminescent P centers. Moreover, we must mention that a considerable fall of $\tau_{rad}$ of the L centers is observed exactly in the region of the rapid rise of the relative concentration of the P centers (~1 wt.% for SrF$_2$ and ~2 wt.% for BaF$_2$). This indicates that energy transfer takes place from the L to the P centers.

It is worth noting also the observation that the lifetime of the excited state of Nd$^{3+}$ in the L centers in BaF$_2$ is approximately seven times longer than for the L centers in CaF$_2$ and SrF$_2$ (cf. Figs. 9a and 10a, as well as Fig. 2 in[6]). The reduction in the transition probability and the increase in the excited state lifetime may be due to the larger lattice constant of BaF$_2$ or the change in the nature of chemical binding because of the stronger polarization.

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