

Time-Resolved Study of Photoluminescence from Excited O_2^- Centers in KCl-KBr Mixed Crystals

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Abstract

We report the optical properties of the O_2^- center in KCl-KBr mixed crystals. The O_2^- ion has different molecular axes in its excited state along the $\langle 110 \rangle$ direction in KCl and along $\langle 111 \rangle$ in KBr. As a result of this, the former system shows double structure sidebands and the latter shows single structure sideband in their emission spectra. It is the motivation of the present work to investigate how the emission of the O_2^- center behaves in a mixed $KCl_{1-x}Br_x$ system. From lifetime measurements, we have determined an activation energy ΔE for the nonradiative process, a frequency factor ν and the oscillator strength of the fluorescence f_{flu0} for the O_2^- center in the $KCl_{1-x}Br_x$ system.

Introduction

Since most of the alkali halides are mutually soluble over a large concentration range, we can easily and systematically investigate the effects on impurities by variation of the host crystal field. Recently the optical properties of $F_A(II)$ centers containing the Li^+ ion in KCl-KBr mixed crystals were investigated [1]. As a result it was observed that the type II emission band in $KCl_{0.78}Br_{0.22} : Li$ crystal shifts to shorter wavelengths by $0.25 \mu m$ compared to the emission of the centers in unmixed KCl. Such a mixed crystal enables us in principle to obtain laser action in a new wavelength range which can not be realized by using a pure host crystal. Moreover such a mixed system makes it convenient to get additional and deeper information about the behavior of impurities, like their basic optical parameters or structural changes of their relaxed excited states.

The optical spectra [2, 3] and structure [4-8] of the O_2^- centers have been investigated in detail in various pure alkali halides. It has been shown that the O_2^- ion substitutes a halide ion and that its molecular axis is oriented at low temperatures in the ground state along the $\langle 110 \rangle$ axis. Furthermore, the O_2^- ion in KCl, RbCl, RbI and RbBr has in its excited state its molecular axis along the $\langle 110 \rangle$ direction and shows double structure phonon sidebands, while in NaCl, KI, KBr and NaBr its axis lies along the $\langle 111 \rangle$ direction and its emission shows single structure sidebands. Several attempts to find out the reason for this difference have been made by using the level schemes and the transition [9, 10] and polarized Raman spectroscopy [8].

In a recent letter we have reported [11] for the first time preliminary results on the optical properties of the O_2^- center in KCl-NaCl mixed crystals in order to clarify how the emission

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of the O_2^- center behaves in such a system. However, the valid difference cannot be observed in a KCl-NaCl system due to its inability to form a solid solution through a large composition range. In this work the KCl-KBr system was selected because such a system can form complete solid solutions through a large composition range and the excited O_2^- center in pure KCl and KBr forms, as described above, different orientations and emission sideband behavior.

In this paper, we present a series of extensive experiments on the optical properties of the O_2^- centers in a KCl-KBr system. We have investigated firstly how the emission of the O_2^- center in a mixed $KCl_{1-x}Br_x$ system behaves in comparison to that in the two pure host systems. Secondly, we have determined from the emission lifetime measurement an activation energy ΔE for the non-radiative process, a frequency factor ν , and the oscillator strength f_{fluo} of the maximum wavelength of the emission for the mixed crystals. These values obtained in this work are compared to similar values obtained by other authors on KCl : O_2^- and KBr : O_2^- .

Experimental

Single crystals of KCl, KBr and a $KCl_{1-x}Br_x$ solid solution were grown in a platinum crucible with 1 mol% potassium super-oxide (KO_2) in the melt by the Kyropoulos method in air. The crystals were cleaved to samples of about $10 \times 10 \times 2$ mm³. Our indicated $KCl_{1-x}Br_x$ compositions represent the doping in the melt. When using this procedure the crystals were always contaminated with significant amounts of OH^- . As previously reported by Florian *et al.* [12], the presence of the OH^- does not influence the O_2^- emission.

The absorption spectra were measured with a Hitachi U-2000 spectrophotometer, while the excitation and emission spectra were recorded with a Hitachi F-3010 spectrofluorometer. The absorption, emission and excitation spectra were measured at 77 K and RT (room temperature). Each absorption spectrum consists of two absorption bands. One is due to the OH^- ions and each absorption peaks shifts towards longer wavelength from 204 nm to 212 nm going from KCl : O_2^- to KBr : O_2^- at 77 K. The other is due to the O_2^- ions and each absorption peaks also shifts from 252 nm to 260 nm going from KCl : O_2^- to KBr : O_2^- at 77 K. The O_2^- concentration was determined by measuring the optical absorption coefficient [13] and estimated to be about 3×10^{17} cm⁻³.

The lifetime measurements were performed with a time-resolved spectrofluorometer (Horiba Ltd., NAES-1100) which was based on the time-correlated photon-counting technique. An outline of this apparatus was given in a previous paper [14]. The sample was mounted in a variable temperature cryostat (Oxford, DN-1754) in conjunction with a temperature controller (Oxford, ITC-4) which keeps a stable temperature between 77 and 475 K. The X-ray diffraction patterns of the mixed crystals correspond to those of a solid solution.

Results and discussion

The emission and excitation spectra of O_2^- centers for the various compositions at 77 K (solid line) and RT (dotted line) are shown in figs. 1a-1d. These figures (a, b, c and d) correspond to the samples of KCl : O_2^- , $KCl_{0.8}Br_{0.2}$: O_2^- , $KCl_{0.4}Br_{0.6}$: O_2^- and KBr : O_2^- ,

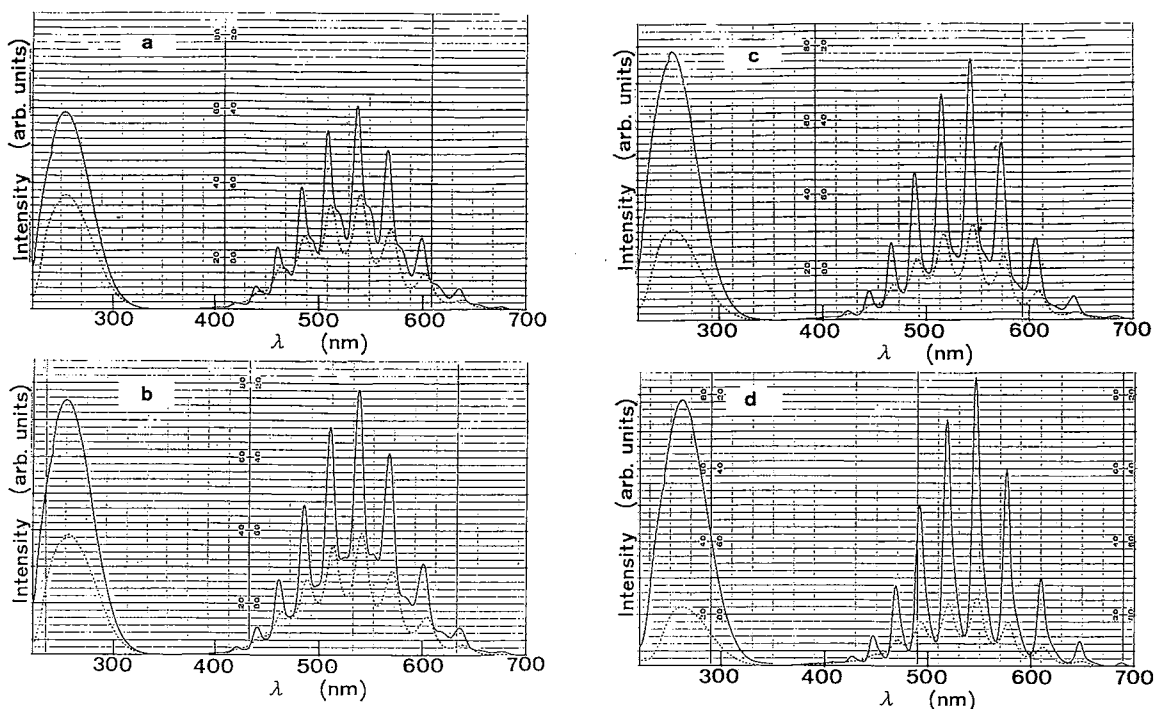


Fig. 1 Emission (right-hand side) and excitation (left-hand side) spectra of KCl : O_2^- (a), $KCl_{0.8}Br_{0.2}$: O_2^- (b), $KCl_{0.4}Br_{0.6}$: O_2^- (c) and KBr : O_2^- (d) at 77 K (solid line) and RT (dotted line).

Table 1 Fluorescence peak positions and relative shifts of O_2^- in a $KCl_{1-x}Br_x$ system at 77 K and RT. The most intense peak is underlined. (λ in nm ; ν and $\Delta\nu$ in cm^{-1}).

Host Crystal Temp.	1	2	3	4	5	6	7	8	9	10	11	
KCl	λ			463.8	486.8	511.8	<u>539.4</u>	568.6	602.4	639.0	678.6	
	ν			21561	20542	19539	<u>18539</u>	17587	16600	15649	14736	
	$\Delta\nu$			1019	1003	1000	952	987	951	913		
$KCl_{0.8}Br_{0.2}$	λ			465.0	488.0	513.2	<u>540.8</u>	570.6	604.2	640.6	681.2	
	ν			21505	20491	19485	<u>18491</u>	17525	16550	15610	14679	
	$\Delta\nu$			1014	1006	994	966	975	940	930		
$KCl_{0.4}Br_{0.6}$	λ			487.8	491.2	516.4	<u>544.2</u>	574.2	608.2	644.8		
	ν			21376	20358	19364	<u>18375</u>	17415	16441	15508		
	$\Delta\nu$			1018	993	989	960	974	933			
KBr	λ		448.4	469.8	493.4	518.8	<u>547.0</u>	577.2	611.2	648.4	690.2	
	ν			22302	21286	20268	<u>19275</u>	18282	17325	16361	15423	
	$\Delta\nu$			1016	1018	992	994	957	964	938	934	
KCl	λ	402.0	419.6	439.2	460.9	483.6	508.6	<u>536.2</u>	566.2	599.2	635.6	675.8
	ν	24876	23832	22769	21697	20678	19662	<u>18650</u>	17668	16689	15733	14797
	$\Delta\nu$	1043	1064	1072	1018	1016	1012	982	979	956	936	
$KCl_{0.8}Br_{0.2}$	λ	402.6	420.8	440.6	461.8	485.0	510.2	<u>537.8</u>	567.6	601.0	637.2	677.0
	ν	24839	23764	22696	21654	20619	19600	<u>18594</u>	17618	16639	15694	14771
	$\Delta\nu$	1074	1068	1042	1036	1018	1006	976	979	945	923	
$KCl_{0.4}Br_{0.6}$	λ	405.0	423.4	443.4	464.8	488.4	514.0	<u>541.8</u>	571.8	605.6	642.6	682.4
	ν	24691	23618	22553	21515	20475	19455	<u>18457</u>	17489	16513	15562	14654
	$\Delta\nu$	1073	1065	1038	1040	1020	998	968	976	951	908	
KBr	λ	407.4	426.4	446.2	468.0	491.4	517.0	<u>545.0</u>	575.6	609.6	646.6	688.0
	ν	24546	23452	22411	21368	20350	19342	<u>18349</u>	17373	16404	15466	14535
	$\Delta\nu$	1094	1041	1044	1018	1008	994	975	969	939	931	

respectively. As the concentration of Br^- ions increases, the emission- and excitation peaks shift towards longer wavelength by about 9 nm going from $\text{KCl}:\text{O}_2^-$ to $\text{KBr}:\text{O}_2^-$. In contrast to this host material dependence, emission and excitation peaks are very little affected by temperature variation. Complete wavelength measurements of the emission spectra at RT and 77 K are presented in table 1. At RT the emission spectra consist of 7 or 9 peaks, while at 77 K they consist of 11 peaks, which are almost equally spaced in energy by about 1000 cm^{-1} . It should be noted that the emission spectra of fig. 1a and 1b at 77 K are quite different from those of fig. 1d. That is, in the case of $\text{KCl}:\text{O}_2^-$ and $\text{KCl}_{0.8}\text{Br}_{0.2}:\text{O}_2^-$, some prominent large peaks with their small associated peaks can be seen. In contrast to this, in the case of $\text{KBr}:\text{O}_2^-$, only the prominent peaks can be seen. The difference is observed more clear, if the experiments are performed at temperatures lower than 77 K. These results can be explained in the same manner as reported earlier by Rolfe *et al.* [7] and Hongo *et al.* [10]. In KCl the molecular axis of O_2^- points along $\langle 110 \rangle$ directions in the excited state. If we assume that O_2^- is centered on the lattice site, the point group of the defect is D_{2h} . Therefore, the excited (ground) state ${}^2\Pi_{u(g)}$ of the O_2^- centers in the $\langle 110 \rangle$ directions splits into $B_{2u(g)}$ and $B_{3u(g)}$ states. Similarly, the O_2^- axis in KBr points along the $\langle 111 \rangle$ directions and the point group is D_{3d} . Both the ground and the excited states do not split in this crystal field.

The typical fluorescence decay curves measured at a set of different temperatures are shown in fig. 2. These curves (a, b, c and d) were obtained by excitation into the 250 nm band and by detection at the maximum wavelength of about 540 nm emission band for $\text{KCl}:\text{O}_2^-$.

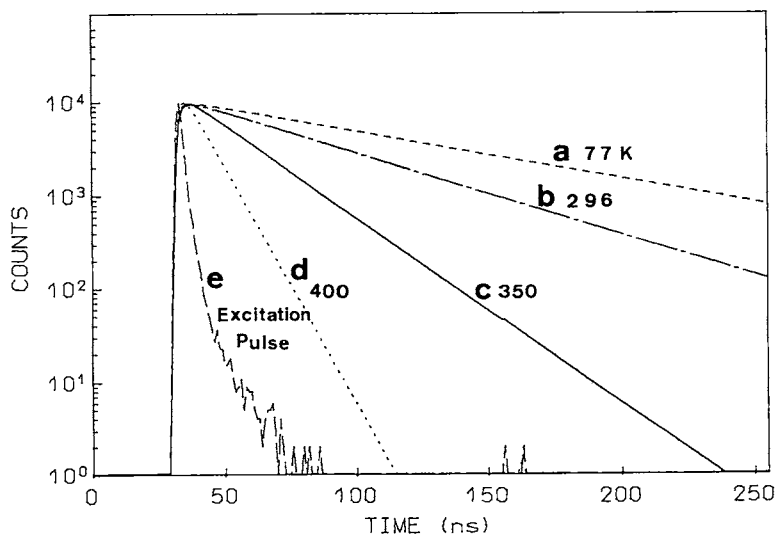


Fig. 2 Decay curves of O_2^- centers in KCl, measured (a) 77 K, (b) 296 K (RT), (c) 350 K and (d) 400 K. Curve (e) is the excitation pulse waveform. Excited at 250 nm; Detected at 540 nm.

Curve (e) shows the excitation waveform. As can be seen in this figure, the decay time τ is $\tau = 85$ ns at 77 K. When raising the temperature, τ decreases slowly about 50 ns at 296 K (RT) and drops more steeply to 8 ns at 400 K. It was found that below 250 K the decay curves are always purely single exponential over nearly 4 orders of magnitude in time and do not depend of the wavelength of observation, though not shown here, parallel to this decrease of τ , the intensity of the fluorescence decays too.

Figure 3 shows typical examples of the measured temperature dependence of the lifetime versus reciprocal temperature $1/T$ for KCl : O_2^- (\circ), $KCl_{0.8}Br_{0.2}$: O_2^- (Δ), $KCl_{0.4}Br_{0.6}$: O_2^- (\square) and KBr : O_2^- (\bullet). The behavior at high temperature above 300 K is shown enlarged in the inset in fig. 3. It should be noted that the curves show the reciprocal lifetime $1/\tau$ dependence versus reciprocal temperature $1/T$ for the various compositions. At temperatures below 250 K the radiative process predominates, while at high temperatures a non-radiative de-excitation process controls the excited state lifetime.

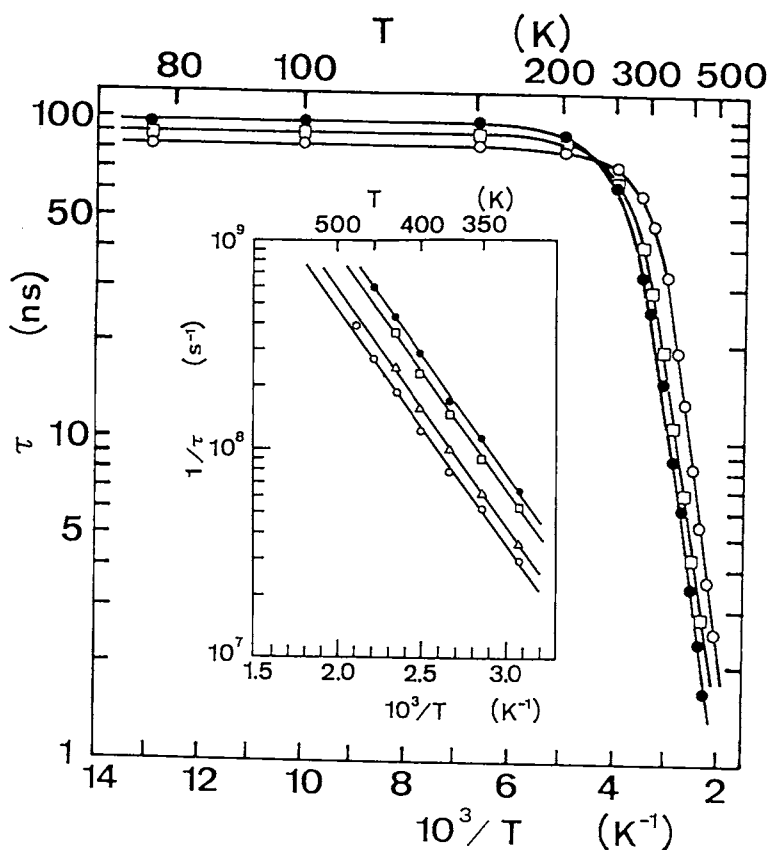


Fig. 3 Fluorescence lifetime τ in log plots vs. $1/T$ for KCl : O_2^- (\circ), $KCl_{0.8}Br_{0.2}$: O_2^- (Δ), $KCl_{0.4}Br_{0.6}$: O_2^- (\square) and KBr : O_2^- (\bullet). The behavior at high temperature above 300 K is shown enlarged in the inset.

From the radiative decay time, τ_R , we can determine the oscillator strength of the fluorescence, f_{flu0} , from the well-known formula

$$f_{flu0} = \frac{1}{8\pi^2} \left(\frac{\lambda^2}{c\tau_R} \right) \left\{ \frac{1}{n[(n^2+2)/3]^2} \right\}, \quad (1)$$

where c is the speed of light, τ_R the radiative lifetime, λ the oscillating wavelength and n the index of refraction of the host. For $\tau_R = 84.4$ ns at 77 K, $\lambda = 540$ nm at the center of the emission and $n = 1.494$ at 540 nm, Eq. (1) yields $f_{flu0} = 0.0302$ for KCl : O₂⁻.

The temperature dependence of the transition probability $1/\tau$ is given by

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \nu \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (2)$$

where τ is the total lifetime, τ_R radiative lifetime, ν frequency factor, k_B the Boltzmann constant and ΔE activation energy for the non-radiative process. All activation energies ΔE and frequency factors ν can be obtained from the curve fitting analysis. The slopes of the curves at high temperatures as shown in the inset in fig. 3 correspond to the activation energy.

All activation energies ΔE , the temperature T_h above which thermal relaxation dominates (h for half of low temperature, $\tau(T_h) = \tau_R/2$), the frequency factor ν , the oscillator strength of the fluorescence, f_{flu0} , are summarized in table 2. The values τ_R and ν increase going from KCl : O₂⁻ to KBr : O₂⁻ as the concentration of Br⁻ ions increases. While the value f_{flu0} at 77 K decrease continuously as the concentration of Br⁻ ions increases. Therefore we can say that the lattice-center interaction is higher in KBr : O₂⁻ than in KCl : O₂⁻ crystals. All activation energies ΔE are the same for all crystals. In the bottom half of table 2, the values obtained here are compared to those obtained by Hongo *et al.* [10] and Hessmann and Fischer [15].

Figure 4 shows the time-resolved spectra measured at 5 ns intervals after irradiation of the exciting pulses for KCl : O₂⁻ crystals at 290 K (RT). It can be seen from this figure that the maximum intensity of the fluorescence was about 25 ns after irradiation of the exciting pulses.

Table 2 Results of data analysis obtained by the present authors. (τ_R radiative lifetime, T_h temperature for $\tau(T_h) = \tau_R/2$, ν frequency factor, ΔE activation energy for the radiationless process and f_{flu0} the oscillator strength of the fluorescence).

Host Crystal	τ_R (ns)	T_h (K)	ν (10 ¹¹ s ⁻¹)	ΔE (10 ² meV)	f_{flu0} at 77 K	Orientation
KCl	84.4	309	0.9	2.3	0.0172	<110>
KCl _{0.8} Br _{0.2}	84.5	298	1.2	2.3	0.0168	↑
KCl _{0.4} Br _{0.6}	90.1	278	1.7	2.3	0.0151	↓
KBr	97.2	268	2.0	2.3	0.0133	<111>

KCl	80	—	1.3	2.5	—	Ref. [10]
KBr	93	—	3.3	2.4	—	Ref. [10]

KCl	76	310	—	2.2	—	Ref. [15]
KBr	84	266	—	2.1	—	Ref. [15]

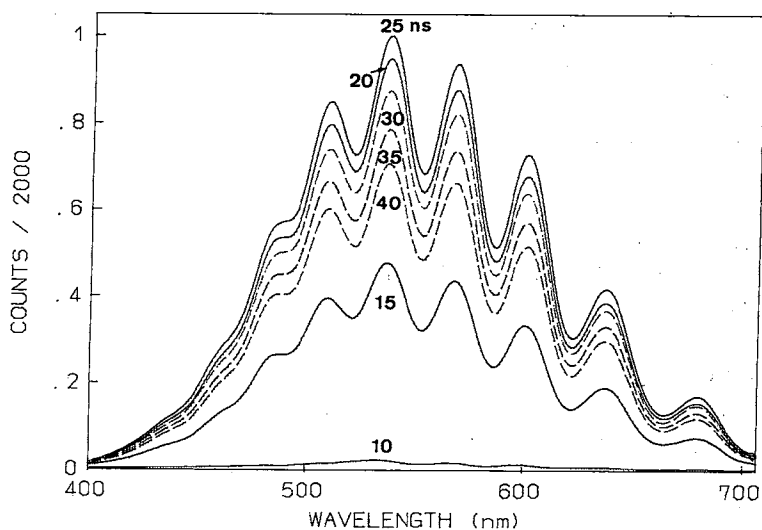


Fig. 4 Time-resolved spectra measured at 5 ns intervals for KCl : O_2^- at RT.

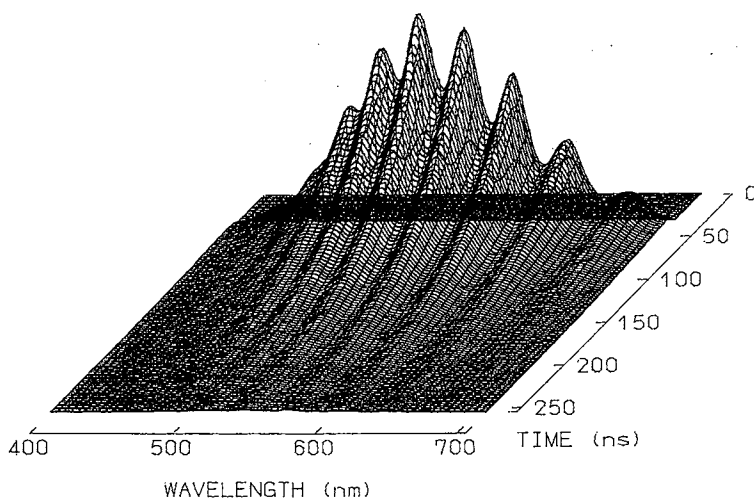


Fig. 5 Three-dimensional fluorescence spectra for KCl : O_2^- at RT.

The three-dimensional graphs of time- and wavelength-dependent fluorescent intensities were obtained by reconstructing the analysis data of time-resolved decays of fluorescence intensity at variable wavelengths, as shown in fig. 5.

In summary we have reported the optical properties of the O_2^- centers in KCl-KBr mixed crystal. Such a $KCl_{1-x}Br_x$ system is a complete solid solution throughout a large composition range, so that we can clearly observe the behavior of the O_2^- ion throughout the different host crystals. Moreover the basic optical parameters such as the activation energy ΔE , the

frequency factor ν and the oscillator strength of fluorescence f_{flu0} can be estimated systematically. Such mixed crystals seem to be convenient systems to investigate other impurity behavior of the ground- and excited states such as Cu^+ and Ag^+ ions which occupy either an on-center or an off-center position in various alkali halides [16].

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