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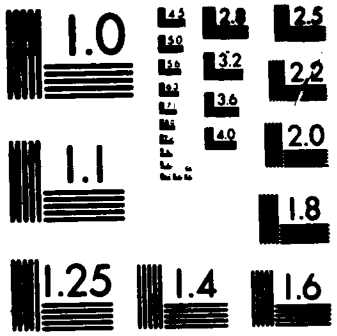

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Luminescence of Cu$^+$ Beta" Alumina

by

J.D. Barrie[1], B. Dunn[1], O.M. Stafsudd[2] and P. Nelson[2]

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1. Department of Materials Science and Engineering,
2. Department of Electrical Engineering
University of California, Los Angeles,
Los Angeles, California 90024

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LUMINESCENCE OF Cu^+-β''-ALUMINA

J.D. Barrie and B. Dunn
Department of Materials Science and Engineering
University of California, Los Angeles, CA 90024

O.M. Stafsudd and P. Nelson
Electrical Engineering Department
University of California, Los Angeles, CA 90024

ABSTRACT

A series of monovalent copper containing β''-alumina single crystals have been prepared by standard ion exchange techniques. The crystals exhibit strong luminescence which we attribute to the $3d^94s \rightarrow 3d^{10}$ interconfigurational transition. The peak wavelength of this transition can be varied by 135nm by the presence of other cations in the β''-alumina conduction plane, allowing the luminescence to be varied throughout the visible spectrum. Single pass gain measurements of several of these crystals show gains of the order of 0.1/cm, suggesting the potential use of these materials for solid state tunable lasers.

I. INTRODUCTION

Recent studies have shown that the two-dimensional solid electrolyte Na^+-β''-alumina is capable of replacing its entire sodium ion content with many monovalent, divalent, and trivalent cations by simple ion exchange reactions [1,2,3]. Such behavior has allowed a wide variety of related compounds to be synthesized, differing only by the chemical species found in the material's so-called "conduction plane," the region in which the mobile ions are situated. (Figure 1) One of these compositions, Nd^{3+} exchanged β''-alumina, has been found to exhibit unique optical behavior [4,5], leading to laser action and degenerate four-wave mixing. Initial studies of transition metal ion exchanged β''-aluminas indicate that these compounds are also capable of exhibiting interesting optical effects [6].

The novel behavior of β''-alumina prompted our interest in applying this material as a host for an ion in which there has been considerable interest, monovalent copper. This ion has been studied extensively in various alkali halide hosts [7]. In addition, several studies have been performed on Cu^+ ions in other halide crystals [8-10], various zeolites [11], and in a number of glassy systems [12-14]. Each of these hosts has some difficulty in being considered for device applications. The glasses are susceptible to color center formation under the ultraviolet radiation required to pump the Cu^+ ions, the halides tend to be sensitive to environmental conditions, e.g. moisture, and the zeolites are generally unavailable in large single crystal form. As such, there would be substantial benefits in finding an oxide material capable of hosting this ion in a crystalline environment. However, introduction of this ion into a crystal during the growth process is typically plagued by the propensity of the ion to oxidize to the Cu^{2+} state, whose absorption bands tend to interfere with luminescence from Cu^+ ions.

The valence instabilities of copper underscore the very advantage of using β''-alumina as an optical host. Like the zeolites, the ion exchange ability of the material makes it possible to separate the crystal growth process from the doping process, which allows far greater control over the experimental conditions to which the dopant ions are subjected. While the growth of β"-alumina crystals requires oxidizing atmospheres and temperatures in excess of 1680°C (which would make retention of the Cu^+ ionic state virtually impossible), the ion exchange process can be performed in inert or reducing atmospheres at temperatures below 600°C. It is this decoupling of the growth and doping processes which makes it possible to achieve ionic states such as Cu^+ in a stable, crystalline oxide host.

The technological significance of monovalent copper ions arises from their efficient luminescent properties in wavelength regions heretofore unobtainable in solid state laser systems (except by doubling processes, etc.). The Cu^+ ion is known to luminesce in the blue-green region of the spectrum in a variety of hosts via transitions from the $3d^94s$ excited state to the $3d^{10}$ ground state [7-14]. Therefore, if the proper host is found, there is a possibility of producing a solid state laser within this spectral region. The vibronic nature of the transition produces wide luminescence bands which should allow any laser produced using this ion to be tunable over a wide frequency range. Wavelength tunability, particularly in the blue-green region should be of interest for a large number of potential applications.

The β"-alumina crystal into which the Cu^+ ions were exchanged possesses two possible sites for the dopant ions, commonly called the Beevers-Ross (BR) and mid-oxygen (mO) sites. The BR site possesses C_{3v} symmetry with respect to the first neighbor oxygen atoms, while the mO site possesses C_{2h} symmetry. The BR site, which is four coordinated, is the site most commonly occupied by sodium ions in undoped β''-alumina [15]. In contrast, many of the divalent and trivalent ions which have been studied in β''-alumina exhibit significant or sole occupation of the mO site [16,17]. This latter site is slightly larger than the BR site, and has eight nearest neighbors (bipyramidal coordination).

In this paper, we describe the synthesis and properties of a family of Cu^+ ion exchanged β''-aluminas. The work demonstrates that not only can monovalent copper be incorporated in the β''-alumina host, but also that it is possible to tune the Cu^+ emission throughout much of the visible spectrum.

II. EXPERIMENTAL PROCEDURES

The preparation of Cu^+ ion exchanged β''-aluminas was performed by standard ion exchange techniques using single crystals of Na^+-β''-alumina of typical composition $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$. The precursor crystals were grown by the flux evaporation technique [18], and typically measured 5x5x0.2mm in size. Crystals were immersed into molten salts containing the ions which were desired for the exchange and were held at temperatures high enough for diffusional processes to proceed at a reasonable rate. A summary of the conditions used for the preparation is found in Table 1. Careful control of the melt composition and atmosphere of the ion exchange allowed for control of the valence state of the copper ions diffusing into the crystal. Flowing nitrogen during the exchange was sufficient to prevent oxidation of the eutectic melts used. The resultant exchanged crystals were colorless and showed no signs of mechanical degradation from the ion exchange process.

An estimate of copper ion concentrations in the exchanged crystals was determined using a variety of approaches. The exchange procedure of β''-aluminas is commonly monitored using the change in weight of crystals which occurs during the ion exchange process. Complete exchange of sodium ions in the crystal with monovalent copper would cause a weight increase of 11.2% in the crystals. This technique is sensitive to exchange levels of approximately 1%, corresponding to Cu^+ ion concentrations of 5×10^{19} ions/cm^3. Approximately this same level of Cu^+ ions is detectable in crystals by x-ray fluorescence techniques. Optical absorption measurements, conversely, may be used to determine the lower bounds of monovalent copper within the crystal. By assuming that absorption transitions are fully allowed (oscillator strength of unity), and that there are no polarization effects, the estimates from optical density measurements can only underestimate the amount of copper ions present. In a typical crystal, the integrated absorption strength gave (assuming a fully allowed transition) a minimum copper ion concentration of $1\text{x}10^{18}$ ions/cm^3. The combination of these techniques allowed for establishing the Cu^+ ion concentrations within fairly narrow ranges. Single crystal x-ray diffraction measurements confirmed the retention of the β''-alumina phase and allowed measurement of the lattice parameters of the exchanged crystals.

Optical properties of the Cu^+ ion exchanged crystals were measured by a variety of techniques. Emission and excitation spectra were obtained using a Spex F112A spectrofluorometer system. The spectra were recorded and digitized via computer control. Temperatures were varied from 77 to 300K using a fused quartz dewar made specifically for this experiment. Absorption spectra were also measured on the same instrument.

Luminescent lifetimes of the crystals were measured using pulsed laser irradiation from a Lambda Physik XeCl excimer laser (nominal pulse duration 20 nsec). The luminescent signal was then discriminated using appropriate laser line filters and focussed onto a Hamamatsu R980 (≈S-11) photomultiplier tube. The system response time was less than 2 μsec, much shorter than any of the lifetimes measured. The signal was digitized using a Data Precision Model 6000 transient digitizer and was stored for analysis. Lifetimes were measured over a range of temperatures using the fused quartz dewar mentioned above.

Small signal single pass gain measurements were performed on selected crystals using the above excimer laser as a pump source, and an argon ion laser or helium-neon laser as a probe. The collection electronics are as described above. Samples were mounted with their c-axis perpendicular to the probe beam. The probe beam was focussed by appropriate microscope objective lenses for coupling into the thin edge of the crystal, and was typically less than 10 microns in diameter. This experimental geometry gave gain path lengths of four to eight millimeters. The excimer pump was at right angles to the probe in order to minimize interactions with the detection optics and to remove any pump depletion effects.

III. RESULTS AND DISCUSSION

(a) Ion Exchange

Using the ion exchange conditions found in Table 1, a variety of Cu^+ exchanged β''-aluminas were prepared. It was found that the ion exchange procedure using melts of pure cuprous salts often resulted in crystals which were discolored and which luminesced only weakly. These crystals typically had 20 to 50 percent of the Na^+ ions replaced by Cu^+ ions after an exchange of several hours. The exact nature of this coloring is unknown, but ESR studies of other similar crystals indicates the presence of Cu^{2+} ions. These results are similar to other attempts to synthesize Cu^+-β''-alumina [19].

When the melts were changed from pure salts to mixtures of salts, such as the eutectic of NaCl and CuCl, it was found that the resultant crystals were colorless. Gravimetric measurements indicated that the crystals had been exchanged only a small amount. For crystals with less than one percent exchanged, (i.e., a Cu^+ concentration of 5×10^{19} ions/cm^3), it was not possible to conclusively establish the Cu^+ ion concentration. However, from optical absorption data, it could be determined that all the crystals had Cu^+ concentrations of at least 5×10^{17} ions/cm^3. Thus at the present time, it can only be estimated that the Cu^+ ion concentration in the β''-alumina host was in the range of 10^{19} ions/cm^3. Despite this relatively low concentration, the luminescence of these crystals was quite strong. In addition, ESR measurements were unable to detect the presence of any Cu^{2+}, which indicates that monovalent copper was the only copper valence present in the conduction plane.

The small percentage of ion exchange is somewhat surprising in that the melt composition of NaCl/CuCl eutectics is approximately 75 mole percent of the cuprous chloride. This suggests that the thermodynamics of copper ion exchange are unfavorable, and that the copper ions are more stable in the melt than they are in the crystal. Such behavior was previously observed for Pb^{2+} and Cd^{2+} exchange in β''-alumina and is associated with a net positive free energy change for the ion exchange reaction [20]. The importance of thermodynamics is confirmed by the fact that ion exchange treatment time has virtually no effect on the final concentration of monovalent copper in the crystal, but changing the melt temperature or copper concentration does influence crystal composition.

(b) Optical Properties

The room temperature excitation and emission spectra of a typical Cu^+ ion exchanged Na^+-β''-alumina crystal are found in Figure 2. Several ultraviolet absorptions are found in the excitation spectrum of Cu^+/Na^+-β''-alumina which result in a broad green luminescence (FWHM=65nm) centered at 535nm. This luminescence shows the typical behavior of a vibrationally allowed transition, weakening in intensity upon cooling. The luminescent lifetime of the transition also follows the behavior expected for transitions dependent upon phonon coupling. The lifetime is shorter at room temperature (65μsec) than it is at liquid nitrogen temperatures (90μsec). The variation of lifetime and intensity of this green luminescence is shown in Figure 3. The decay of the luminescence showed a single exponential nature at all temperatures.

Interpretation of the observed spectra of Cu^+ ions exchanged in small concentration into Na^+-β''-alumina begins with the knowledge that the primary site for sodium ions is the BR site. Assuming that the Cu^+ ion would have an equal propensity for both available sites, it would seem more favorable from an electrostatic viewpoint for the initial dopant ions to occupy the same sites as the sodium ions which they replaced. This would place the Cu^+ ions in a C_{3v} symmetric environment, coordinated with three oxygen atoms below the conduction plane and one above the conduction plane. (The nearest oxygen atoms in the conduction plane are at least 30 percent further away than the first nearest neighbors. Their arrangement is such that even considering their effects, they do not lower the C_{3v} symmetry of the site.)

Group theory predicts that the symmetric $3d^{10}$ ground state of the Cu^+ ion will be unaffected by the field imposed by this site and will remain one level, $^1A_1$. The $3d^94s$ first excited state, however, will be split into levels consisting of singlet and triplet states arising from the combined spins of electrons in two different principal quantum shells. It is expected that two or more peaks should be found in the excitation (or absorption) spectra of such an ion as a result of the absorptions from the $^1A_1$ ground state to the singlet excited states. These levels should possess differing polarization behavior, but due to the platelet geometry of the crystals, this has yet to be confirmed. The question of the identity of the emitting state is not clear at this time. For the case of an isolated Cu^+ ion, emission would be expected to occur from the lowest triplet state. The spin forbidden nature of this transition is in good agreement with the observed lifetimes.

However, the large energy gap between excitation and emission indicates that the spectra may not arise from isolated Cu^+ ions, but may be further complicated by interactions of the Cu^+ ions within the conduction plane. Studies by Hoffmann suggest that such interactions may be energetically favorable [21], and spectra observed by Payne, et al., attributed to copper dimers in $SrCl_2$, show a marked resemblance to the emission in β''-alumina [8].

(c) Tunable Emission

The Cu^+ ion is expected to be sensitive to its crystal field environment not only because the electronic transitions involve d-orbitals (which are relatively unshielded in comparison to other electrons), but also from the fact that Cu^+ ions in the excited state have electron density in the 4s orbitals. These electrons tend to interact with the 2p orbitals of the oxygen ligands [23]. The rich ion exchange chemistry of β''-alumina enables us to easily alter the crystal field imposed upon the Cu^+ ions. The c-axis lattice parameter of β''-alumina is known to be highly sensitive to the ions which are found in the conduction plane [2]. Total replacement of Na^+ ions by K^+ ions typically increases the c-axis length from 33.54 Å to 34.09 Å. Thus if we keep the Cu^+ ion concentration constant and small, replacing the remainder of the Na^+ ions with K^+ ions by ion exchange should result in (1) expansion of the c-axis lattice parameter for β''-alumina and (2) a lower crystal field imposed upon the copper ions. Since the energy levels in copper are shifted to higher levels than in the free ion under an imposed crystal field (due to the strong antibonding nature of the interaction between copper 4s and oxygen 2p orbitals), lessening of this field should lower the energies observed for excitation and emission. This variation of transition energies with crystal lattice parameter does indeed exist. The replacement of the residual sodium ions with a variety of other ions (monovalent, divalent, and trivalent) produces a series of emissions from Cu^+ ion exchanged β''-alumina. Ions which contract c_o relative to Na^+-β''-alumina cause blue shifts relative to Cu^+/Na^+ emission (Figure 2) while ions that increase c_o produce red shifts. From this behavior, we have found that the emission peak could be varied by as much as 135nm. That is, the emission of Cu^+ in β''-alumina can be varied throughout the visible spectrum simply by the introduction of "co-dopants" into the β''-alumina conduction plane (Figure 4).

Most of the emission spectra shifts seem to arise from the above explained effect. The co-dopant serves to expand or contract the β''-alumina conduction plane about the Cu^+ ions, and result in smaller or larger crystal fields. The two extreme shifts which were observed, however, did not follow this trend. (Figure 5) Replacement of the residual sodium ion content with silver ions tends to produce emission bands shifted to much lower energies than with any other combination. This luminescence is unexplained by the above lattice parameter argument, and seems to arise from some other effect. The temperature dependence of Cu^+/Ag^+ emission varies from that of the Cu^+/Na^+ exchanged crystals. In the Ag^+ containing crystals, a second, green emission occurs as the temperature is decreased. The emission maximum, which is quite strong, occurs at a wavelength which is consistent with that expected from the lattice parameter of the Cu^+/Ag^+ crystals. The position of the emission peak of these crystals at 300K and 77K is shown in Figure 5. This behavior suggests that the red emission is from some other species, as yet unknown, which competes with the green emission at elevated temperatures.

In addition to the behavior observed for the Cu^+/Ag^+ ion exchanged samples, the Cu^+/Ba^{2+} ion exchanged β''-aluminas also exhibit two emission peaks. In this case, however, both are observed at room temperature. They are found at 480nm, the most blue shifted observed, and at 575nm. The latter peak is expected from the lattice parameter argument. The peak at 480nm, however, seems to arise from a second type of Cu^+ environment in the conduction plane, showing a distinctly different excitation spectrum. The relative amounts of these two peaks at room temperature can be varied depending upon the conditions used for the synthesis of the crystals.

(d) Applications

Small signal single pass gain measurements were performed on several of the Cu^+ ion exchanged β''-aluminas. In Cu^+/Na^+-β''-alumina crystals (fluorescence maximum at 533nm) the single pass gain at 514.5 nm was measured to be of the order of 0.1/cm. This gain was measured at several locations in each of several crystals, with path lengths varying from 4 to 8 mm. The long path length resulted in signal gains of from 4 to 8 percent, at least ten times greater than the experimental uncertainties. The temporal profile of this small signal gain showed behavior similar to the luminescent lifetime. Moreover, very little gain was observed at the 488nm line from an argon ion laser, further confirming that the observed gain was valid and not due to impurities or transient color centers. No effect at all was observed at 632.8nm in the Cu^+/Na^+ exchanged crystals. Assuming that the room temperature luminescent lifetime of 65μsec is dominated by radiative processes, the population inversion achieved was approximately 10^{19} ions/cm^3. This is of the same order of magnitude as the concentration of Cu^+ ions in the crystals, and is consistent with the high intensity of the XeCl excimer laser pump beam. This gain is nearly two orders of magnitude greater than has been reported for Cu^+ in any other solid state host [14].

In addition to the Cu^+/Na^+ system, single pass gain for the red emission of Cu^+/Ag^+ exchanged β''-alumina was also measured. The probe beam in this case was the 632.8nm emission of a helium/neon laser, and the gain was found to be of the order of 0.1/cm. No effects were observed using 488nm or 514.5nm probe beams. These gain measurements suggest that Cu^+ doped β''-aluminas may be useful laser materials over a broad wavelength range. More detailed single pass gain measurements are in progress.

One issue of considerable practical importance is the stability of the cuprous ions in the β''-alumina host. We have begun to explore some of these questions. Very high intensity UV radiation from an excimer laser (5 MW/cm^2 at 308nm) produces no indication of either transient or long lived color centers in these materials. In addition, subjecting these crystals to a variety of annealing treatments up to 400°C in nitrogen produces no change in their fluorescence behavior. Past experience has shown that some of the ion exchanged β''-aluminas are sensitive to hydration of the conduction plane due to water diffusion. Initial studies indicate that the emission behavior of Cu^+ ions in β''-alumina is not effected by either prolonged exposure to ambient atmospheres or shorter term exposure (days) in water vapor at temperatures up to 80°C.

IV. CONCLUSIONS

The Cu^+ ion exchanged β''-aluminas appear to exhibit a range of interesting and useful properties. The unique ion exchange behavior of β''-alumina enables the material to be prepared such that the monovalent copper ions are selectively incorporated into the structure. The ability to completely exclude the cupric state is extremely difficult to accomplish in other oxide hosts and is of central importance if practical devices based on Cu^+ are to be realized. A second significant result is that we are able to alter the emission spectrum of the Cu^+ ion exchanged materials by using a series of co-dopants. This behavior is based upon the sensitivity of the Cu^+ ion to its surroundings and by the propensity for β''-alumina to expand or contract its c-axis lattice parameter with the size of the co-dopant. However, not all the emission shifts can be explained by lattice parameter changes. The spectroscopy of Cu^+-β''-alumina has yet to be detailed and it is likely that the spectroscopy for most of these systems will be more involved than that of isolated Cu^+ ions in a host structure. In this regard, it is important to recognize that monovalent cations are mobile in the β''-alumina structure and this may lead to effects which are not known to occur in traditional close-packed host materials. Finally, single pass gain coefficients measured for some of the Cu^+-β''-alumina crystals suggest that these materials may exhibit tunable laser action over a wide region of the visible spectrum.

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Table 1: Ion Exchange Conditions

Ion(s)	Media (mol%)	Temp(C)	Time(hr)
Cu^+	75CuCl/25NaCl	460-600	1-4
Cu^+/Ag^+	50CuCl/50AgCl	460	1-4
Cu^+/K^+	50-75CuCl/50-25KCl	460	2
Cu^+/Ba^{2+}	50-90CuCl/50-10BaCl$_2$	460-600	1-2
Cu^+/Cd^{2+}	70CuCl/30CdCl$_2$	460-600	2-3
Cu^+/Ca^{2+}	75CuCl/25CaCl$_2$	460	2-5
Cu^+/La^{3+}	100CuCl*	600	1.5

* - Starting crystal was La^{3+}-β"-Alumina

FIGURE CAPTIONS

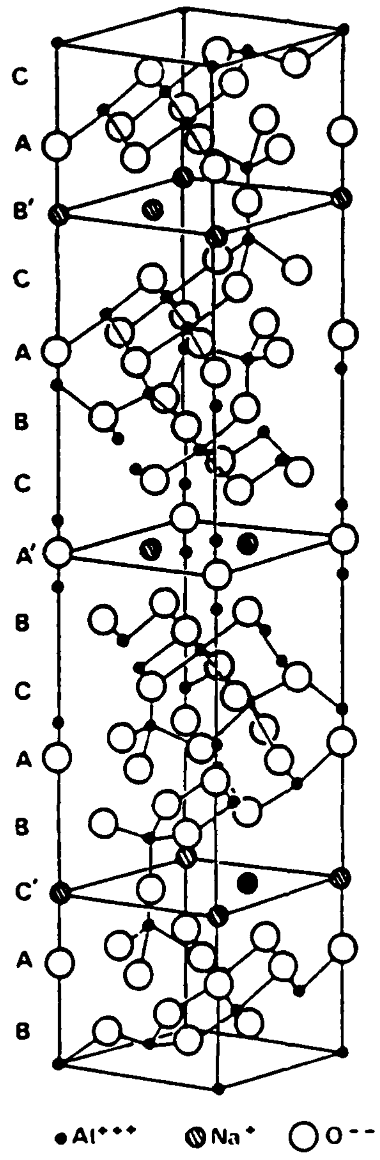
Figure 1 - (a) The unit cell for β''-Alumina. Alternating with closely packed regions called spinel blocks are the more loosely packed "conduction planes."

Figure 2 - Room temperature excitation and emission spectra of Cu^{+}/Na^{+}-β''-alumina.

Figure 3 - Lifetime and intensity of Cu^{+}/Na^{+}-β''-alumina luminescence versus temperature in the region 80-400K. Lifetimes are indicated by □, and intensity by +.

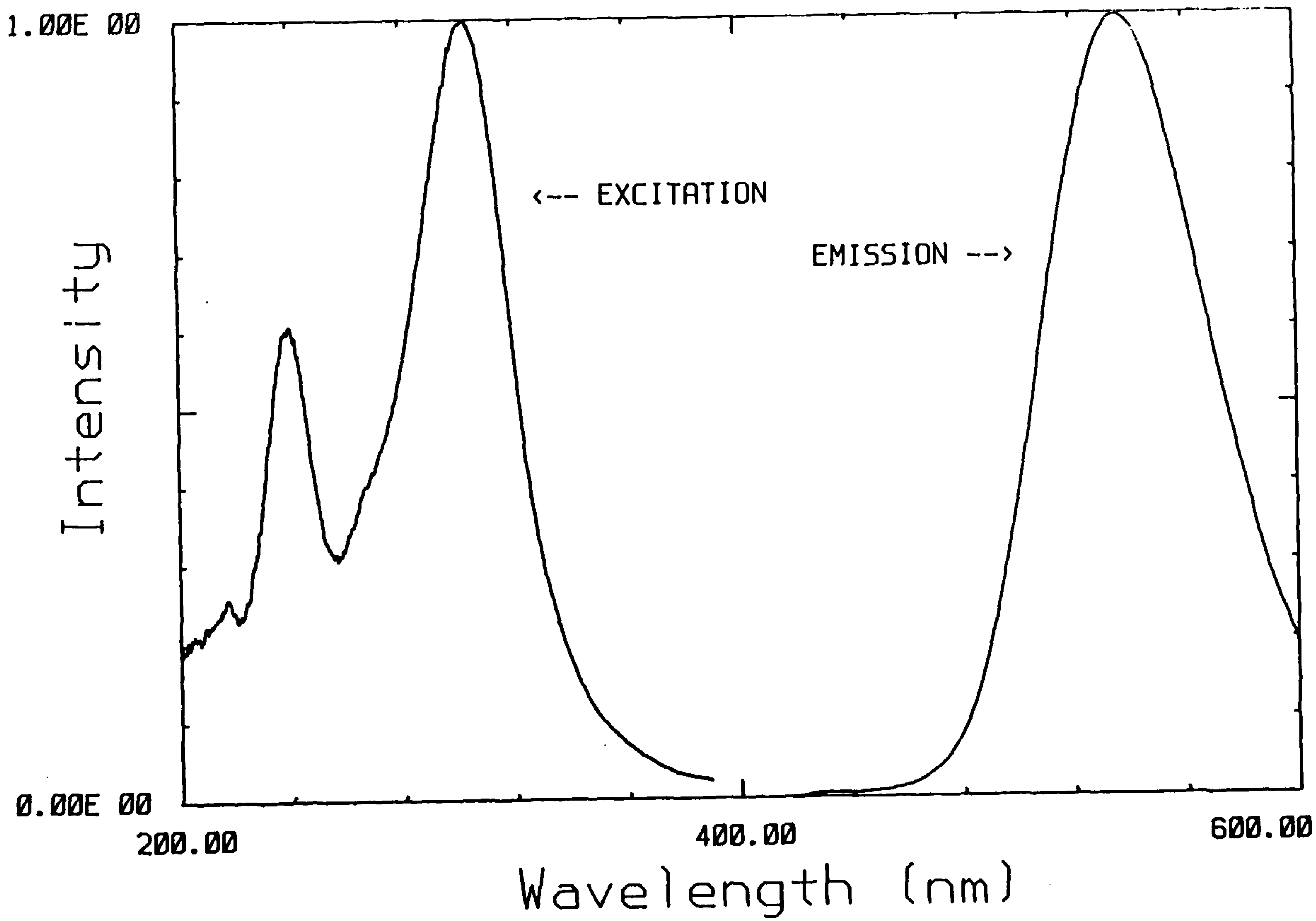
Figure 4 - Normalized emission spectra of various co-doped Cu^{+}-β''-aluminas. The co-dopant ion for each spectrum is as indicated.

Figure 5 - Position of peak emission from Cu^{+}-β''-aluminas as a function of the c-axis lattice parameter of the crystal. The various conduction plane co-dopants are labeled. All spectra recorded at 300K unless otherwise noted.



← Spinel Block

← Conduction Plane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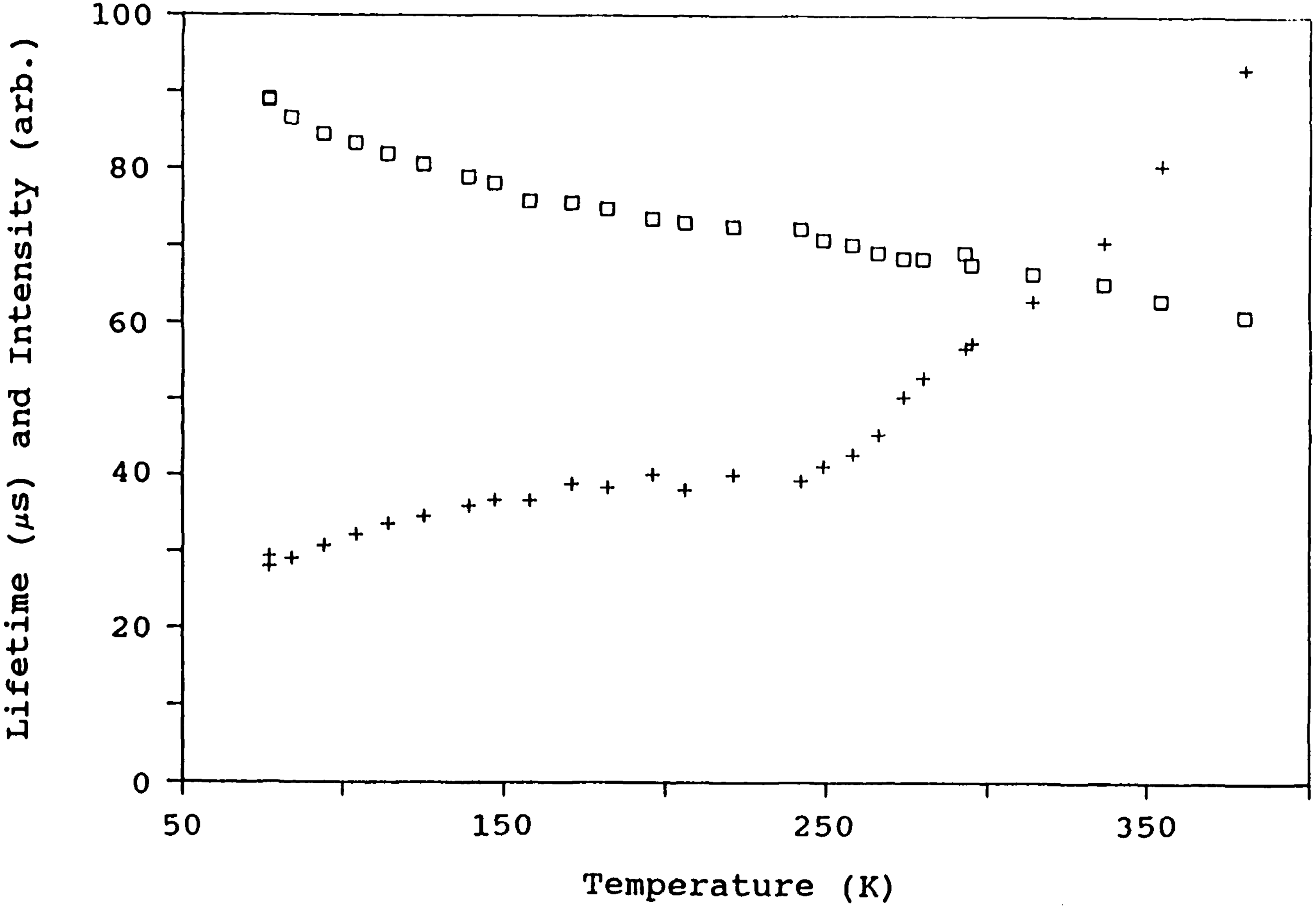
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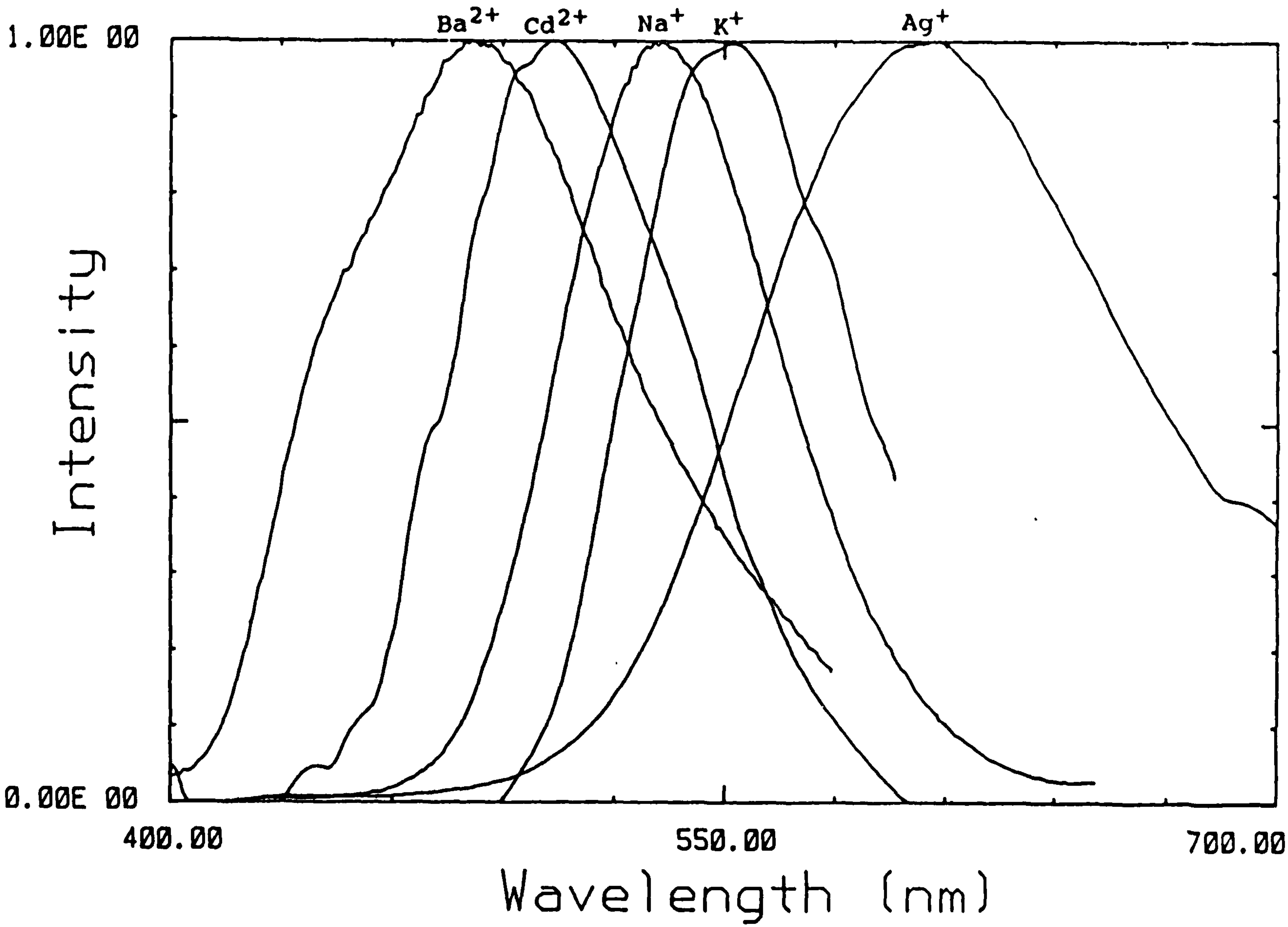
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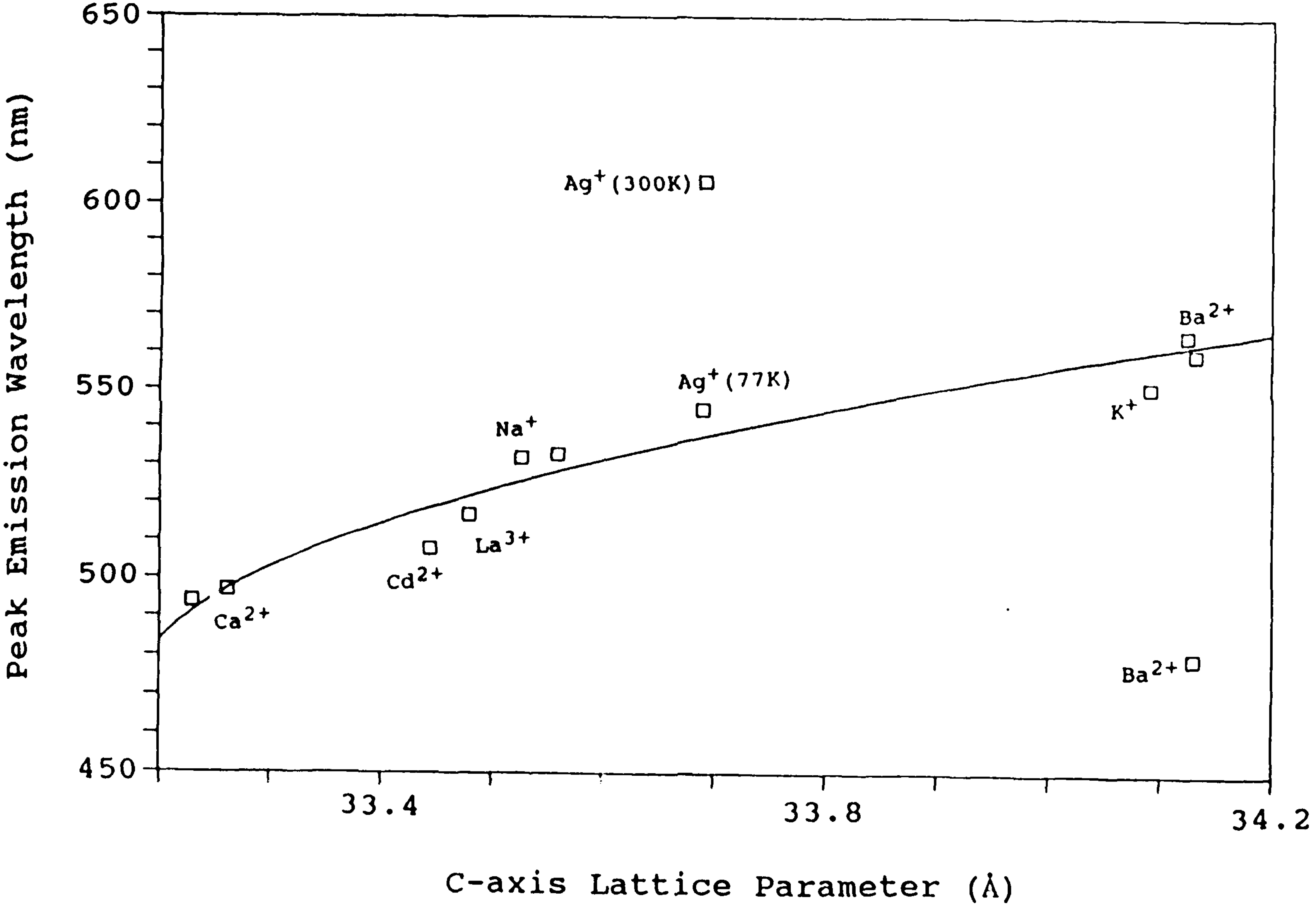
Wavelength (nm)


Peak Emission Wavelength (nm)
650
600
550
500
450
33.4
33.8
34.2
C-axis Lattice Parameter (Å)
Ag+(300K)
Ag+(77K)
Na+
La3+
Cd2+
Ca2+
K+
Ba2+
Ba2+

END

9-87

DTIC