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Optical Spectroscopy of Cu^+/Ag^+ Doped β''-Alumina

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Abstract: Crystalline β''-alumina doped with both Ag^+ and Cu^+ is luminescent at temperatures between 10 and 450 K. The mobility of the ions in the conduction plane at room temperature gives rise to unusual spectroscopic properties. The dominant emission band at 640 nm originates from $[CuAg]^{2+}$ exciplex emission. Absorption of a photon by mobile monomeric ions leads to excited state dimer formation. Emission from $[CuCu]^{2+}$ excimers at 550 nm and from Cu^+ monomers at 400–450 nm are also observed. No emission from Ag^+ monomers or $[AgAg]^{2+}$ excimers is found. The Cu^+/Ag^+ doped crystals exhibit optical memory. Irradiation of a spot on a crystal during cooling of the crystal preferentially forms dimers in the irradiated region which are trapped when the ion mobility decreases. The luminescence spectrum from the written spot is different from that of the unirradiated portions of the crystal. The written spot can be erased by heating the crystal to a temperature at which the ions are again mobile. The emission, absorption, and excitation spectra of this optical memory material as a function of temperature and of the relative concentrations of Ag^+ and Cu^+ are discussed.

Introduction

The luminescence properties of metal-ion-exchanged Na^+-β''-alumina are attracting increasing interest.[2] The parent compound, $Na_{1+x}Mg_xAl_{11-x}O_{17}$ (where x is typically 0.66 ± 0.03), first reported by Yamaguchi,[3] is a Na^+ ion conductor. Recent studies have shown that the sodium ion content of β''-alumina can be exchanged for virtually any +1, +2, or +3 cation in the periodic table.[4-6] The remarkable ion transport properties of β''-alumina are the result of its unusual structure.[7] The framework of the material consists of close-packed blocks of Al, Mg, and O, referred to as "spinel blocks" because of their resemblance to the mineral spinel, separated by more open regions containing the mobile cations. These regions are about 4-Å thick and are referred to as "conduction planes". The spinel block layers are connected by Al–O–Al bonds. The linking oxygens are known as column oxygens. Ion motion occurs in two-dimensional honeycomb-like pathways around the column oxygen. The structure of the conduction plane is shown in Figure 1.

The unusual luminescence properties of β''-alumina doped with both Ag^+ and Cu^+ are a result of the ion motion occurring in the two-dimensional conduction plane. The most stable sites in the conduction plane are the Beevers–Ross (BR) and mid-oxygen (mO) sites in which the ion is in a crystal field of C_{3v} and C_{2h} symmetry, respectively. The C_{3v} site is formed by oxygens in the spinel block above and below the conduction plane. The C_{2h} site is produced by spinel block oxygens along with the column oxygens. The lowest energy transitions in an individual ion are spin-forbidden transitions between the ground-state d^{10} electronic configuration and the excited-state d^9s^1 configuration. The spectroscopy of the Ag^+ and Cu^+ ions is itself unusual because the low oxidation state metals are in an oxide lattice. However, as will be discussed in this paper, the most interesting effects occur because of dimer formation upon excitation when an excited ion attracts another ion to an adjacent site and forms a chemical bond.

Previous studies of the luminescence spectra of Cu^+ doped Na^+-β''-alumina single crystals revealed emission bands due to both Cu^+ monomers and Cu^+–Cu^+ dimers.[8] At low temperature, two monomer emissions (410 and 440 nm) and two dimer emissions (515 and 540 nm) were observed. The relative intensities of the emission bands were dependent on the sequence of irradiation and cooling. Changes in the relative intensities were caused by ion-hopping processes and the photoaggregation of the mobile Cu^+ ions to form dimers. The dynamics of ion motion that produce the green dimer emission band were quantified by a diffusion model based upon the thin-film solution of Fick's second law.[8]

We report here the luminescence properties of Cu^+/Ag^+ doped β''-alumina. Emission, absorption, and excitation spectra of crystals containing both copper and silver ions are reported. These spectra are compared to those from crystals containing copper ions and silver ions (but not both simultaneously). When a spatially defined region of a crystal is irradiated and the crystal is cooled, the irradiated region has luminescence properties different from those of the unirradiated portions. The process is reversible; heating the crystal restores its original properties. This sequence forms the basis for a write/read/erase optical memory. The results are interpreted in terms of photoformation of $[CuCu]^{2+}$ and $[CuAg]^{2+}$ dimers, i.e., a type of excimer or exciplex formation,[9] between the mobile ions in the conduction plane.

Experimental Section

Single crystals of Cu^+ doped β''-alumina were prepared by using ion-exchange techniques.[10] In this approach precursor crystals of Na^+ β''-alumina, nominally $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, were immersed in molten salts (75 mol% CuCl/25 mol% NaCl) at temperatures of 400–600 °C. The Cu^+ ion concentration was shown to be approximately 5×10^{18} ions/cm^3 by chemical analysis and optical absorption techniques, while ESR measurements were unable to detect the presence of any Cu^{2+}.

In the present studies, both Cu^+ and Ag^+ were doped into the β''-alumina conduction plane. The precursor crystals were doped under similar conditions to those mentioned above, and spectroscopic measurements indicated that the Cu^+ concentration was comparable to that obtained previously. However, the Ag^+ was doped to two different levels of concentration. Low level Ag^+ doping was achieved by adding a small amount of AgCl to the molten salt mixture (melt composition: 75 mol% CuCl/24 mol% NaCl/1 mol% AgCl). The exchange occurred at 500 °C for 4 h in flowing nitrogen. The resulting material (termed Cu^+/low Ag^+ doped β''-alumina) replaced approximately 1 mol% of the initial Na^+ ions with Ag^+ ions. A high level of Ag^+ doping was obtained by immersing the precursor single crystals in a molten salt containing 50 mol% CuCl and 50 mol% AgCl at temperatures from 460 to 500 °C and for times ranging from 1 to 4 h. In this material (termed Cu^+/high Ag^+ doped β''-alumina) virtually all the Na^+ was replaced by Ag^+. The amount of Ag^+ exchange was determined gravimetrically in both types of the Cu^+/Ag^+ doped β''-aluminas (The small amount of Cu^+ entering the crystal does not affect the weight change measurement.). The Cu^+/Ag^+ ratio for the two materials is quite different. The ratio is about 1:10 (Cu^+/Ag^+) in the low Ag^+ composition and 1:1000 (Cu^+/Ag^+) in the high Ag^+ material.

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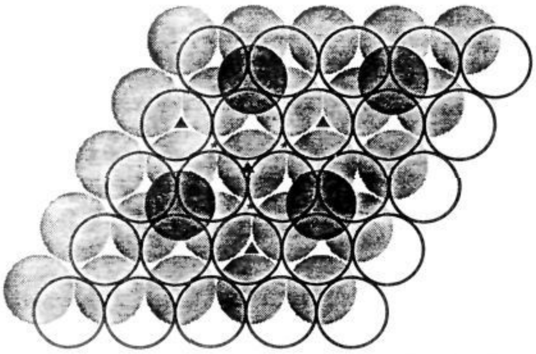

Figure 1. Conduction plane of Na(I)-β''-alumina. The view is parallel to the c-axis, looking down on the conduction plane. Open circles are oxygens above the plane; dark fill indicates column oxygens within the plane; and light fill indicates oxygens below the plane. The small black triangles are BR sites and the small stars are mO sites.

After the ion exchange, the crystal was withdrawn from the molten salt, and the majority of the residual salt on the crystal drained back into the crucible. The crystal was then cooled to room temperature under flowing nitrogen. The remaining external CuCl/AgCl salts were removed from the crystals by using warm ammonium hydroxide solutions, while the CuCl/NaCl salts were removed by using warm aqua regia. The resultant crystals were clear and colorless.

Emission spectra were taken by exciting with 351.1 nm or visible lines between 454.5 and 488.0 nm from an argon ion laser. The exciting light is focussed onto the sample mounted on a copper block which was affixed to the cold tip of an AirProduct Displex closed cycle helium refrigerator. The emitted light was focussed onto the slit of a Spex Model 1702 3/4 m single monochromator equipped with a 1200 groove/mm grating. The detector is a cooled RCA C31034 photomultiplier tube and an EG & G Model 1105 photon counter. The photon counter and monochromator controller are interfaced to a computer. The spectra are digitized and recorded under computer control. All spectra are uncorrected for wavelength response characteristics of the detector.

Optical laser writing is done by irradiating the crystal with a focussed laser beam (351.1 nm), while the crystal is cooled from room temperature to 16 K. The size of the crystal is about 3 × 3 mm, and the diameter of the focussed laser beam is about 100 μ. The emission originating from only the written spot on the crystal can be selectively detected by using a diaphragm.

Excitation spectra were obtained by using a Spex F112A spectrofluorometer system equipped with a 150-W xenon arc lamp. A fused quartz dewar was used to take spectra at 77 K. Absorption spectra were measured on the same instrument or on a Shimadzu UV-260 spectrophotometer.

Luminescence lifetimes of the crystals were measured by using pulsed laser irradiation from a Lambda Physik XeCl excimer laser (nominal pulse duration 20 ns). The luminescence signal was then discriminated by using dielectric line filters and focussed onto a Hamamatsu R980 photomultiplier tube. The system response time was typically 2 μs, much shorter than any of the lifetimes measured. The signal was collected by using either a Data Precision Model 6000 transient digitizer or a Tektronix 2230 digitizing oscilloscope and was stored for analysis. The lifetimes were determined by a least-squares regression fit of the slope of plots of the log of intensity versus time. The data at long times (microseconds) show single exponential behavior. The lifetimes are accurate to about ±1 μs. Lifetimes were measured over a range of temperatures.

Results

The mixed Cu^+/Ag^+ doped crystals are luminescent when irradiated in the visible and UV regions of the spectrum. Spectra were obtained from crystals at low (16 K) and room temperatures. A general summary of the wavelengths of the luminescence bands and a comparison with the luminescence of crystals doped only with copper is given in Table I. The unique feature of the luminescence spectra is the strong dependence on the temperature and the conditions under which the crystal was cooled. The spectroscopic results discussed below are organized in terms of the dopants in the crystals, i.e., those containing Cu^+ and a high Ag^+ concentration, those containing Cu^+ and a low Ag^+ concentration, and the comparison crystals containing Cu^+ with no silver ions and Ag^+ with no copper ions.

1. Cu^+/High Ag^+ Doped β''-Alumina. Samples of Cu^+/high Ag^+ doped β''-alumina (copper/silver ratio of about 1:1000) show a bright orange luminescence centered at 620 nm when excited at 351.1 or 363.8 nm at room temperature. When these samples are cooled to low temperatures in the dark, the emission spectrum is dominated by a band at 570 nm with a long tail to the red. Figure 2a,b shows the emission spectra of a crystal at 298 and 16 K, respectively, when excited at 351.1 nm.

Table I. Assignments of the Emission Bands[a-c]

assignment	Cu^+ doped crystal, nm	Cu^+/low Ag^+, nm	Cu^+/high Ag^+, nm
Cu^+, BR site	410	~420	
Cu^+, mO site	440	450	450 sh
$[CuCu]^{2+}$, BR–BR site	515	~530	
$[CuCu]^{2+}$, mO–mO site	540	550	550
$[CuAg]^{2+}$, mO–mO site		640	640

[a] The uncertainty of the peak positions in Cu^+/Ag^+ doped crystals is ±10 nm. [b] The bands are observed at both 16 K and room temperature. The relative intensities are temperature dependent. See text. [c] Ag^+ doped β''-aluminum does not luminesce.

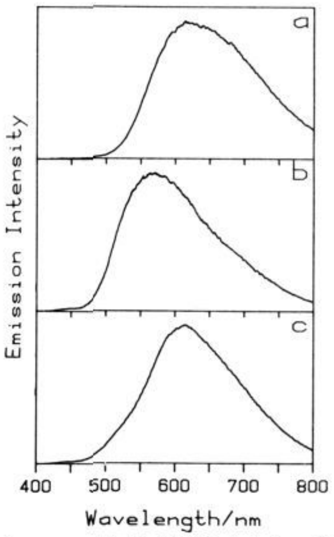

Figure 2. Emission spectra for Cu^+/high Ag^+ doped β''-alumina (a) at 298 K, (b) at 16 K, cooled in the dark, and (c) at 16 K, irradiated with 351.1 nm during cooling. The excitation wavelength is 351.1 nm for all spectra.

In contrast, when the sample is irradiated with 351.1-nm light during cooling, the low temperature emission spectrum from the irradiated spot on the sample excited with 351.1-nm light is very similar to the room-temperature spectrum. It shows a bright orange luminescence centered at 620 nm. Figure 2c shows the emission spectrum from the irradiated spot of the crystal at 16 K when excited with 351.1 nm.

When the crystals are excited with visible wavelengths between 454.5 and 488.0 nm at low temperature (16 K), different spectra are observed. Both ~550- and 640-nm emission peaks are observed which have narrower widths than those emission peaks excited with UV excitation. The 640-nm band has much stronger emission intensity than that of the 550-nm band. Figure 3a shows the emission spectrum of a crystal at 16 K when excited with 476.5 nm.

The luminescence lifetimes of the green and orange emission peaks confirm that they are different in origin. The orange emission band at 640 nm shows an emission lifetime of 90 μs at 77 K, while the green emission band at 550 nm has a lifetime of 61 μs. When the crystals are heated to 250 K (the highest temperature at which the green band shows significant intensity), the lifetime of the orange emission decreases to 76 μs, while that of the green emission increases to 71 μs. The decay of the luminescence in the long time (microsecond) regime of each of these bands is single exponential at all of the temperatures studied.

The absorption spectrum of Cu^+/high Ag^+ doped β''-alumina shows two distinct peaks at 305 and 330 nm. Neither of these peaks are present in the absorption spectra of Ag^+ doped β''-alumina (no copper doping) and Cu^+ doped Na^+-β''-alumina (no silver doping).

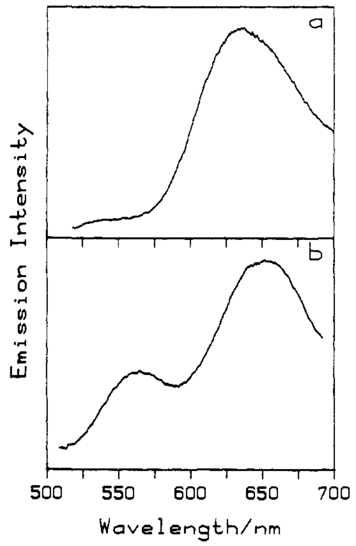

Figure 3. (a) Emission spectrum of Cu$^+$/high Ag$^+$ doped β″-alumina at 16 K, cooled in the dark. The excitation wavelength is 476.5 nm. (b) Emission spectrum of Cu$^+$/low Ag$^+$ doped β″-alumina at 16 K, cooled in the dark. The excitation wavelength is 472.7 nm.

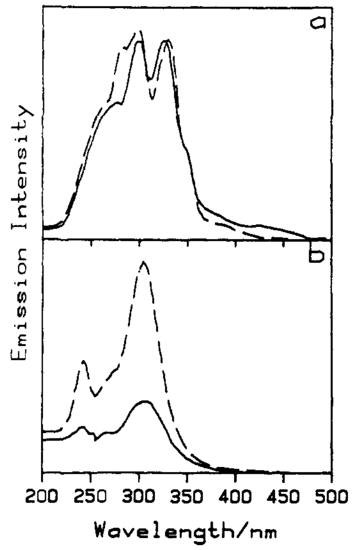

Figure 4. Excitation spectra of the green (at 550 nm, --) and orange (at 620 nm, —) emissions of (a) Cu$^+$/high Ag$^+$ doped β″-alumina and (b) Cu$^+$/low Ag$^+$ doped β″-alumina. All of the spectra are taken at 77 K.

The excitation spectra of Cu$^+$/high Ag$^+$ doped β″-alumina obtained by monitoring the green and orange emissions at 77 K are shown in Figure 4a. The excitation spectra show peaks at 270, 280, 305, 330, 350, 390, and 425 nm. The excitation spectra of the two emissions at 77 K are similar. Part of the similarity probably arises from energy transfer between the two emitting species. The most important difference is the presence of a long tail extending to about 480 nm in the spectrum obtained by monitoring the orange emission.

2. Cu$^+$/Low Ag$^+$ Doped β″-Alumina. Samples of Cu$^+$ doped Na$^+$-β″-alumina with a small portion of Na$^+$ replaced by Ag$^+$ (copper/silver ratio of about 1:10) show a green luminescence centered at 560 nm with a long tail to the red when excited with 351.1 or 363.8 nm at room temperature. When these samples are cooled to low temperatures and excited in the UV, blue emission bands are observed at 420 and 450 nm. In general, the band at 450 nm dominates. In addition, the green emission band is centered at 570 nm, shifted slightly to the red compared to the green band at room temperature. Figure 5a,b shows the emission spectra of a crystal at 298 and 16 K, respectively, when excited with 351.1-nm light.

If the sample is irradiated with 351.1-nm light during cooling, the emission spectrum from the irradiated spot on the sample at low temperature when excited with UV light contains a green emission band which is narrower than that at room temperature. The band at 450 nm is still present in the spectrum. Figure 5c shows the emission spectrum from the irradiated spot of the crystal at 16 K when excited with 351.1 nm.

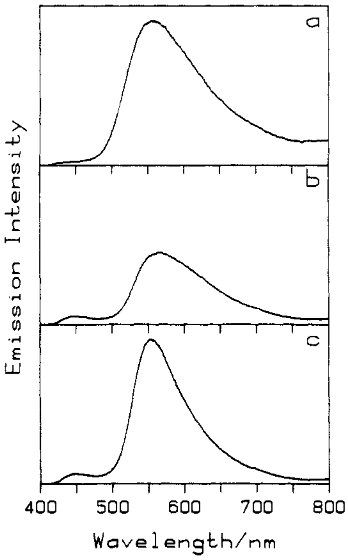

Figure 5. Emission spectra for Cu$^+$/low Ag$^+$ doped β″-alumina (a) at 298 K, (b) at 16 K, cooled in the dark, and (c) at 16 K, irradiated with 351.1 nm during cooling. The excitation wavelength is 351.1 nm for all the spectra.

When the sample is excited with visible wavelengths between 454.5 and 472.7 nm at low temperature, two weak green emission bands at ~530 and 550 nm (although not resolved in Figure 3b) and an orange band at 650 nm are found. The relative intensity of the green band to the orange band is greater in the spectra of the Cu$^+$/low Ag$^+$ crystals than in those of the Cu$^+$/high Ag$^+$ crystals. Figure 3b shows the emission spectrum of a crystal at 16 K when excited with 472.7 nm.

The excitation spectra obtained by monitoring the green and orange emission bands at 77 K are shown in Figure 4b. The excitation spectra show peaks at 240, 270, and 305 nm for both the blue and the orange emission bands.

3. Cu$^+$ Doped Na$^+$-β″-Alumina. The luminescence spectra of crystals of Cu$^+$ doped Na$^+$-β″-alumina (no silver dopants) excited with a variety of ultraviolet wavelengths at room temperature and low temperatures are reported in detail elsewhere.[8,11] The two blue emissions at 410 and 440 nm have been assigned to monomeric Cu$^+$ ions located in the BR and mO sites within the conduction plane. The two green emissions at 515 and 540 nm have been assigned to [CuCu]$^{2+}$ dimers situated in adjacent BR sites and adjacent mO sites, respectively.[8,11]

When crystals of Cu$^+$ doped Na$^+$-β″-alumina are excited with 457.9 or 454.5 nm at low temperature, the emission spectra show a green emission which consists of a distinct band at 515 nm and a shoulder at 530 nm. In contrast to the spectra from the Cu$^+$/Ag$^+$ doped β″-alumina crystals, no orange band appears in the spectra.

4. Ag$^+$-β″-Alumina. There is no measurable luminescence from Ag$^+$-β″-alumina (no copper dopants) at temperatures between 16 K and room temperature when excited at wavelengths between 351 and 514 nm.

Discussion

1. Assignment of the Luminescence Bands. The Orange (620–650 nm) Emission Band. The assignment of the luminescence bands in the mixed Cu$^+$/Ag$^+$ doped crystals is simplified by three observations. First, the luminescence spectra from the mixed Cu$^+$/Ag$^+$ doped crystals contain an orange band which is absent from the spectra of both the Cu$^+$ doped and Ag$^+$ doped crystals. Second, no luminescence is observed from either Ag$^+$

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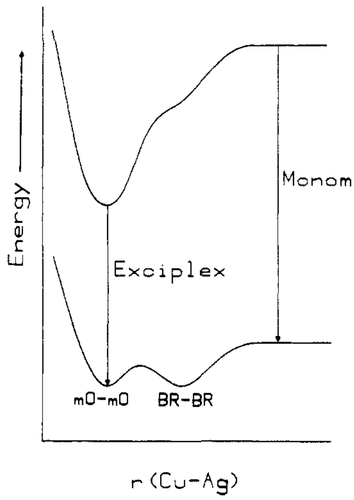

Figure 6. Schematic potential energy surface diagram depicting the interaction of a closed shell Cu$^+$(d^{10}) ion with a Ag$^+$(d^{10}) ion.

doped Na$^+$-β''-alumina or Ag$^+$-β''-alumina (i.e., in the absence of copper). Thus, none of the bands to be assigned in the mixed Cu$^+$/Ag$^+$ doped crystals arise from silver alone. Third, Cu$^+$ doped Na$^+$-β''-alumina (i.e., in the absence of Ag$^+$) has luminescence peaks only at wavelengths shorter than about 550 nm.[8] These green and blue peaks are also observed in the mixed Cu$^+$/Ag$^+$ doped crystals. However, they only involve the copper component in the mixed crystal and are independent of the presence of the silver ion. The new orange luminescence peak which is observed in the mixed Cu$^+$/Ag$^+$ doped crystal, but which is absent in both the Cu$^+$ doped and Ag$^+$ doped crystals, is thus an emission from an excited state which requires the presence of both the silver and copper ions. It is assigned to the HOMO to LUMO, $\sigma_{(4s-5s)} \rightarrow \sigma^*_{(3d-4d)}$, transition of [CuAg]$^{2+}$ dimers in the conduction plane (vide infra).

The existence of a new species in the conduction plane involving both silver and copper is supported by other spectroscopic evidence. The absorption spectra of Ag$^+$ doped, Cu$^+$ doped, and the mixed Cu$^+$/Ag$^+$ doped β''-alumina are consistent with the interpretation based on the formation of mixed dimers. The spectrum of the mixed Cu$^+$/Ag$^+$ doped crystal contains two new peaks at 305 and 330 nm which are not present in the spectra of either Cu$^+$ doped or Ag$^+$ doped β''-alumina.[12] These new absorption bands probably arise from $\sigma_{(3d-4d)} \rightarrow \sigma^*_{(4s-5s)}$ transitions in the [CuAg]$^{2+}$ dimer.

The excitation spectrum of the mixed Cu$^+$/Ag$^+$ doped crystal at room temperature obtained by monitoring the orange emission peak contains peaks at about 305 and 330 nm as shown in Figure 4. These peaks were not observed in the excitation spectra of Cu$^+$ doped Na$^+$-β''-alumina. In addition, this excitation spectrum contains a long tail extending out to about 470 nm. This tail was also not found in the excitation spectra of Cu$^+$ doped Na$^+$-β''-alumina. Again these results are consistent with the interpretation based on the formation of a new species in the mixed Cu$^+$/Ag$^+$ β''-alumina crystals.

Bands Attributed to Cu$^+$ Monomers and Dimers in the Mixed Cu$^+$/Ag$^+$ Doped Crystals. In addition to the orange luminescence band, the Cu$^+$/Ag$^+$ doped crystals exhibit blue and green emission. The blue bands at 420 and 450 nm are assigned to the Cu$^+$ monomer emissions, and the green bands at 530 and 550 nm are assigned to the [CuCu]$^{2+}$ dimer emissions. These assignments are based on the previous studies of Cu$^+$ doped Na$^+$-β''-alumina.[8,11] All of the observed emission peaks are listed and compared to those observed in Cu$^+$ doped Na$^+$-β''-alumina in Table I.

The emission peaks from Cu$^+$ monomers and dimers observed in the mixed Cu$^+$/Ag$^+$ doped crystals are shifted to the red by about 10–15 nm compared to those observed in Cu$^+$ doped Na$^+$-β''-alumina. This red shift is a result of the change in the *c*-axis lattice parameter of β''-alumina caused by replacing Na$^+$ ions in the conduction plane by Ag$^+$ ions.[10]

2. Excimers, Exciplexes, and Trapped Dimers. Ionic motion of cations in the β''-alumina structure gives rise to novel spectroscopic features. In Cu$^+$ doped β''-alumina, Cu$^+$ mobility led to the quenching of monomer emission, the formation of [CuCu]$^{2+}$ dimers, and an increase in dimer emission.[8] The present study is influenced by similar considerations, with the exception being that two types of luminescent species can be formed: [CuCu]$^{2+}$ dimers and [CuAg]$^{2+}$ dimers. Cu$^+$ mobility and the relative concentration of Ag$^+$ determine which type of dimer dominates the emission spectra.

The interaction between Cu$^+$ and Ag$^+$ ions can be understood by using the schematic potential energy surface diagram shown in Figure 6. The state energy is shown as a function of Cu–Ag distance in a two-dimensional conduction plane.

The surface of the ground electronic state has two shallow minima at the two stable sites in the conduction plane (mO–mO sites at r(Cu–Ag) $\cong$ 2.6 Å and BR–BR sites at r(Cu–Ag) $\cong$ 3.2 Å) because of the stability of the ions in the sites themselves and the weak bonding interaction between ions situated in these sites. The interaction of d^{10} closed shell ions has been discussed in detail.[13-15] The bonding arises from the interaction between the d and s valence shells of Cu$^+$ and Ag$^+$ ions. The molecular orbitals from the ten d orbitals are filled with the 20 valence electrons of the dimer. The HOMO is the σ antibonding orbital from the 3d (Cu$^+$) and the 4d (Ag$^+$) orbitals. The LUMO is the σ bonding orbital from the 4s (Cu$^+$) and the 5s (Ag$^+$) orbitals.

The potential surface of the excited electronic state has one deep minimum at $r \cong$ 2.6 Å (mO–mO) and an inflection point at $r \cong$ 3.2 Å (BR–BR) caused by the strong bonding interaction between ions in the excited state. The bonding interaction is much stronger in the excited state than in the ground state because an electron occupies the σ bonding LUMO and an electron has been removed from the σ antibonding HOMO. The most stable exciplex is assumed to occur at the adjacent mO–mO sites in [CuAg]$^{2+}$ dimers because the distance between the ions in these sites is smallest. Calculations of Cu$_2^{2+}$ show that the binding energy is greater when the internuclear distance is 2.58 Å than when it is 3.18 Å.[13]

At room temperature, the ions are mobile in the conduction plane because kT at room temperature is high enough to overcome the two shallow minima. Therefore, there is no trapping in sites. At large separations between the ions (r > 4 Å), monomer absorption occurs. This transition is shown at the far right of the potential surface. As one of the excited monomers (e.g., Cu^{+*}) approaches the other monomer (e.g., Ag$^+$), the bonding between them occurs and an exciplex forms. Emission from the exciplex will occur vertically from the excited-state minimum (at $r_{\text{mO-mO}}$).

At low temperature, the ions are immobile and trapped in two minima. Absorption occurs from these two minima, which leads to two new absorption bands in Cu$^+$/high Ag$^+$ crystals. Emission can occur from the trapped [CuAg]$^{2+}$ dimers.

In the following discussion, the terms "exciplexes" and "excimers" are reserved for the mobile situation and "trapped dimers" for the situation at low temperature when ions are trapped in the stable sites, and absorption bands as well as emission bands originate from electronic transitions of the site-trapped dimers.

3. Effects of Concentration and Temperature on Peak Intensities. The emission spectra of the mixed Cu$^+$/Ag$^+$ doped crystals are dominated by two intense emission bands, one in the green region of the spectrum arising from [CuCu]$^{2+}$ dimers and one in the orange region arising from [CuAg]$^{2+}$ dimers in the conduction plane. The relative intensities of these two bands change with the relative concentrations of the two ions in the crystal, the excitation wavelength, and the temperature. However, they are present in all of the emission spectra, and the positions of these bands are not changed.

The trends in the relative intensities of the emission bands follow the trends in the relative concentrations of the Cu$^+$ and Ag$^+$ ions in the conduction plane. Quantitative correlations between the intensities and the concentrations cannot be made because the

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doping level of the β″-alumina crystals cannot be precisely controlled. In the following discussion, the mixed Cu^+/Ag^+ doped crystals are categorized into two concentration regimes, those containing Cu^+ and a high Ag^+ concentration (i.e., Cu^+/Ag^+ = 1:1000) and those containing Cu^+ and a low Ag^+ concentration (i.e., Cu^+/Ag^+ = 1:10).

Room Temperature Emission Spectra of Cu^+/Low Ag^+ and Cu^+/High Ag^+. The emission spectra of Cu^+/low Ag^+ crystals excited at 351 nm are dominated by the emission band of the $[CuCu]^{2+}$ excimers. These spectra are very similar to those of Cu^+ doped Na^+-β″-alumina. The similarity between the spectra shows that the most intense emission arises from $[CuCu]^{2+}$ excimers in the conduction plane in spite of the fact that the ratio between Cu^+ and Ag^+ is 1:10. The excited-state interaction between the Cu^+ and Ag^+ ions is apparently weaker than that between the Cu^+ ions and/or the quantum yield of the emission of the mixed exciplex is lower than that of the copper excimer.

In contrast, when the relative concentration of the silver ions is increased to about 1000:1 in the Cu^+/high Ag^+ crystals, the emission spectrum excited at 351 nm is dominated by the orange emission band of the $[CuAg]^{2+}$ exciplexes. The majority of the emission at room temperature now originates from $[CuAg]^{2+}$ exciplexes because of the high concentration of Ag^+ ions. A very large excess of Ag^+ ions is required in order to increase the probability of Cu^+–Ag^+ interactions and overcome the stronger Cu^+–Cu^+ interactions.

Low Temperature Emission Spectra of Cu^+/High Ag^+ and Cu^+/Low Ag^+ When the Crystals Are Cooled in the Dark. The emission spectra for all of the copper-containing crystals which were excited in the UV at 16 K (cooled in the dark) are very similar despite the differences in the concentration of Ag^+ ions present in the crystal. That is, the emission spectra for Cu^+/high Ag^+ and Cu^+/low Ag^+ as well as Cu^+ doped β″-alumina are dominated by the green emission band. Therefore, the dominant emitting species at low temperature are $[CuCu]^{2+}$ trapped dimers even for Cu^+/high Ag^+ crystals.

The dominance of the green $[CuCu]^{2+}$ emission band can arise from at least two origins. First, the emission quantum yield of the trapped $[CuCu]^{2+}$ dimers is larger than that of the $[CuAg]^{2+}$ trapped dimers. On the basis of the relative concentration of the ions in the crystals and the emission intensities, the quantum yield of the $[CuCu]^{2+}$ trapped dimers is about 10^1–10^2 times larger than that of the $[CuAg]^{2+}$ dimers. Second, if the Cu^+–Cu^+ ground-state interaction is larger than the Cu^+–Ag^+ ground-state interaction, then as the crystal is slowly cooled in the dark, each Cu^+ ion will preferentially pair with another Cu^+ ion in a neighboring site. The room temperature emission spectra already indicated that the excited state Cu^+–Cu^+ interaction is larger than the excited-state Cu^+–Ag^+ interaction. Thus, the trapped $[CuCu]^{2+}$ dimers will emit even though each Cu^+ ion also has Ag^+ ions as its neighbors.

In order to reveal further details in the spectra, visible excitation was used. Examples are shown in Figure 3. The excitation spectra show that the orange $[CuAg]^{2+}$ peak and the green $[CuCu]^{2+}$ peak should have different relative intensities when visible excitation is used compared to those under UV excitation. When Cu^+/low Ag^+ crystals are excited with visible wavelengths between 454.5 and 472.7 nm, the emission spectra show two distinct bands, an intense orange band and a weaker green band. The presence of the orange emission band establishes that some Cu^+–Ag^+ interaction is present in the Cu^+/low Ag^+ crystal. Under UV excitation its relative intensity is much weaker, and the $[CuAg]^{2+}$ species appear as the long tail to the red in the spectrum. When Cu^+/high Ag^+ crystals are excited with visible wavelengths between 454.5 and 488.0 nm, the emission spectrum also shows the green and orange bands. However, the intensity of the green emission relative to the orange emission in Cu^+/high Ag^+ crystals is much lower than that in Cu^+/low Ag^+ because of the larger Ag^+ ion concentration.

Low Temperature Emission Spectra of Cu^+/High Ag^+ and Cu^+/Low Ag^+ When the Crystals Are Irradiated with UV Light during Cooling. When the Cu^+/high Ag^+ crystals and the Cu^+/low Ag^+ crystals are irradiated with UV light while they are being cooled, the resulting emission spectra at 16 K are the same as those at room temperature. The unirradiated portions of the crystal give the same emission spectra as those obtained from the crystals which were cooled in the dark.

The changes in the spectra of the irradiated portions of the crystals are a result of the bonding which occurs in the excited state. When the crystal is irradiated as it is cooled, the metal ions in the portion being irradiated are held together by the increased bonding in the excited state. As the temperature is lowered and the mobility decreases, the dimers become trapped.

The Cu^+/Ag^+ doped β″-aluminas exhibit different behavior depending upon the Ag^+ content. The spectra of Cu^+/high Ag^+ doped β″-alumina crystals are dominated by $[CuAg]^{2+}$ dimer emissions at room temperature, while that of the Cu^+/low Ag^+ doped β″-alumina crystals are dominated by $[CuCu]^{2+}$ dimer emissions. When both of these crystals are cooled during UV irradiation, the species trapped in the irradiated portions are the same as those which emit at room temperature. Thus, in the Cu^+/high Ag^+ crystals, the $[CuAg]^{2+}$ dimers are the dominant-emitting species from the irradiated spot at 16 K and give an orange emission. Also, in the Cu^+/low Ag^+ crystals, the $[CuCu]^{2+}$ dimers are the dominant-emitting species. Irradiation during cooling increases the concentration of $[CuCu]^{2+}$ dimers and produces a more intense green emission band than that in the unirradiated portions.

It is interesting to note that some $[CuAg]^{2+}$ dimers are trapped in the Cu^+/low Ag^+ crystal in addition to the dominant $[CuCu]^{2+}$ dimers. The emission of the trapped $[CuAg]^{2+}$ dimers can be selectively excited by using visible irradiation. When the irradiated spot is excited at 472.7 nm at 16 K, the orange $[CuAg]^{2+}$ emission is clearly seen.

4. Optical Memory in Crystals of Cu^+/Ag^+ Doped β″-Alumina. The spectral feature which can be produced in a well-defined part of a crystal when that part is illuminated during cooling of the crystal is a form of optical writing which can be incorporated in a write/read/erase sequence. The write step consists of irradiating a spot on the crystal with UV light (351-nm laser light in the above experiments) during cooling. The read step is the detection of the new emission band which is obtained from that spot compared to those from a spot which was not irradiated. The above sequence is reversible because heating of the written spot restores its spectral properties to those of the unwritten spots.

The most dramatic optical memory effects are observed in the Cu^+/high Ag^+ crystals. At room temperature they luminesce bright orange as the luminescence is dominated by the orange $[CuAg]^{2+}$ exciplex emission. When the crystal is cooled in the dark, the resulting low-temperature luminescence is dominated by $[CuCu]^{2+}$ trapped dimer emission. When a spot is written on the crystal by irradiating it at 351 nm during the cooling, the spectrum obtained from the written spot is dominated by the orange $[CuAg]^{2+}$ dimer emission. The spectrum obtained from the unirradiated portions of the crystal is the same as that obtained from the crystal cooled in the dark.

The Cu^+/low Ag^+ crystals also exhibit optical memory. In this case, the silver concentration is low, and the spectral changes are dominated by the copper dimer emission. The intensity of the copper dimer emission from the written spot is two to three times as intense as that from the regions of the crystal which were cooled in the dark.

The experiments discussed above demonstrate that optical reading and writing can be carried out on silver and copper ion doped β″-alumina crystals. The temperature requirement is not stringent; the above effects occur at liquid nitrogen temperature. However, the requirement of temperature change to effect the writing step may preclude the use of this system in practical optical memory applications.

Conclusions

The high ionic mobility for cations in β″-alumina gives rise to novel spectroscopic features in Cu^+/Ag^+ doped single crystals. Absorption of a photon by a mobile monomeric ion at room temperature leads to exciplex formation and the green emission from the $[CuCu]^{2+}$ excimer and the orange emission from the $[CuAg]^{2+}$ exciplex. No emission from a $[AgAg]^{2+}$ excimer is found. Cooling of a crystal during irradiation of a spot causes trapping of the dimers in that spot. The luminescence spectrum and intensity from the trapped dimers in the written spot are different from those of the unirradiated portions of the crystal. These changes are an example of optical memory. The emission, absorption, and excitation spectra of the crystals are dependent on the temperature and the Ag^+ ion concentration.

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Registry No. Ag, 14701-21-4; Cu, 17493-86-6; alumina, 1344-28-1.

An Integral Equation Theory Study of the Solvent-Induced Reaction Barrier in the Nucleophilic Addition of Hydroxide to Formaldehyde

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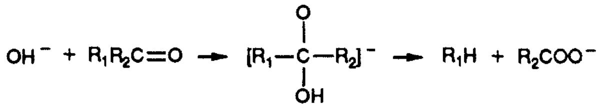
Abstract: The solvent-induced reaction barrier in water for the nucleophilic addition of hydroxide anion to formaldehyde is studied by integral equation theory and compared with Monte Carlo [Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517] and molecular dynamics results. The free energy profile correlates well with the charge transfer during the reaction. The position of the transition state is shifted from $R_{C-O2} = 2.39$ Å in the gas phase to 2.0 Å in water, in agreement with the Monte Carlo simulation. The activation free energy of 21 kcal/mol is in approximate agreement with experimental data on esters and amides (15-19 kcal/mol for alkaline hydrolysis of esters and 22-24 kcal/mol for amides) but is significantly larger than an experimental estimate (9 kcal/mol) for formaldehyde from a rate constant measurement at a single temperature. Since the Monte Carlo simulation also gave values of 24-28 kcal/mol, the difference is surprising and suggests that a more detailed experimental study of the reaction rate as a function of temperature would be of interest. The tetrahedral complex is 13 kcal/mol lower in free energy than the transition state, in agreement with 10-14 kcal/mol from the simulation. Detailed analyses of the enthalpic and entropic terms are made and the potential of mean force is decomposed into contributions from the individual sites. The reaction profile is dominated by an enthalpy barrier of 26-28 kcal/mol for addition and 12 kcal/mol for dissociation. The success of the present thermodynamic calculation demonstrates the utility of the computationally less demanding analytic integral equation theory for exploration of alternative reaction mechanisms. However, the fact that radial distribution functions show only qualitative agreement with the simulation results suggests that there may be a cancellation of errors and that care must be used in interpreting the results.

1. Introduction

Organic reactions involving the carbonyl group, -CO-, are widespread in chemistry and biology. Amide or ester hydrolysis and synthesis, for example, play essential roles in the formation and destruction of the peptide unit, -NH-CO-, that links amino acids together to form proteins. The carbonyl carbon is the site of nucleophilic attack and the hydrolysis may be catalyzed by acid or base.[1] A case of biological interest is provided by the family of serine proteases.[2] For the forward reaction, in which the peptide substrate is hydrolyzed, it is generally accepted that a serine side-chain hydroxyl attacks the carbonyl carbon to form an acyl intermediate.[2] In the deacylation stage, a hydroxide anion or otherwise activated species derived from water is the nucleophile that displaces the acyl polypeptide by attacking the same carbonyl carbon. Schematically the deacylation can be represented as



$$\mathrm{OH^- + R_1R_2C{=}O \longrightarrow [R_1{-}\overset{\displaystyle O}{\underset{\displaystyle OH}{C}}{-}R_2]^- \longrightarrow R_1H + R_2COO^-} \qquad (1)$$

where R_1- is the enzyme, and R_2CO- is the leaving acyl group. A pair of peptide backbone NHs contribute to the catalysis by coordinating the carbonyl oxygen in the same proteases. An imidazole side chain is involved in activating the water.[3]

We report here an extended reference interaction site model (RISM) integral equation study[4] of the first step in scheme 1 for a simplified model reaction where both R groups are hydrogens; i.e., the attack of OH^- on the carbonyl of formaldehyde. We study this system because of its role as a well-studied prototype of nucleophilic addition to the carbonyl group.[5] Also, there exist a large number of gas-phase theoretical studies,[6-9] as well as the Monte Carlo (MC) solvation study of Madura and Jorgensen.[10] This work provides an opportunity to compare in detail the performance of the integral equation theory with an MC simulation of a reaction. Of particular interest is the result that while in the gas phase the approach of OH^- to H_2CO is dominated by an attractive ion-dipole interaction; the variation in solvation free energy along the reaction coordinate gives rise to a barrier. In nature, formaldehyde interacts with water to form a diol;[11] in the present model study, this reaction is not considered.

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