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EPR Investigation of UV-Irradiated Single Crystals of Chromate-Doped Methylammonium and Potassium Aluminum Alums

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Electron paramagnetic resonance (EPR) has been used to identify and analyze a CrO_4^{3-} species produced by UV irradiation in single crystals of chromate-doped methylammonium aluminum alum and in potassium aluminum alum lightly codoped with the methylammonium ion. The photoreduction is a simple reduction of the type $CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$, where the odd electron is a photoelectron liberated by the methylammonium ion.

1. Introduction

It is known that by itself the chromate ion, CrO_4^{2-}, is insensitive to UV light (*1*). This insensitivity has been explained in terms of a "hot" ground state; namely, the absorbed photon energy is transformed into the vibrational energy of the ground state. However, in the presence of a reducing agent, photoreduction of the chromate ion is possible. A brief review on the photoreduction of the chromate ion was given by Adamson *et al.* (*1*). The materials previously investigated were in liquid solutions or glassy matrices (*1*). The mechanism and product of the UV photochemical reaction of the chromate ion in the solid state could be different from those in the liquid state. We have investigated the UV photochemical reaction of the chromate ion doped into single crystals of methylammonium and potassium aluminum alums. The method of investigation is electron paramagnetic resonance (EPR). The Cr^{6+} ($3d^0$) ion of CrO_4^{2-} is diamagnetic and hence EPR silent. However, if reduced to either Cr^{5+} ($3d^1$) or Cr^{3+} ($3d^3$), it is detectable by EPR.

We have found, via EPR, a Cr(V) species (which we will call simply the species) in chromate-doped single crystals of methylammonium aluminum alum, $CH_3NH_3Al(SO_4)_2 \cdot 12\ H_2O$ (which we abbreviate as MASD), irradiated with UV light at room temperature. Neither Cr(V) nor Cr(III) species can be detected by EPR in single crystals of chromate-doped potassium aluminum alum, $KAl(SO_4)_2 \cdot 12\ H_2O$ (which we will call simply potassium alum) irradiated with UV. However, a Cr(V) species can be detected in single crystals of potassium alum lightly codoped with the methylammonium ion, $CH_3NH_3^+$ (nominally 1% in solution). The EPR spectrum of this species in potassium alum is similar to the species in MASD. Furthermore, the EPR spectrum of this species in potassium alum is identical to that exhibited by the CrO_4^{3-} species produced by γ-irradiation in chromate-doped potassium alum. The UV-photolyzed Cr(V) species can thus be identified as a CrO_4^{3-} ion, and the UV photochemical reaction as a simple reduction of the type $CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$. It can be inferred that the photoelectron is liberated by the methylammonium ion.

The paramagnetic CrO_4^{3-} ion is conventionally produced via either X- or γ-irradiation. Yu and co-workers (*2*, *3*) recently re-

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ported a thermal method of production. They have investigated via EPR the production of a CrO_4^{3-} species in single crystals of $(NH_4)_3H(SeO_4)_2 : CrO_4^{2-}$ (*2*) and in single crystals of $(NH_4)_2SnCl_6$ and K_2SnCl_6 doped with NH_4^+ (*3*), via thermal treatment at temperatures well below the decomposition temperature of the host compound. The thermal electron acquired by CrO_4^{2-} to form CrO_4^{3-} is released by the ammonium ion (*2, 3*). The UV production reported in this paper represents a new method of producing the CrO_4^{3-} ion.

2. Experimental

Pure MASD crystals were crystallized at 20°C from aqueous solutions made up of appropriate quantities of $CH_3NH_2 \cdot HCl$, H_2SO_4, and $Al_2(SO_4)_3 \cdot 18H_2O$. $MASD : CrO_4^{2-}$ crystals were grown by dissolving MASD crystals and Li_2CrO_4 in distilled water. The concentration of CrO_4^{2-} in MASD crystals was apparently very low, because the characteristic color of the chromate ion was light at best. MASD normally crystallizes as irregularly shaped crystals, showing mainly {111} and {021} crystal faces (*4*). We have found that the chromate ion is a very efficient habit modifier for the growth of octahedral crystals; octahedral crystals showing {111} and {001} crystal faces can be obtained for MASD. The availability of {001}-type crystal faces greatly facilitates the analysis of the single-crystal EPR spectrum.

If the chromate ion was doped during the initial preparation and growth of MASD (sulfuric acid was present in the growth solution), then the $MASD : CrO_4^{2-}$ crystals obtained frequently exhibited a Cr^{3+} EPR spectrum which is identical to that of the Cr^{3+} ion intentionally doped into MASD crystals (*4*). This indicates a $CrO_4^{2-} \rightarrow Cr^{3+}$ reaction in solution. The EPR spectrum intensity of this unintentional Cr^{3+} ion is much weaker in recrystallized $MASD : CrO_4^{2-}$ crystals, especially for crystals obtained within a few days after the preparation of the growth solution. We usually took an EPR measurement prior to UV irradiation, to make sure that the spectrum intensity of Cr^{3+} is very weak. However, this phenomenon does not adversely affect the investigation of the UV photochemical reaction ($CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$) reported in this paper, since photoreduction of the type $CrO_4^{2-} \rightarrow Cr^{3+}$ was not observed.

Crystals of potassium alum doped with CrO_4^{2-} were grown at 20°C from aqueous solutions. Crystals of deuterated potassium alum doped with the chromate ion, $KAl(SO_4)_2 \cdot 12\ D_2O : CrO_4^{2-}$, were grown at 20°C by dissolving anhydrous potassium alum and potassium chromate into 99.75% pure D_2O. The unintentional doping of Cr^{3+} is not as significant as the case of MASD.

We used a Bruker 200 W UV irradiation system. UV irradiation was carried out at room temperature by placing the crystal in front of the UV lamp for 20–70 hr, with or without a bandpass filter (220–420 nm). The results are identical, but the yield of the photolyzed Cr(V) species is greater for unfiltered UV irradiation. Furthermore, the observed Cr(VI) → Cr(V) reaction cannot be detected in $MASD : CrO_4^{2-}$ crystals thermally treated at 40°C for 3 days (for unfiltered UV irradiation, the temperature of the crystal increased at most by a few degrees). This indicates that the observed reduction of the chromate ion is definitely photochemical in origin. γ-irradiation was carried out at ambient temperature, using a Co^{60} source, for a total dosage of approximately 2–5 MRad. An X-band (microwave cavity frequency about 9.5 GHz) Bruker ER 200 D spectrometer, equipped with goniometers and low-temperature accessories, was used to make EPR measurements.

3. Results and Discussion

A. EPR Spectrum

A spin $S = \frac{1}{2}$ paramagnetic species which can be identified as a Cr(V) species can be observed by EPR in UV-irradiated $MASD : CrO_4^{2-}$ crystals. This EPR spectrum

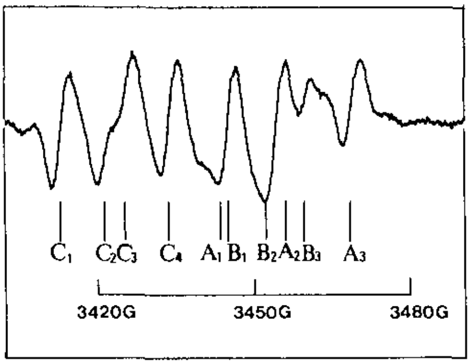

FIG. 1. A 160 K, [100]-oriented EPR spectrum of the UV-photolyzed Cr(V) species in a MASD : CrO_4^{2-} crystal. There are three degenerate inequivalent sites at this orientation, and the corresponding EPR lines are designated as the A, B, and C lines. The inequivalence of the two proton splittings (see the four lines marked C_1–C_4) is most evident at orientations perpendicular to the quasi-symmetry axis of this Cr(V) species

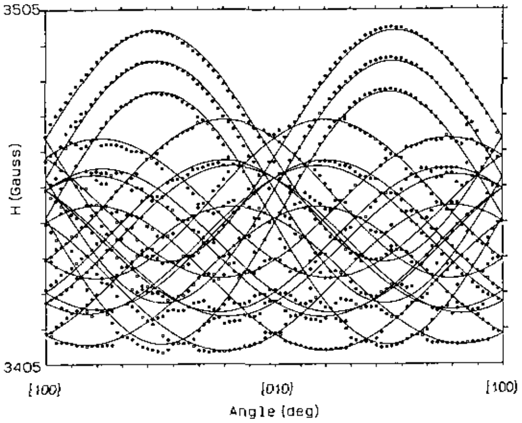

FIG. 2. The observed and fitted (001) rotation patterns at 160 K of the UV-photolyzed Cr(V) species in MASD : CrO_4^{2-} crystals. This pattern shows six degenerate inequivalent sites. The experimental evidence of the inequivalence of the two proton splittings is very conclusive.

can be observed at room temperature, but the spectrum resolution is improved at low temperatures. Figure 1 shows a 160-K, [100]-oriented EPR spectrum of the species in a MASD : CrO_4^{2-} crystal irradiated with UV for 50 hr. The resolution of the EPR spectrum at 160 K is still incomplete (down to about 100 K), such that it is difficult to interpret the observed EPR spectrum at any orientation. This can be accomplished only through an analysis of the (001), (111), and (110) rotation patterns. Figure 2 shows the observed and fitted (001) rotation pattern and Figure 3 the (111) rotation pattern. At 160 K, the observed rotation pattern can be analyzed by assuming that the odd electron of the species interacts with two nearby protons (of the hydration waters). At 160 K, these two protons are magnetically inequivalent in MASD. The g-factor can be analyzed by the effective g-factor (5)

$$R = [l^2T_{xx} + m^2T_{yy} + n^2T_{zz} + 2lmT_{xy} + 2mnT_{yz} + 2nlT_{zx}]^{1/2}, \quad (1)$$

where the 3 × 3 T_{ij} matrix is the square of the g-matrix, which is assumed to be symmetric, and l, m, n are the directional cosines of the magnetic field with respect to the reference axes which were chosen as parallel to the three cubic axes of the host lattice. Because the observed proton hyperfine splitting is much smaller than the Zeeman splitting, the former can be regarded as a perturbation to the latter; the effective hyperfine splittings can also be analyzed using an equation similar in form to Eq. (1). The evaluated principal values and principal

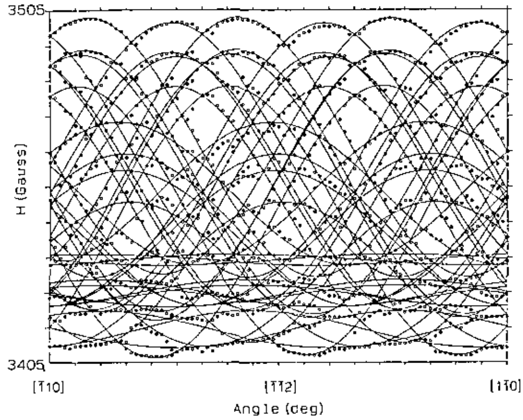

FIG. 3. The observed and fitted (111) rotation patterns at 160 K of the photolyzed Cr(V) species in MASD : CrO_4^{2-} crystals. This pattern shows 12 inequivalent sites.

TABLE I

The Evaluated Principal Values and Principal Axes for the g-Factor and the Two (H_1 and H_2) Proton Hyperfine Splittings (in Gauss) at 160 K, for the CrO_4^{3-} Species Produced via Either UV- or γ-Irradiation in MASD and Potassium Alum

Host lattice	g-factor	Hyperfine splitting	Irradiation
$CH_3NH_3Al(SO_4)_2 \cdot 12\ H_2O$		H_1	UV
	1.9388: [0.6986, 0.6704, 0.2501]	12.2: [0.8249, 0.4691, −0.3153]	
	1.9831: [0.0205, −0.3681, 0.9296]	8.0: [−0.2521, 0.8047, 0.5375]	
	1.9811: [−0.7152, 0.6442, 0.2709]	8.8: [0.5059, −0.3639, 0.7821]	
		H_2	
		14.3: [0.6676, 0.0066, −0.7445]	
		10.7: [0.4435, 0.7997, 0.4047]	
		5.6: [0.5981, −0.6003, 0.5310]	
$KAl(SO_4)_2 \cdot 12\ H_2O$		H_1 and H_2	UV and γ
	1.9400: [0.6924, 0.6749, 0.2553]	12.9: [0.7661, −0.3389, 0.5461]	
	1.9845: [0.2343, −0.5449, 0.8051]	8.9: [0.5858, 0.0185, −0.8103]	
	1.9816: [−0.6824, 0.4976, 0.5354]	7.6: [0.2645, 0.9406, 0.2127]	
$KAl(SO_4)_2 \cdot 12\ H_2O$	1.9406: [0.6683, 0.7036, 0.2416]		γ
	1.9838: [0.3556, −0.0018, 0.9341]		
	1.9816: [−0.6528, 0.7104, 0.2630]		

Note. Only one set of the principal axes is listed; the other 11 sets can be obtained by similarity transformations.

axes for the g-matrix and the two proton hyperfine matrices are listed in Table I.

The diagonal elements of the T_{ij} matrix for the g-factor (and proton hyperfine splittings) and the absolute values of the off-diagonal elements were evaluated from the observed (001) rotation pattern, and the relative signs of the off-diagonal elements were determined from the observed (111) or (110) rotation pattern.

Crystals of MASD commonly crystallize in a cubic $Pa3$ (T_h^6) structure (*6*). The proper rotation group of this structure is the cubic T group, so that there are twelve potentially magnetically inequivalent sites associated with each paramagnetic species (*7*, *8*). The species shows rhombic symmetry. Although the magnetic symmetry is almost axial (see Table I), the direction of this quasi-symmetry axis deviates from a [111] direction. Consequently, there are 12 distinguishable inequivalent sites in a (111) or a (110) plane, and 6 degenerate inequivalent sites in a (001) plane.

The observed rotation patterns at room temperature also indicate hyperfine splittings due to two protons. Because the resolution is poor, we are uncertain whether these two protons are magnetically inequivalent or not. However, there is no definite evidence of inequivalence. Because this is not directly related to the purpose of this present paper, we refrain from any further discussion on this topic.

Crystals of potassium alum doped singly with CrO_4^{2-} and UV-irradiated did not exhibit any Cr(V) or Cr(III) EPR spectrum. However, when lightly codoped (about 1 mole% in solution) with MASD, a UV-photolyzed (for 50 hr of irradiation) Cr(V) species can be detected. The EPR spectrum exhibited by this species is almost identical to that of the species produced by UV-irradiation in MASD. Furthermore, this EPR spectrum is identical to that exhibited by the CrO_4^{3-} species produced by γ-irradiation in crystals of chromate-doped potassium alum. Chowdari and Ravi Sekhar (*9*) reported the EPR of the CrO_4^{3-} ion produced by γ-irradiation in crystals of chromate-

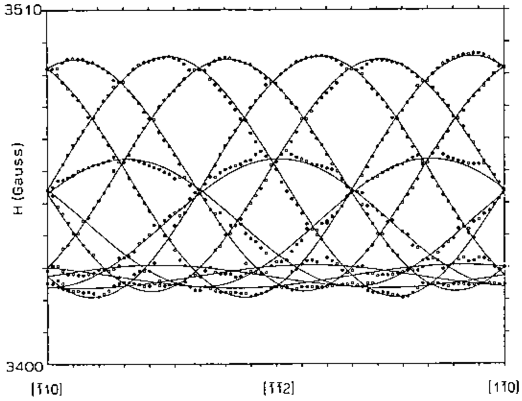

FIG. 4. The observed and fitted (111) rotation patterns at 160 K of the CrO_4^{3-} species produced via γ-irradiation in a $KAl(SO_4)_2 \cdot 12\,D_2O \cdot CrO_4^{2-}$ crystal. The deuteron splittings are not resolved.

doped potassium alum, but their analysis of the EPR spectrum was incorrect. A correct analysis of this EPR spectrum was given by Chou and Yu (*10*), although they did not analyze the proton hyperfine splittings. We have found that the yield of the species for 50 hr of UV-irradiation is comparable to that for 2 MRad of γ-irradiation.

The EPR spectrum of the species produced in crystals of potassium alum is also complicated, due to the presence of a large number of inequivalent sites (12) and the proton hyperfine structure. The EPR spectrum of the species in $KAl(SO_4)_2 \cdot 12D_2O$ crystals is simpler, because deuteron hyperfine splittings are not resolved. Figure 4 shows the observed and fitted (111) rotation patterns at 160 K of the species produced by γ-irradiation in $KAl(SO_4)_2 \cdot 12D_2O : CrO_4^{2-}$ crystals. The evaluated principal values and principal axes for the g-factor are listed in Table I. The principal values and axes for the g- and the proton hyperfine matrices (see Table I) of the species produced by either γ- or UV-irradiation in $KAl(SO_4)_2 \cdot 12H_2O$ were determined from the observed rotation patterns at 160 K in a (001) plane (not shown, but quite similar to Fig. 2) and a (110) plane (see Fig. 5). In crystals of normal potassium alum, the odd electron of the species also interacts with two nearby protons of the hydration waters, but these two protons can be regarded as magnetically equivalent at room temperature and at 160 K.

B. Nature of the Photolyzed Cr(V) Species

The EPR of Cr(V) species ($3d^1$; $S = \frac{1}{2}$), in the forms of CrO_4^{3-}, CrO_3^-, and Cr^{5+} ions coordinated to oxygen or other type of ligands, has been investigated in many different crystal lattices. Cr(V) species can be classified into two types: Those that can be detected by EPR at room temperature and those that can be detected by EPR only at very low temperatures. In the former case, the orbital ground state is observed to be a $3d_{x^2-y^2}$ state. If the magnetic symmetry is axial or quasi-axial, then $g_\parallel < g_\perp$ for such an orbital ground state. The CrO_4^{3-} ion produced via either γ- or UV-irradiation in MASD and potassium alum belongs to such a type. The EPR of CrO_4^{3-} produced in KH_2PO_4-type ferroelectrics and antiferroelectrics has been reviewed by Dalal (*11*). The orbital ground state of CrO_4^{3-} in KH_2PO_4-type crystals is the $x^2 - y^2$ state. Greenblatt (*12*) reviewed the EPR of

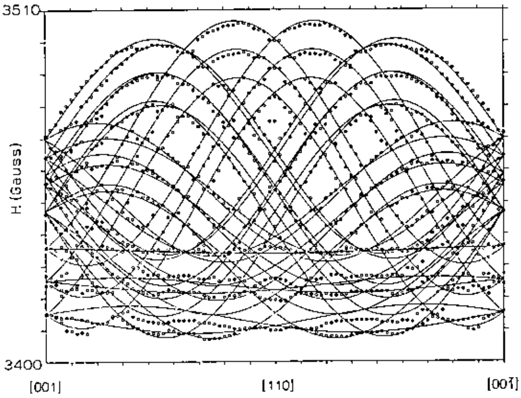

FIG. 5. The observed and fitted (110) rotation patterns at 160 K of the Cr(V) species produced via either γ- or UV-irradiation in $KAl(SO_4)_2 \cdot 12\,H_2O \cdot CrO_4^{2-}$ crystals.

CrO_4^{3-} ions produced in some phosphate-type compounds; the ground state is other than the $x^2 - y^2$ state and can be detected by EPR only at very low temperatures.

The sulfate tetrahedron in crystals of either MASD or potassium alum possesses trigonal symmetry (*6*), with a [111] axis as the threefold axis. The observed symmetry of the CrO_4^{3-} ion produced either via γ- or UV-irradiation in MASD or potassium alum is almost axial, but the quasi-axis deviates from the [111] axis. The angle of deviation is 20.8° in MASD at 160 K and 20.5° in potassium alum at 160 K. This deviation can be explained by assuming that when a CrO_4^{2-} tetrahedron replaces a SO_4^{2-} tetrahedron, it becomes distorted. The oxygens of the sulfate tetrahedron are hydrogen-bonded to hydration waters in alums; therefore the two protons observed to be coupled to the CrO_4^{3-} ion belong to these hydration waters.

C. Origin of the Photoelectron

It is known that radicals such as SO_4^- and/or SO_3^- can be produced in sulfate crystals via either γ- or x-irradiation (*13*). Free electrons may be liberated in the radiolysis of the sulfate group and can be absorbed by CrO_4^{2-} to form CrO_4^{3-}. The SO_3^- radical produced by γ-irradiation has been detected by EPR in crystals of potassium alum (*14*). However, crystals of potassium alum irradiated with UV did not exhibit any EPR-detectable radical species such as SO_4^-, SO_3^-, SO_2^-, or O_3^-. Therefore, it is unlikely that the odd electron of the species originates from the sulfate group.

It is also known that OH radical can be produced via the radiolysis of hydration waters (*15, 16*); it can be produced via electron, X-ray, γ-ray, or even *UV* irradiation. Free electrons may be liberated in the radiolysis of the hydration waters. But since the $CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$ reduction cannot be detected by EPR in crystals of chromate-doped potassium alum for 50 hr of UV irradiation, this mechanism cannot be responsible for the production of the species.

The most significant experimental evidence that we have gathered is the fact that the species can be produced in crystals of potash alum lightly (1% in solution) doped with the methylammonium ion, $CH_3NH_3^+$. This experimental result indicates that the odd electron originates from the $CH_3NH_3^+$ ion. The actual concentration of the $CH_3NH_3^+$ ion has not been determined, but it should not exceed the nominal value too much. Hence, the odd electron acquired by the species in crystals of potash alum lightly doped with $CH_3NH_3^+$ is in the form of a free electron (photoelectron). These free electrons can apparently travel over a large distance (on a microscopic scale) before it is absorbed by the chromate ion. It can be concluded that photoelectrons are liberated by the $CH_3NH_3^+$ ion in potassium alum when it is irradiated with UV light.

A stable free radical, in the form of $NH_2CH_3^+$, has been detected by EPR in γ-irradiated MASD crystals (*17*), but cannot be detected by EPR in UV-irradiated (for 50 hr) MASD crystals. We have found that UV light very efficiently bleaches the $NH_2CH_3^+$ radical produced by γ-irradiation in MASD crystals. UV irradiation for 1 hr reduced the population of the $NH_2CH_3^+$ radical to 45% of its original value. This may explain the absence of any EPR-detectable $NH_2CH_3^+$ radical in UV-irradiated (at room temperature) MASD crystals. The $CH_3NH_3^+$ ion can be formed in aqueous solutions by the reaction of CH_3NH_2 and HCl. This third hydrogen of the ammonium group of $CH_3NH_3^+$ can be regarded as an "acid" hydrogen, which should be more unstable and chemically reactive than the other hydrogens of $CH_3NH_3^+$. We postulate that the free electron is liberated when this N–H bond is broken by the UV photon, but the $NH_2CH_3^+$ radical produced is very quickly bleached by UV light. The final product of the UV photodissociation of the $CH_3NH_3^+$ ion in MASD is diamagnetic and cannot be identified by EPR.

4. Conclusions

We have found via EPR that, although the CrO_4^{2-} ion is by itself UV-photo insensitive, photoreduction of the type $CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$ can be accomplished with the assistance of the $CH_3NH_3^+$ ion. $CH_3NH_3^+$ is apparently a strong source of UV photoelectrons. $CH_3NH_3^+$ has been found to be a powerful reducing agent for the thermal reduction of the doped chromate ion in solids (*3*). Interestingly, when $CH_3NH_3^+$ was used as the reducing agent (its concentration was kept at low levels), the only kind of thermal reduction for the chromate ion detected by EPR is $CrO_4^{2-} \rightarrow Cr^{3+}$; namely, simple reduction of the form $CrO_4^{2-} + e^- \rightarrow CrO_4^{3-}$ was not found (*3*). One could assume that when thermally excited, $CH_3NH_3^+$ dissociates thermally with the liberation of free electrons and protons which react with the chromate ion to produce the Cr^{3+} detected by EPR (*3*).

On the other hand, UV photoreduction of the type $CrO_4^{2-} \rightarrow Cr^{3+}$ was not observed in MASD : CrO_4^{2-} crystals. One reason for this could be that the UV irradiation we have experimented was conducted at room temperature, so the chromate ion was insufficiently thermally excited to react with the free electrons and protons released by the photodissociated $CH_3NH_3^+$. However, we have recently observed, via EPR, an UV photoreduction of the type $CrO_4^{2-} \rightarrow Cr^{3+}$ in chromate-doped $(CH_3NH_3)_2SnCl_6$ and $[NH(CH_3)_3]_2SnCl_6$ crystals (the details will be reported at a later date). Both $CH_3NH_3^+$ and $[NH(CH_3)_3]^+$ have been found to be powerful reducing agents for the reduction of the chromate ion to Cr^{3+} (*3*). It is known that compounds of methylammonium have been used in the UV photopassivation of defects in semiconductors. The mechanism is apparently the passivation of defects by the free hydrogens released via the photodissociation of the $CH_3NH_3^+$ ion. In this respect, it seems worthwhile to investigate the role played by the $CH_3NH_3^+$ or $[NH(CH_3)_3]^+$ ion in the photodissociation of the chromate ion.

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