Absorption Spectra of Cr$^{3+}$
in Al$_2$O$_3$ Under Shock Compression

Tsuneki Goto*, Thomas J. Ahrens, and George R. Rosman
Division of Geological and Planetary Sciences, California Institute of Technology,
Pasadena, California 91125, U.S.A.

Abstract. Unpolarized absorption spectra of single crystals of Cr$^{3+}$ doped
Al$_2$O$_3$ (synthetic ruby) have measured using a new, time-resolving, dispersive,
streak photographic system over the range ~ 350 to ~ 700 nm during a series
of shock loading experiments. The crystal field absorptions assigned to the
transition $^4$A$_2$ $\rightarrow$ $^2$T$_1$ were observed to shift in a series of experiments from
555±1 nm at atmospheric pressure to 503±5 nm at 46 GPa. In a single
experiment at 32 GPa the $^4$A$_2$ $\rightarrow$ $^2$T$_1$ transition was observed to shift from
405±1 to 386±5 nm. The present data extrapolate downwards in compres-
sion toward the 10 GPa data of Stephens and Drickamer (1961) although
both crystal field absorption energies increase considerably less with com-
pression than predicted by the simple ionic point charge model. The single
datum observed for the Raush parameter B, 388±38 cm$^{-1}$ at 32 GPa, is
consistent with previous results to 10 GPa and the trend of decreasing B,
with compression expected from the divergence of the data from the
point charge model due to increasing covalency.

Introduction
Spectral absorption measurements on minerals carried out while these are at
dynamically induced high pressure states provide constraints on their shock
compressed crystal structure. The observed spectra in the optical range may be
compared with those obtained using static high pressure methods (Drickamer
and Frank, 1973; also Mao, 1976; Abu-Frid, 1976). Both techniques provide
information on the crystal field environment of transition elements.
Absorption spectra measured in static high pressure apparatus can be
recorded over a spectral range which includes the infrared, whereas similar
measurements carried out under dynamic pressures have been limited to the
optical range. The pressure calibration used in recently reported static
absorptive

* Present address: The Research Institute for Iron, Steel and other Metals, Tohoku University,
Sendai, Japan.
tion experiments have employed the decrease in energy of the $R$, ruby spectral fluorescence with increasing compression (Block and Piermarini, 1976; Bell and Mao, 1977). To the degree that the shock compression produces hydrostatic states, the pressures associated with spectral measurements under dynamic conditions are known absolutely to within several percent. The errors in the pressure arise from uncertainties in the Hugoniot and the shock state induced in a specific experiment. Presently, the only other technique which is capable of examining the state of solids shocked to high pressure are flash X-ray diffraction methods (Johnson et al., 1970; Johnson and Mitchell, 1972).

On the basis of zero-pressure crystal field transition energies Burns (1976) has inferred that Cr$^{3+}$ will have a strong octahedral site preference in mantle minerals. He proposes that Cr$^{3+}$ is enriched as follows: spinel $>$ garnet $>$ pyroxene $>$ olivine. Previous static high pressure spectral measurements to 10 GPa on ruby are reported by Stephens and Dichtlamer (1961) and previous dynamic pressure measurements of only the optical spectra are reported by Gaffney and Ager (1973).

The development of intense xenon flash tube which operates for a duration of $\sim 30 \mu s$ with 3.8 KJ of capacitor stored energy (Goto et al., 1979) has provided sufficient illumination such that a conventional rotating mirror streak camera can be used to obtain spectra over the extended range ($\sim 350$ to $700$ nm). The new streak spectrometer system provides a broader spectral sensitivity than previously obtained with an image-converter camera, and produce more precise measurements because of the lack of spectral complexities in the xenon light sources compared to the confined, air-spark light sources previously used for these measurements.

In the initial tests of the system the spectral properties of Cr$^{3+}$ in Al$_2$O$_3$ were chosen for study because spectra are available for comparison obtained under both static and dynamic conditions. The current series of experiments extends the pressure range previously studied (by static techniques) by more than 20 GPa.

Experimental Technique

In the improved spectrographic streak camera system (Fig. 1), the light from a 3.8 KJ xenon flash lamp is focussed onto a sample by a single lens, L1 (200 mm, f/4) and is internally reflected via a mirrored surface onto the back of the sample. The reflected light is, in turn, focussed onto a vertical entrance slit of a spectrometer (250 mm, long) with a diffraction grating (590 lines/mm blazed at 550 nm) the output of which is projected onto a slit in the horizontal plane which is orthogonal to the sweeping direction of the streak camera. By the use of a field lens, L3 (95 mm, f/2.5), a relay lens, L4 (200 mm, f/2.7), and the streak camera objective lens, L5 (300 mm, f/4), the image of the dispersed light is in turn formed on the slit of the streak camera (Beckman and Whitley, 1959 B). The camera records continuously the time variation of the slit image (transmission spectrum) on the film. The apparatus is operated at a writing speed of 70 mm/s using Kodak $\# 2475$ film. This film is sensitive over the range 300
Spectra of Al$_2$O$_3$ \textsuperscript{3+}

Fig. 1. Experimental configuration of apparatus for obtaining optical spectroscopy data under shock compression. Interception intervals of the He–Ne laser beam are used to measure projectile velocity. The xenon flash lamp is triggered by a pulse from a photodiode and achieves full brightness at the time when the projectile impacts the target. The light beam from the xenon flash enters the vacuum chamber via lens $L_1$, is filtered into the target by an inclined ($-45^\circ$) mirror, and is reflected internally by a mirror coating on the back of the sample. All images of the central 6 mm diameter region of the sample is focused at the entrance slit of the spectrometer. The image of the dispersed spectrum is focused via $L_3$, $L_4$, and $L_5$ at the split plate within the spectrometer.

to 700 nm. Spectral and time resolutions obtained with the present system are $\sim$ 8 nm and $\sim$ 50 ns, respectively, over the spectral range, $\sim$ 350 nm to $\sim$ 700 nm.

With the above geometry, the spectral range recorded in any given experiment was $\sim$ 225 nm. The $\sim$ 225 nm bandwidth recorded can be varied by rotating the orientation of the diffraction grating within the spectrometer.

Shock waves of various amplitudes are driven into the samples by the impact of a flyer plate which interacts with a series of driver plates upon which the samples are mounted. In the present experiments both plates were oxygen-free copper. The flyer plate is embedded in a Lexan plastic sabot which is accelerated to velocities of 1.1 to 2.1 km/s by a 40 mm bore propellant gun. Because the impedance-matching method is employed to obtain the high-pressure shock state in the sample, the velocity of the projectile must be accurately measured. We utilize the time intervals between intersection of three He–Ne laser beams propagating across the gun axis over a total distance of $\sim$ 75 cm to obtain the velocities.

The samples studied were single crystals of Cr$^{3+}$-doped (0.07 wt%) Al$_2$O$_3$ (Union Carbide, Crystal Product Division) 6 mm thick and 19 mm in diameter, with their crystallographic $c$-axis oriented at $60^\circ$ with respect to the impact surface. These were polished, such that the surface were specularly reflecting and flat to within $\pm$0.002 mm. One surface was coated with an optically thick layer of aluminum to form a back surface mirror. A disk of single crystal Al$_2$O$_3$, 1 mm thick and 25 mm in diameter, is inserted between the sample and driven plate to smooth the shock front, which because of the polycrystallinity of the copper, is believed to be rough on the scale of a wavelength of visible light. The
light path through the sample (Fig. 1), permits observation of the time-resolved spectrum, initially through the unshocked sample and then during the shock transit through the sample.

Experimental Results

The spectrum of Cr$^{3+}$ in Al$_2$O$_3$ at atmospheric pressure has been measured on a Cary 17 spectrophotometer (Fig. 2). The absorption bands arise from the electronic transitions of Cr$^{3+}$ ions substituting in an Al$^{3+}$ site. The observed absorption bands are assigned to transitions from the $^4T_2$ ground state to the excited states $^2E_g$ (at $\sim$555 nm) and $^2T_2$ (at $\sim$405 nm) (Sugane and Tanabe, 1958). Trigonal distortion which splits each excited state into two components with a separation of about 500 cm$^{-1}$ at atmospheric pressure (Stephens and Drickamer, 1961) is too small to be resolved in the unpolarized spectra observed here.

The time-resolved spectra have been obtained at five shock pressures (23.5 to 45.7 GPa) above the Hugoniot elastic limit (12-21 GPa), depending on crystallographic orientation and final shock state (Graham and Brooks, 1971). In four of the experiments the spectrometer was set to observe the 555 nm transition. Figure 3 shows a typical streak record of the transmission spectrum of a sample shocked to 301$\pm$0.5 GPa. A microdensitometer trace of the streak camera image signal of the record at different times is also indicated on the right. In the upper part of the record (Fig. 3a) we can see the spectrum of the unshocked sample which is dominated by the 555 nm absorption. When the shock front

![Figure 2](https://example.com/figure2.png)

**Fig. 2.** Transmission versus wavelength for ruby oriented 40° from c-axis, measured on a modified Cary 17 spectrophotometer.
Fig. 3. Transmission spectrum of Cr\textsuperscript{3+} (605 Å) in A\textsubscript{2}O\textsubscript{3} as 30.1 ± 0.5 GPa shock propagates through sample. The two spectral calibration lines are the emission lines of a standard mercury light source. The microphotometer traces are plotted on the right: (a) Prior to impact; (b) Shock front enters sample (line of reflectivity observed by streak camera); (c) Spectrum observed at (1) shock front in zero-pressure spectra; (d) Shock wave reaches free-surface and the observed spectrum corresponds to that of sample at high pressure. The absorption band arising from the \textit{\chi_{4s}} → \textit{\lambda}_{3g} transition is observed to shift from 555 nm to 509 nm as shock exceeds the sample

arrives at the internal mirror (Fig. 3b), the intensity of the spectrum decreases sharply. This may be due to absorption in the shock front or by degradation of the mirror by the shock. As the shock wave propagates through the sample (Fig. 3c and d), the absorption at zero-pressure is gradually replaced by that due to material in the shock compressed region. The 555 nm band at zero-pressure is observed to shift to 509 nm in the 30.1 ± 0.5 GPa shock compressed state. After the shock front arrives at the free surface of the sample, we can no longer record the spectrum because a rarefaction wave originating from the free surface releases the sample from the shock compressed state to the zero-pressure state. This process probably severely fractures the crystal, rendering it immediately opaque. From the difference between the arrival times of the shock front at the internal mirror and free surface the shock velocity is calculated to be 8.76 ± 0.12 km/s for the 30.1 GPa shot. The uncertainty in shock velocity is estimated to be ±1.4% from the time resolution (±10 ns) and transit time of shock wave through the sample (~0.72 μs). The value of the shock velocity is consistent with the plastic shock velocities obtained by McQueen and Marsh (1966), and
Table 1. Crystal field absorption spectra for ruby shocked to high pressure

<table>
<thead>
<tr>
<th>Shock pressure (GPa)</th>
<th>Relative volume $Y/Y_T$</th>
<th>$\Delta E_{\text{exc}} - \Delta E_{\text{abs}}$ Absorption band (nm)</th>
<th>$\Delta E_{\text{exc}} - \Delta E_{\text{abs}}$ Absorption band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>555 ± 1</td>
<td>405 ± 1</td>
</tr>
<tr>
<td>23.5 ± 0.5</td>
<td>0.934 ± 0.0002</td>
<td>514 ± 4</td>
<td>398 ± 4</td>
</tr>
<tr>
<td>30.1 ± 0.5</td>
<td>0.916 ± 0.0004</td>
<td>509 ± 4</td>
<td>397 ± 4</td>
</tr>
<tr>
<td>44.3 ± 0.5</td>
<td>0.814 ± 0.0003</td>
<td>513 ± 5</td>
<td>396 ± 5</td>
</tr>
<tr>
<td>45.7 ± 0.5</td>
<td>0.870 ± 0.0002</td>
<td>508 ± 5</td>
<td>380 ± 5</td>
</tr>
<tr>
<td>31.2 ± 0.5</td>
<td>0.912 ± 0.0004</td>
<td></td>
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</tr>
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Graham and Brooks (1971), as shown in Fig. 4. In this figure the particle velocity behind the shock front is obtained from the projectile velocity using the impedance-match method. Because the 16 GPa Hugoniot elastic limit wave for the shock propagation direction of the present experiments is not overdamped until the final shock state of 30.1 ± 0.5 GPa is achieved, we infer that the absorption due to the region compressed by the elastic precursor wave does not measurably affect the spectra resolvable with the present system.

The spectra data obtained in the present study are summarized in Table 1. The centers of the absorption bands have been determined using a data reduction procedure described in Appendix A. Splitting of the absorption bands was not observed which suggests that the splitting of $\Delta E_{\text{exc}}$ or $\Delta E_{\text{abs}}$ states due to distortion of the octahedral site in the high pressure state above the Hugoniot elastic limit remains small compared with the absorption bandwidths ($\sim 1,500 \text{ cm}^{-1}$ at zero-pressure). On the other hand, below the Hugoniot elastic limit a large splitting of the $\Delta E_{\text{exc}}$ state caused by the highly anisotropic stress configuration in the sample was observed by Gaffney and Ahrens (1973). These
results support the conclusions of Graham and Brooks (1971) which suggest that the stress configuration in shock compressed single crystal Al₂O₃ is almost hydrostatic above the Hugoniot elastic limit.

Discussion

The energy for the transition to the 4T₁₂ state is equal to the crystal field splitting parameter, δ (Tanabe and Sugano, 1954). Figure 6 shows the relative change of this energy, δ/δ₀, (Tanabe and Sugano, 1954) plotted versus relative volume, V/V₀. The quasi-hydrostatic data of Stephens and Drickamer (1961) are also indicated for comparison. The values of volume compression for the static data are determined using the hydrostatic compression curve of Hart and Drickamer (1965). In the point charge model, δ/δ₀ varies as (V₀/V)² if the local compressibility about the substituting transition metal ion is equal to the bulk compressibility (McClure, 1959). Thus

\[ \delta/\delta_0 = (V_0/V)^2. \]  

(1)

Hydrostatic data for δ/δ₀ are in good agreement with the curve calculated from this model up to about 3% volume compression, but gradually deviate from the curve at higher compression. This result indicates that at low compression the point charge model is applicable to Cr³⁺ in Al₂O₃ and the local compressibility about Cr⁺⁺ ion is equal to the bulk compressibility at low compression. However, the present data indicate that the change in crystal field splitting energy (McClure, 1959) becomes considerably lower in the volume compression range 6% - 12% than what this model would predict. On the other hand, previous lower resolution shock data (Gaffney and Abrass, 1973) are not reproducible and are inconsistent with the newer results. Minomura and Drickamer (1961) found that for Ti⁺⁺, V⁺⁺, Ni⁺⁺, and Ni⁺⁺⁺ ions in Al₂O₃, the relative changes in crystal field splitting energy are also consistent with the point charge model up to 6% (volume compression 2%).

In MgO, for comparison, the relative change in crystal field splitting energy depends strongly on the substituting transition ion even in the low compression range. Figure 7 shows typical examples of δ/δ₀ plotted versus V/V₀ for Ni⁺⁺⁺, Co⁺⁺⁺ (Minomura and Drickamer, 1961) and Fe⁺⁺⁺ ions (Shankland, 1968) in MgO. The ionic radii for an octahedral environment increases, as follows (Shannon and Prewitt, 1969):

\[ R_{Ni}^{++} > R_{Co}^{+++} > R_{Fe}^{+++}. \]  

(2)

where R_0 is ionic radius for M⁺⁺⁺ ion. The data shown in Fig. 6 demonstrate that as R₀ increases, the impurity ion decreases, δ/δ₀ increases, for a given compression within the host material (MgO). This suggests that the local compressibility about the substituting transition metal ion is usually different from the bulk compressibility of its host crystal and depends on its ionic radius. If the substituting ion is much larger than that of the host element normally
occupying the site, the local compressibility about the ion will be less than the bulk compressibility. In this case the crystal field splitting energy will be less than that predicted by the $(5/3)$-power law, as in the case of $\text{Fe}^{3+}$ in $\text{MgO}$.

The local compressibility about the substituting transition metal ion in $\text{Al}_2\text{O}_3$ is almost equal to the bulk compressibility up to $2\%$ volume compression (Minomura and Drickamer, 1961). At higher compressions, however, the local compressibility appears to depend on the size of the substituting ion. Since the ionic radius of $\text{Cr}^{3+}$ is larger than that of $\text{Al}^{3+}$, the local compressibility about $\text{Cr}^{3+}$ is expected to be lower than the bulk compressibility of $\text{Al}_2\text{O}_3$ at higher compression, as inferred from substitution systematics in $\text{MgO}$ and observed in this study. In addition to the simple effects of changing ionic radii, covalency and local asymmetry about transition element ions with the lattice undoubtedly play a role in the effect of ion substitution on local compressibility and thus on $\beta$. The present results suggest that the generalizations of Burns (1976) regarding $\text{Cr}^{3+}$ partitioning may change with pressure and that either static or dynamic spectral studies should be undertaken to observe crystal field spectra of ions other than $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ as these data can be used to predict partitioning trends between minerals in the mantle.

Figure 7 shows the relative volume dependence of the Racah parameter $B$ for $\text{Cr}^{3+}$ in $\text{Al}_2\text{O}_3$. For $\text{Cr}^{3+}$ in octahedral site, $B$ is calculated from the equation (Tanaske and Sugano, 1954).

$$\frac{3}{2} + \frac{1}{2} B = [\langle \Delta E - 9 \Delta^2 \rangle - 144 B^2]^{1/2} = E(T_{1u})$$

where $E(T_{1u})$ is the transition energy to the $^4T_{1u}$ state. The spectrometer was adjusted to observe this transition at a shock pressure $31.5 \text{ GPa}$ (Table 1) for
one experiment. The Racah parameter, $B$, describes the effects of the repulsion between electrons of a given ion. An increase in the degree of covalency between a metal ion and its ligands, would be accompanied by a spreading out of the electron charge cloud and therefore a reduction of the repulsion and thus the value of $B$. Jorgensen (1962, 1966) has suggested that the ratio $\beta$ between the Racah parameter $B$ of the bonded cation and the value of $B$ for the free ion, is a measure of cation-union covalency. In the case of $\text{Cr}^{3+}$ in $\text{Al}_2\text{O}_3$, the value of $\beta$ decreases from 0.71 at zero-pressure to 0.64 at 32 GPa ($\sim 9\%$ volume compression), indicating an increase in covalency of $\text{Cr}^{3+}-\text{O}^{2-}$ bonding in $\text{Cr}^{3+}$-doped $\text{Al}_2\text{O}_3$ with compression. The increase in covalency will decrease the value of $\Delta$, at a given compression, from that calculated via the $(T/T_0)^{\beta}$ law which assumes complete ideal ionic behavior. This result is qualitatively consistent with the observed decrease of $\Delta$ with compression which is significantly less than predicted by the $(T/T_0)^{\beta}$ law.

Appendix

A. Data Reduction of Shocked Cr$^{3+}$-Doped Al$_2$O$_3$ Spectra

The data from the spectrophotometric system was recorded on 35 mm Kodak 4245 film. The films are developed in Acufix developer at 20°C for 10 min, yielding an effective ASA number of 1600. The films are then scanned by a microdensitometer. The photographic density of the exposed film is defined by the equation,

$$D = \log_{10} \frac{I}{I_0}$$

(1a)

where $I_0$ is transmission of the film. Since the transmission is proportional to the microdensitometer voltage signal $V$, the film density is given by:

$$D = \frac{V}{V_0} = \text{const.}$$

(1b)

The relation between incident light energy, $E$, impinging onto the film (photographic exposure), and photographic film density is given by the relation,

$$\frac{dD}{d\log_{10}E} = (\gamma)^2$$

(1c)

where $(\gamma)^2$ is conventionally defined as the gamma value of the film. Eq. (1a) assumes, at least over the film densities and energies recorded in the present experiments, light flux rate independence.

The reflectivity of the shock-damaged interior; $R_s$, will be given constant while the shock wave propagates through the sample. The intensity of light transmitted through the sample, $I$, is written in the form,

$$I = R_sT_{1h}$$

(1d)
where $T$ is transmission of the sample and $I_0$, the intensity of incident light on the surface of the sample. In general the three terms on the right hand side of Eq. (4a) are dependent on wavelength. We neglect the small effect of light reflection from the sample free-surface. Therefore the transmittance ratio of unshocked to shocked sample is given by

$$\frac{I_0}{I_1} = \frac{T}{T_1}$$  \hspace{1cm} (5a)

where $I_0$ is the light intensity transmitted through the sample and $T$ is the transmittivity of the sample just after the shock arrival in the sample mirror (Fig. 1a) and $I_1$ and $T_1$ light intensity transmitted and transmittivity of the sample just before the shock arrival at the free surface of the sample (Fig. 1b). Since the photographic density $D$ is proportional to the intensity of light transmitted through the sample, we obtain the difference between the densities of film, $D_0$ and $D_1$, exposed just after the shock arrival in the sample and just before the shock arrival at the free surface of the sample from the Eqs (2a), (14a) and (5a) in the form

$$D_0 - D_1 = \log \left( \frac{I_0}{I_1} \right) = \log \left( \frac{T}{T_1} \right)$$  \hspace{1cm} (6a)

where $I_0$ and $I_1$ are microphotometer signals corresponding to the densities of $D_0$ and $D_1$, respectively. In the Eq (6a) absorption in the shocked region of the sample will appear as positive features while those in the unshocked region will be negative features. We calculated the value of $\log \left( \frac{I_0}{I_1} \right)$ at various wavelengths and determined the absorption energies from the positions of positive peaks in the values of $6a$.

References


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