Dependence of R fluorescence lines of rubies on Cr\(^{3+}\) concentration at various temperatures

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Abstract

The R fluorescence lines of rubies that contain 0.022, 0.068, 0.211, 0.279, 0.556, 1.221 and 1.676 wt% of Cr\(_2\)O\(_3\) were measured at temperatures of 100-600 K and at atmospheric pressure. The R\(_1\) line wavenumbers of all of the ruby samples shifted
linearly as the temperature increased from 298 to 600 K at atmospheric pressure, and
the temperature dependence increased from \(-0.157 \pm 0.001\) cm\(^{-1}\)/K to \(-0.149 \pm 0.001\) cm\(^{-1}\)/K as the Cr\(_2\)O\(_3\) content in the rubies increased from 0.022 wt% to 1.676 wt%,
which suggests a significant dependence on Cr\(^{3+}\) concentration. At room temperature
and atmospheric pressure, the full width at half maximum (FWHM) of the peak height
of the R lines also appears to be linearly related to the Cr\(^{3+}\) concentration. The relative
intensity ratios of the R\(_2\) to R\(_1\) lines \((I_2/I_1)\) of ruby samples with different Cr\(^{3+}\)
concentrations show several non-linear variations with temperature from 100 to 600 K,
and the maximum values, \((I_2/I_1)_{\text{max}}\), occur near room temperature. The effect of Cr\(^{3+}\)
doping on the temperature dependence of the R line wavenumbers should be
considered when rubies are used to calibrate the pressure or temperature in
high-pressure and high-temperature experiments.

**Keywords:** R fluorescence lines; pressure calibration; temperature correction; ruby;
Cr\(_2\)O\(_3\) content

**Introduction**

Rubies are important photonic crystals, and their R fluorescence lines vary with
pressure and temperature. The variations of the wavenumbers of R lines with pressure
are commonly used to calibrate the pressure in diamond anvil cells (DACs) (Forman
et al. 1972; Mao et al. 1986). The variations in the intensity of R lines have also been
used to calibrate temperature in scientific research (Weinstein 1986). Because the R
lines are caused by the excitation of the 3d electrons in their ground states and their
subsequent de-excitation from their excitation states and because there are inevitable interactions between Cr$^{3+}$ in the ruby lattice, the concentration of Cr$^{3+}$ in rubies may affect both the pressure and temperature dependence of the R lines at high temperature and high pressure conditions. Therefore, the quantitative investigation of the effect of Cr$^{3+}$ doping on the pressure and temperature behaviors of R lines is important for the accuracy of pressure and temperature calibrations in simultaneous high pressure and high temperature DAC experiments, which are often used to study the Earth’s interior (Chou 2003) and in other high-pressure sciences, such as high-pressure physics, chemistry, life science and material science.

Variations in the peak position and the width and intensity of the ruby R$_1$ line as a function of temperature have been analyzed in several studies, but the results vary widely (Kokhanenko and Antipov 1969; Barnett et al. 1973; Yamaoka et al. 1980; Wunder and Schoen 1981; Ragan et al. 1992; Yen and Nicol 1992; Goncharov et al. 2005). For example, Ragan et al. (1992) determined a temperature dependence of 0.158 cm$^{-1}$/K from 390-600 K for the R$_1$ line wavenumber, which was approximately 11% greater than the value of 0.0068 nm/K (equivalent to approximately 0.141 cm$^{-1}$/K) that was reported by Barnett et al. (1973) and Yamaoka et al. (1980). When calibrating the pressure or temperature in a heating DAC experiment from 300 to 600 K using the R$_1$ line, this difference would lead to a maximum temperature discrepancy of 34 K or a maximum pressure discrepancy of 675 MPa. In fact, the reference contents of Cr$_2$O$_3$ in rubies used by previous researchers (0.062 wt%, 0.5 wt%, ~1 wt%, and 2 wt% Cr$_2$O$_3$ by Yen and Nicol 1992; Barnett et al. 1973; Yamaoka et al.
1980; and Wunder and Schoen 1981, respectively) were not the same. Does the
concentration of Cr$^{3+}$ contribute to this discrepancy? This study attempts to answer
this question by measuring the temperature variations of the R lines of rubies with
varying Cr$^{3+}$ concentrations at atmospheric pressure.

**Experimental methods**

Pink to blood red synthetic rubies were cut into disks that were ~0.5 mm in diameter
and ~0.2 mm thick and then polished. The concentrations of Cr$^{3+}$ in the rubies were
measured using an EPMA-1600 type electron probe (beam size 10 μm) with WDS
(wavelength-dispersive spectroscopy) mode and an Atomic Absorption
Spectrophotometer (AAS). Three to five spots were measured in each sample. The
average values are listed in Table 1. The Cr$_2$O$_3$ contents in rubies were from 0.022 to
1.676 wt%.

In the fluorescence measurement experiments that were conducted at high
temperatures and atmospheric pressure, the samples were heated and cooled in a
Linkam heating stage with a liquid nitrogen flowing system. The temperature was
increased by 15 K/min and measured with a thermocouple. The precision of the
temperature measurements was ± 0.1 K. The fluorescence spectra of the samples were
excited and recorded using a con-focal Renishaw inVia Micro-Raman Spectroscopy
system. The system uses a 514.5 nm laser beam, which is produced by a Spectra
Physics 2017 2 W argon ion laser and is focused on a spot on the sample by a Leica
microscope system, as the excitation light source of the fluorescence. A
high-resolution white light image of the samples that covers the sampling spot can be displayed on a screen of the Leica microscope system. In our experiments, (1) the silicon 520 cm\(^{-1}\) peak calibration was performed before the fluorescence spectra were collected, and the accuracy of the spectrum collection was up to ± 0.01 cm\(^{-1}\); (2) the excitation laser powers ranged from 0.0002 mW to 0.05 mW; (3) a 20X Olympus ULWD objective was used for the Leica microscope system, so the excitation laser beam was focused onto a ~2-μm-diameter spot; and (4) all of the fluorescence spectra were collected near the spots where the electron microprobe measurements were made.

In the fluorescence measurement experiments that were conducted at high pressures and room temperature, the fluorescence spectra of each ruby sample were measured at pressures of 0-2.0 GPa using the fluorescence measurement system described above and a DAC. The anvil culets of the DAC were approximately 500 μm in diameter. The T301 stainless steel gasket (300 μm thick with a sample hole that was 280 μm in diameter) and a mixture of methanol, ethanol and water at 16:3:1 volume proportions were used as the sample chamber and pressure medium, respectively, and could maintain a hydrostatic pressures up to ~10.5 GPa at room temperature (Angel et al. 2007). The pressures in the cell were measured using the wavenumber shift of the R\(_1\) fluorescence peak of ruby #5, which contained 0.556 wt% of Cr\(_2\)O\(_3\). The uncertainty of this technique below 2.0 GPa was estimated to be ± 50 MPa (Schmidt and Ziemann 2000).
The wavenumber of each fluorescence peak was obtained using the peak fitting program of the WIRE 3.1 software package from Renishaw Co. The R₁ line generally had a Lorentzian-type shape, but the R₂ line at high temperature was fit better by a Voigt type line that included Gaussian and Lorentzian components, and the Gaussian proportion increased with increasing temperature and Cr³⁺ concentration in the ruby samples.

Finally, the electron densities of state (DOS) of the Cr³⁺ 3d band in the rubies at ambient pressure and 10 GPa were calculated by the first principle calculation method using the crystal structure data of Al₁.₉₈Cr₀.₀₂O₃, Al₁.₉₂Cr₀.₀₈O₃, Al₁.₈₉₆Cr₀.₁₀₄O₃ and Al₁.₅₄Cr₀.₄₆O₃ in the ICSD database. The calculations used the Generalized Gradient Approximation (GGA) method, the PBE exchange-correlation function (Perdew et al. 1996) and ultra-soft potentials, and a 3×3×3 k-point mesh and 300 eV cut-off energy were chosen.

Results and discussions

1. Fluorescence peaks and their positions

The fluorescence spectra and the Raman spectra of the ruby samples with the lowest and highest Cr₂O₃ contents used in this study are shown in Figure 1. In addition to the well-known R₁ and R₂ peaks, several new peaks were present in the fluorescence spectra of rubies with Cr³⁺ concentrations greater than 0.5 wt%, and the relative intensities of the new peaks increased with increasing Cr₂O₃ content. A high Cr³⁺ concentration would lead to strong Cr³⁺-Cr³⁺ interactions, which change the electron
structure of the Cr$^{3+}$. Thus, the new peaks might be attributed to Cr$^{3+}$-Cr$^{3+}$ interactions in the ruby lattice because the fluorescence spectra of rubies originate from the excitation of the 3d electrons in their ground states and their subsequent de-excitation from their respective excitation states. However, because the Raman spectra were similar, the increase of Cr$^{3+}$ concentration likely does not cause the separation of a new phase from the ruby matrix.

Significantly varying shifts of the wavenumber positions of the R lines with Cr$^{3+}$ concentration were observed at room temperature and atmospheric pressure. As shown in Figures 2a and 2b, the wavenumbers of the R$_1$ and R$_2$ lines decreased with increasing Cr$_2$O$_3$ content up to 0.3 wt%, whereas a reversal of this trend occurred at Cr$_2$O$_3$ contents greater than 0.3 wt%. The latter observation might be attributed to the fact that the ionic radius of Cr$^{3+}$ is larger than that of Al$^{3+}$. The behavior at Cr$_2$O$_3$ contents below approximately 0.3 wt% is not fully understood, but it might be related to the internal stress that commonly remains in ruby samples because we did not attempt to eliminate the residual stress in our samples before making the fluorescence measurements.

From 300 to 600 K and at atmospheric pressure, the R lines red-shifted linearly with increasing temperature. The relationship between the slope of the R$_1$ shift with temperature and Cr$_2$O$_3$ content is shown in Figure 3a. The absolute values of the slopes decrease with increasing Cr$_2$O$_3$ content. The corresponding relationship for R$_2$ is shown in Figure 3b. In this case, the absolute values of the slopes of the wavenumber shift with temperature also decrease with increasing Cr$_2$O$_3$ content.
below 1.2 wt% content of Cr$_2$O$_3$ but recover at higher contents. Rangan et al. (1992) observed slopes of the $R_1$ and $R_2$ shifts with temperature of -0.158 cm$^{-1}$/K and -0.162 cm$^{-1}$/K from 300-600 K, respectively, with an unknown Cr$^{3+}$ concentration. They attributed the discrepancy between their results and those of other researchers (-0.14 cm$^{-1}$/K for $R_1$ measured by Barnett et al. 1973; -0.153 cm$^{-1}$/K for $R_1$ by Yen and Nicol 1992) to the different methods used to determine the peak positions in the spectra fitting. Spectrum fitting to a double Lorentzian line can allow us to accurately separate the $R_1$ and $R_2$ components from overlapping R lines and thereby obtain precise line positions, while obtaining the peak positions by eye (as in Barnett et al. 1973 and Yen and Nicol 1992) will give a $R_1$ position that does not shift as fast as it should because at high temperatures, the $R_1$ and $R_2$ lines overlap and yield a visual $R_1$ peak that is located at a higher frequency than the line’s true resonant frequency. However, significant differences are still present in the slopes of the R line shift among the samples in this study (see Table 2 and Figures 3 (a) and (b)) even though the wavenumber positions of the R lines were obtained by fitting the spectrum to a double Lorentzian line using high-precision software. Therefore, the discrepancies in the slopes of the R line shift with temperature between various studies cannot be fully explained by the difference in the methods of determining the peak positions. We believe that the major factor was the difference in the Cr$^{3+}$ concentrations in the ruby samples used in this study. The mechanism is discussed in a subsequent section. The anomalous slope of $R_2$ in sample #1006 and #8 might be attributed to the crystal orientation (Shen and Gupta 1993). The relative intensity of
R1 and R2 can reflect the crystal orientations in the rubies to some extent. The shifts of the slopes of the R2 lines with temperature were more closely related to the intensity ratios of R2 and R1 (I2/I1) (see Figures 3c and 3d), which is consistent with the greater dependence on the crystal orientation of the R2 line shift than the R1 line shift (Shen and Gupta 1993). Moreover, of all the samples, sample #1006 and #8 had the higher I2/I1 value (Table 2). In sample #1006 and #8, the fast shift of the R2 line indicates that the crystal orientation might be closer to the crystal’s c axis. However, the anomalous fast shift of the R1 line in sample #1006 might be attributed to the lower Cr3+ concentration, the crystal orientation and the internal stress.

In the high pressure DAC experiments (0-2.0 GPa), we found no significant pressure difference in the cell when we used the ruby samples with different Cr2O3 contents as pressure calibrants. Figure 4 shows the differences between the pressure that was measured using sample #5 and used as the reference pressure in our high pressure experiments and the pressures measured using the other ruby samples with different Cr2O3 contents. All of the differences between the reference pressure and the other measured pressures are within ± 50 MPa, which is a commonly-used uncertainty for pressure calibrations when rubies are used as a pressure calibrant in hydrostatic DACs below 2 GPa (Schmidt and Ziemann 2000).

**2. Additional discussion of the impact of Cr3+ concentration on the R line shift**

Temperature and pressure both have significant impacts on the red-shift of R lines due to the Cr3+ doping in rubies. In this study, we found that the Cr3+ concentration in a ruby also has an important impact on shift of the R lines. This
impact can be summarized as a decrease of the \( \frac{d\nu}{dT} \) value of the R lines and a blue-shifting of the R lines with increasing Cr\(^{3+}\) concentration in a ruby.

McCumber and Sturge (1963) theoretically interpreted the shift of the R\(_1\) line with temperature. Based on Equation (3a) of McCumber and Sturge, we calculated the derivative of the wavenumber of the R\(_1\) line with respect to temperature as follows,

\[
\frac{d\nu_1(T)}{dT} = a \cdot \left[ 4 \times \frac{T^3}{T_D} \int_0^{T^{\nu/T}} \frac{x^3}{e^{x} - 1} \, dx - \frac{1}{T(e^{x/T} - 1)^2} \right] \tag{1}
\]

where \( a \) is the electron-phonon coupling constant, and \( T_D \) is the effective Debye temperature. McCumber and Sturge (1963) found that using \( a = -400 \text{ cm}^{-1} \) and \( T_D = 760 \text{ K} \) provided a good fit to the experimental results for 0-700 K. However, Yen and Nicol (1992) found that \( a = 400 \text{ cm}^{-1} \) gives good results for this temperature range. Table 3 shows the values of the constant \( a \) that provided the best fits to the measurement results in this study. The rates of the wavenumber shift of the R lines with temperature are closely related to the electron-phonon coupling constant, and the electron-phonon coupling constant \( a \) decreases monotonously with increasing Cr\(^{3+}\) concentration. According to McCumber and Sturge (1963), the electron-phonon coupling constant \( a \) measures the probability of the scattering of phonons from the 3d electrons of Cr\(^{3+}\); the larger the value of \( a \), the smaller the probability of scattering. In our case, an increase of the Cr\(^{3+}\) concentration in the ruby samples indicates an increase of the density of the scattering center, Cr\(^{3+}\), for the phonon. As a result, the probability of scattering would increase, and the value of the phonon-electron coupling constant \( a \) decreases with increasing Cr\(^{3+}\) concentration. Therefore, our experimental results are consistent with the theoretical model of McCumber and
Sturge (1963) of the impact of Cr$^{3+}$ concentration on the value of $(d\nu/dT)$ of R lines.

To theoretically explain the blue-shift of ruby R lines with increasing Cr$^{3+}$ concentration, we used the first principle calculation method and conducted a series of calculations of the electronic density of state (DOS) of the Cr$^{3+}$ 3d band for rubies with different Cr$^{3+}$ concentrations at room temperature and atmospheric pressure and at room temperature and 10 GPa. The results (Figures 5 and 6) show that the peaks of the DOS of the Cr$^{3+}$ 3d electrons are blue-shifted with increasing Cr$^{3+}$ concentration at room temperature and atmospheric pressure and red-shifted with increasing pressure at room temperature and a constant Cr$^{3+}$ concentration. Moreover, with increasing Cr$^{3+}$ concentration at room temperature, the amplitude of the pressure-induced red-shift of the DOS peaks increased when the pressure increased from atmospheric pressure to 10 GPa. Because the red-shift of the DOS peaks of the Cr$^{3+}$ 3d electrons with increasing pressure is a well-known mechanism for the red-shift of ruby R lines with pressure (Xie 2004), the blue-shift of the DOS peaks of the Cr$^{3+}$ 3d electrons with increasing Cr$^{3+}$ concentration should also be the mechanism for the blue-shift of the ruby R lines with increasing Cr$^{3+}$ concentration. This behavior was observed from the experimental results in this study.

The analysis presented above indicates that the Cr$^{3+}$ concentration might have a significant influence on the R line shift of rubies in addition to the important factors of temperature and pressure. It is possible that with increasing Cr$^{3+}$ concentration, there could be increasingly important coupling effects of the influences of temperature, pressure and Cr$^{3+}$ concentration on the ruby R line shift because the Cr$^{3+}$ - Cr$^{3+}$...
interactions in the ruby lattice would become stronger (Ohnishi and Sugano 1982; Winter et al. 1990).

3. Full width at half maximum (FWHM) of the R lines

The full width at half maximum of the R₁ line (FWHM₁) at atmospheric pressure and temperature increased significantly with increasing Cr³⁺ concentration, whereas the full width at half maximum of the R₂ line (FWHM₂) increased moderately (Figure 7). By linear fits to the experimental data for the R₁ and R₂ lines, we obtained $FWHM₁ (\text{cm}^{-1}) = 11.44348 + 2.33563 \times \text{Cr}_2\text{O}_3 \text{ (wt\%)}$ with a $r^2$ value of 0.9978 and $FWHM₂ (\text{cm}^{-1}) = 8.94403 + 1.1267 \times \text{Cr}_2\text{O}_3 \text{ (wt\%)}$ with a $r^2$ value of 0.9986. In contrast, Ragan et al. (1992) reported that the FWHM values of the R lines of rubies that contained 0.12% and 0.5% Cr³⁺ were nearly identical. Theoretically, if two 3d electrons are located in the same type of orbit but belong to two different Cr³⁺ in the ruby lattice, there is always a slight difference in their energy levels due to subtle differences in the electromagnetic environments in which the two Cr³⁺ are located. The difference in energy level changes the energy level into an energy band. With increasing Cr³⁺ concentration in rubies, the energy bands of both the ground states and the excited states of the 3d electrons of Cr³⁺ would widen, and the FWHMs of the ruby R lines that originate from the excitation of 3d electrons from their respective ground states and the subsequent de-excitation from their corresponding excitation states of Cr³⁺ would also widen. As shown in Figure 7, both $FWHM₁$ and $FWHM₂$ show significant linear increases with Cr³⁺ concentration in the range of 0.022-1.67 wt%. Our experimental results are consistent with the theoretical analysis presented...
At high temperatures and ambient pressure, $FWHM_1$ increased with temperature from 298-600 K (Figure 8). These results are consistent with common knowledge. However, two interesting phenomena in our results are worth noting. First, the increasing width of the $FWHM$s of the R lines with increasing Cr$^{3+}$ concentration observed at room temperature (Figure 7) was also observed for the R$_1$ line at higher temperatures. Second, the positive dependence of $FWHM_1$ on temperature became stronger with increasing temperature.

4. Relative intensity ratios of R$_2$ to R$_1$ ($I_2/I_1$)

Similar to the results described above, the relative intensities of the R$_1$ and R$_2$ lines of all the ruby samples in this study decreased with increasing temperature at atmospheric pressure. However, the relative intensity of the R$_2$ line ($I_2$) decreased more slowly than that of the R$_1$ line ($I_1$) at temperatures from 100 K to approximately 298 K and subsequently decreased faster than $I_1$ until 600 K, which indicates a significant temperature dependence of $I_2/I_1$ (Figure 9a in the supplement information). Moreover, the maximum $I_2/I_1$ values, ($I_2/I_1$)$_{max}$, occurred at different temperatures in samples with different Cr$_2$O$_3$ contents, and the values of ($I_2/I_1$)$_{max}$ and $I_2/I_1$ at 298 K, i.e., ($I_2/I_1$)$_0$, were both related to the Cr$_2$O$_3$ contents in the samples. As shown in Figure 9b in the supplement information, the temperatures that correspond to the values of ($I_2/I_1$)$_{max}$ were inversely related to the Cr$_2$O$_3$ content. However, it is interesting to note that the relationship between ($I_2/I_1$)$_{max}$ and the Cr$_2$O$_3$ content was weaker than that between ($I_2/I_1$)$_0$ and the Cr$_2$O$_3$ content at atmospheric pressure. By
further linear fitting, we obtained a relationship between \((I_2/I_1)_{\text{max}}\) and \((I_2/I_1)_0\), which can be expressed as \((I_2/I_1)_{\text{max}} = -0.02036 + 1.04067 \times (I_2/I_1)_0\) with a \(r^2\) value of 0.997 (Figure 9c in the supplement information).

**Implications**

Pressure calibration is of primary importance for high pressure experiments. Ruby is the most commonly used pressure calibrant, especially in high pressure DAC experiments. Temperature corrections in ruby pressure calibrations are especially important at elevated temperatures. The results of this study show that the wavenumber shifts of ruby R lines are related not only to variations of pressure and temperature but also to variations in the \(\text{Cr}^{3+}\) concentrations of the rubies. Moreover, the three influential factors, temperature, pressure and \(\text{Cr}^{3+}\) concentration, have important coupled effects on the wavenumber shifts of the ruby R lines. At room temperature and pressures of 0-2.0 GPa, the results of our DAC experiments show that the differences in the cell pressures calibrated by the ruby samples with different \(\text{Cr}^{3+}\) concentrations were less than ± 50 MPa, which is a commonly accepted pressure calibration uncertainty for a ruby calibrant in hydrostatic DACs below 2.0 GPa (Schmidt and Ziemann 2000). However, this does not mean that the differences would be within ± 50 MPa at higher temperatures and/or pressures. For example, if we conduct a heating DAC experiment from 300 to 600 K and calibrate the temperature or pressure using the temperature shift rates of the R between 1 line wavenumber of samples #1006 and #8 (Table 2), the maximum temperature and pressure differences would be...
16 K and 315 MPa, respectively. We conclude that before conducting a DAC experiment, it is important to know the dependence of the ruby R line shift on the temperature, pressure and Cr\(^{3+}\) concentration if rubies are used as the temperature or pressure calibrant. The precision of the ruby temperature or pressure calibration could be improved significantly if these dependences are known in detail. However, a large number of experiments at higher pressures and/or temperatures should be conducted in the future to completely resolve the complicated coupled effects of temperature, pressure, and Cr\(^{3+}\) concentration on the wavenumber shifts of the R lines of rubies.

References


Table 1. Weight percentages of major and trace elements in the ruby samples.

<table>
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<tr>
<th>Sample No.</th>
<th>1006</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>5</th>
<th>7</th>
<th>8</th>
</tr>
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<tbody>
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<td>Cr₂O₃</td>
<td>0.022*</td>
<td>0.068</td>
<td>0.211</td>
<td>0.279</td>
<td>0.556</td>
<td>1.221</td>
<td>1.676</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
<td>0.011</td>
<td>0.024</td>
<td>0.004</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
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<td>0.005</td>
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<td>0.005</td>
<td>0.039</td>
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<td>NiO</td>
<td>-</td>
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<td>0.006</td>
<td>0.001</td>
<td>0.007</td>
<td>0.004</td>
<td>0.011</td>
</tr>
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<td>MnO</td>
<td>-</td>
<td>0.008</td>
<td>0.012</td>
<td>0.002</td>
<td>0.015</td>
<td>0.005</td>
<td>0.000</td>
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<td>SiO₂</td>
<td>-</td>
<td>0.012</td>
<td>0.096</td>
<td>0.016</td>
<td>0.016</td>
<td>0.017</td>
<td>0.033</td>
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<td>0.008</td>
<td>0.002</td>
<td>0.001</td>
<td>0.000</td>
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<tr>
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<td>0.013</td>
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<td>0.000</td>
<td>0.010</td>
<td>0.003</td>
<td>0.000</td>
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<tr>
<td>K₂O</td>
<td>-</td>
<td>0.004</td>
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<td>0.010</td>
<td>0.011</td>
<td>0.003</td>
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<tr>
<td>Al₂O₃</td>
<td>99.796</td>
<td>98.541</td>
<td>99.524</td>
<td>98.737</td>
<td>97.122</td>
<td>98.029</td>
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</tr>
<tr>
<td>Total</td>
<td>99.904</td>
<td>98.895</td>
<td>99.845</td>
<td>99.396</td>
<td>98.440</td>
<td>99.800</td>
<td></td>
</tr>
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</table>

*Cr₂O₃ wt% of sample #1006 was measured by AAS, and the other data were measured by electron microprobe.

Table 2. Relative intensity ratios of R₂ to R₁ at room temperature and atmospheric pressure ((I₂/I₁₀)₀) and the slopes of the wavenumber shifts of R₁ and R₂ with temperature (dν₁/dT, dν₂/dT) at atmospheric pressure for ruby samples with different Cr₂O₃ contents.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cr₂O₃ (wt%)</th>
<th>(I₂/I₁₀)₀</th>
<th>dν₁/dT (cm⁻¹/K⁻¹)</th>
<th>dν₂/dT (cm⁻¹/K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1006</td>
<td>0.022</td>
<td>0.856 ± 0.003</td>
<td>-0.1574 ± 0.0011</td>
<td>-0.1561 ± 0.0015</td>
</tr>
<tr>
<td>4</td>
<td>0.068</td>
<td>0.678 ± 0.011</td>
<td>-0.1533 ± 0.0010</td>
<td>-0.1542 ± 0.0010</td>
</tr>
<tr>
<td>3</td>
<td>0.211</td>
<td>0.620 ± 0.012</td>
<td>-0.1530 ± 0.0008</td>
<td>-0.1541 ± 0.0012</td>
</tr>
<tr>
<td>2</td>
<td>0.279</td>
<td>0.626 ± 0.007</td>
<td>-0.1525 ± 0.0007</td>
<td>-0.1543 ± 0.0014</td>
</tr>
<tr>
<td>5</td>
<td>0.556</td>
<td>0.651 ± 0.009</td>
<td>-0.1519 ± 0.0008</td>
<td>-0.1522 ± 0.0014</td>
</tr>
<tr>
<td>7</td>
<td>1.221</td>
<td>0.611 ± 0.001</td>
<td>-0.1501 ± 0.0012</td>
<td>-0.1494 ± 0.0021</td>
</tr>
<tr>
<td>8</td>
<td>1.676</td>
<td>0.748 ± 0.005</td>
<td>-0.1495 ± 0.0011</td>
<td>-0.1560 ± 0.0013</td>
</tr>
</tbody>
</table>

Table 3. Calculated values of the electron-phonon coupling constant $a$ for ruby samples with different contents of Cr₂O₃ ($T_D = 760$ K, $T = 298.15$ K).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cr₂O₃ (wt%)</th>
<th>$a$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1006</td>
<td>0.022</td>
<td>257.2 ± 1.6</td>
</tr>
<tr>
<td>4</td>
<td>0.068</td>
<td>250.4 ± 1.5</td>
</tr>
<tr>
<td>3</td>
<td>0.211</td>
<td>250.7 ± 1.1</td>
</tr>
<tr>
<td>2</td>
<td>0.279</td>
<td>250.7 ± 1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.556</td>
<td>248.2 ± 1.1</td>
</tr>
<tr>
<td>7</td>
<td>1.221</td>
<td>245.4 ± 1.8</td>
</tr>
<tr>
<td>8</td>
<td>1.676</td>
<td>244.3 ± 1.6</td>
</tr>
</tbody>
</table>
Figures

Figure 1

Figure 2

Figure 3

Figure 4
Figure 3

Figure 4

(a) 
(b)
Figure 5
Figure 6

Figure 7

Figure 8
Figure captions

**Figure 1.** (a) Fluorescence spectra of rubies at 298 K and atmospheric pressure, and (b) Raman spectra of rubies at room temperature and atmospheric pressure.

**Figure 2.** Wavenumber values of R lines at room temperature and atmospheric pressure versus Cr$_2$O$_3$ contents in ruby samples, (a) line R$_1$ and (b) line R$_2$.

**Figure 3.** Slopes of the wavenumber shift of (a) line R$_1$ and (b) line R$_2$ with temperature at atmospheric pressure versus the Cr$_2$O$_3$ contents of different ruby samples, and slopes of the wavenumber shifts of (c) line R$_1$ and (d) line R$_2$ with temperature versus the relative intensity ratios of R$_2$ to R$_1$ for different ruby samples at room temperature and atmospheric pressure.

**Figure 4.** Pressure differences between the reference pressure calibrated using ruby sample #5 and those calibrated using the other ruby samples with different Cr$_2$O$_3$ contents at 2.0 GPa and room temperature.

**Figure 5.** Electronic densities of state (DOS) of the Cr$^{3+}$ 3d band in rubies with different Cr$_2$O$_3$ contents at room temperature and atmospheric pressure.

**Figure 6.** Electronic densities of state (DOS) of the Cr$^{3+}$ 3d band in rubies with different Cr$_2$O$_3$ contents at room temperature and 10 GPa.

**Figure 7.** Variations of the full width at half maximum ($FWHM$) of ruby R lines with Cr$_2$O$_3$ contents in different ruby samples at atmospheric pressure and room temperature.

**Figure 8.** Variations of the full width at half maximum of the R$_1$ line ($FWHM_1$) of different ruby samples at atmospheric pressure and a temperature range of 298-600 K.
Figure 9. (a) Variations of the relative intensity ratio of R₂ to R₁ ($I₂/I₁$) at temperatures from 100-600 K at atmospheric pressure for different ruby samples. (b) Plot of the temperatures at which the maximum $I₂/I₁$ values, $(I₂/I₁)_{max}$ occurred at ambient pressure versus the Cr₂O₃ contents of the ruby samples. (c) Relationship between $(I₂/I₁)_{max}$ at atmospheric pressure and $(I₂/I₁)₀$, the relative intensity ratio of R₂ to R₁ at room temperature and atmospheric pressure, for ruby samples with different Cr₂O₃ contents.