Alexandrite as a high-temperature pressure calibrant, and implications for the ruby-fluorescence scale

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The wavelength shifts of the $R1$ and $R2$ fluorescence lines of alexandrite ($BeAl_2O_4$:Cr^{+3}) have been experimentally calibrated against the ruby-fluorescence scale as a function of both hydrostatic and nonhydrostatic pressures between 0 and 50 GPa, and simultaneously as a function of temperatures between 290 and 550 K. The results can be expressed in nm as $\lambda(R1) = 680.26(\pm 0.01) + 8.7 \times 10^{-3}(\pm 0.3)(T - 273) + 0.292(\pm 0.003)P + 1.3(\pm 0.1) \times 10^{-3}P^2$ and $\lambda(R2) = 678.63(\pm 0.01) + 7.8 \times 10^{-3}(\pm 0.2)(T - 273) + 0.031(\pm 0.003)P + 0.8(\pm 0.1) \times 10^{-3}P^2$, with pressure P in GPa and temperature T in K. Notably, we find that the pressure-temperature cross derivative of the fluorescence wavelength shifts are negligible for both ruby and alexandrite.

INTRODUCTION

The ruby-fluorescence scale has become a standard method for determining pressures in the diamond cell.[1,2] However, because the fluorescence wavelength of ruby has a significant temperature shift, in addition to the well-calibrated pressure shift, and because the fluorescence intensity rapidly degrades with increasing temperature, there is an interest in other materials that can be used as pressure calibrants at elevated temperatures.[3] Alexandrite ($BeAl_2O_4$:Cr^{+3}) is one of the materials which has the potential for use as a secondary standard, the fluorescence of the $R1$ and $R2$ lines having been measured up to 30 GPa by other workers.[4,5]

Two approaches have been suggested for pressure calibration at simultaneously high pressures and temperatures: (i) the use of x-ray diffraction with materials, such as gold, having a well-determined thermal equation of state,[6–9] and (ii) the application of fluorescence standards other than ruby.[10–14] The former are considered primary standards, whereas the latter are secondary standards. A significant uncertainty for all secondary standards, including ruby fluorescence, is that the combined pressure and temperature dependencies of the calibrations have not yet been determined for pressures above 20 GPa.[13,15–17] Thus, our goal in the present study is not only to present a possible alternative to the ruby-fluorescence standard at elevated pressures and temperatures, but also to calibrate the effect of temperature on the ruby pressure scale at high pressures.

EXPERIMENT

The synthetic alexandrite (chrysoberyl structured $BeAl_2O_4$ with 1500 ± 500 ppm Cr used in this study was obtained from Allied Signal Inc. (Morristown, NJ), and was ground to a powder with a grain size of approximately 3 μm. Because ruby and alexandrite react with the methanol:ethanol pressure transmitting medium at high temperatures and pressures, some of the data were collected using 20μm-thick pieces of alexandrite and ruby. The decrease in the surface-to-volume ratio of this larger piece reduced the amount of reaction with the methanol:ethanol, thus allowing more data to be collected per loading.

All fluorescence measurements were made using a 14-mW He–Cd laser (441.6-nm wavelength) as an excitation source, and a 0.25-meter Jarrel-Ash monochromator with an RCA C31034 photomultiplier tube to collect spectra.[18] Fluorescence wavelengths were determined at the point of maximum recorded intensity, with no attempt to fit the line shapes or deconvolve the spectra. Any spectra requiring deconvolution were considered too unreliable to quote in this study.

The pressure dependencies of the fluorescence wavelengths of alexandrite were measured in a gasketted Mao-Bell type diamond anvil cell, with the ruby-fluorescence technique being used to determine the pressure.[1,19] For the entire study, 1/5 carat type I diamonds having either 350- or 500-μm culets were used with gaskets made of spring steel.

Two sets of measurements were carried out: one with 4:1 methanol:ethanol as the pressure transmitting medium, in which the maximum pressure reached was 50 GPa, and another with Ar as the pressure transmitting medium which was taken to 35 GPa. For pressures greater than 11 GPa the methanol:ethanol was no longer hydrostatic,[20] leading to a broadening of both ruby and alexandrite fluorescence lines. In contrast, the Ar remained quasihydrostatic up to 35 GPa, and no line broadening was observed with this medium. Accordingly, the pressures were determined using the calibration of Ref. 2 for the runs in which methanol:ethanol was the transmitting medium, while for the measurements made with Ar as the medium, the quasihydrostatic pressure calibration of the ruby fluorescence was used.[21] We note that the difference between the
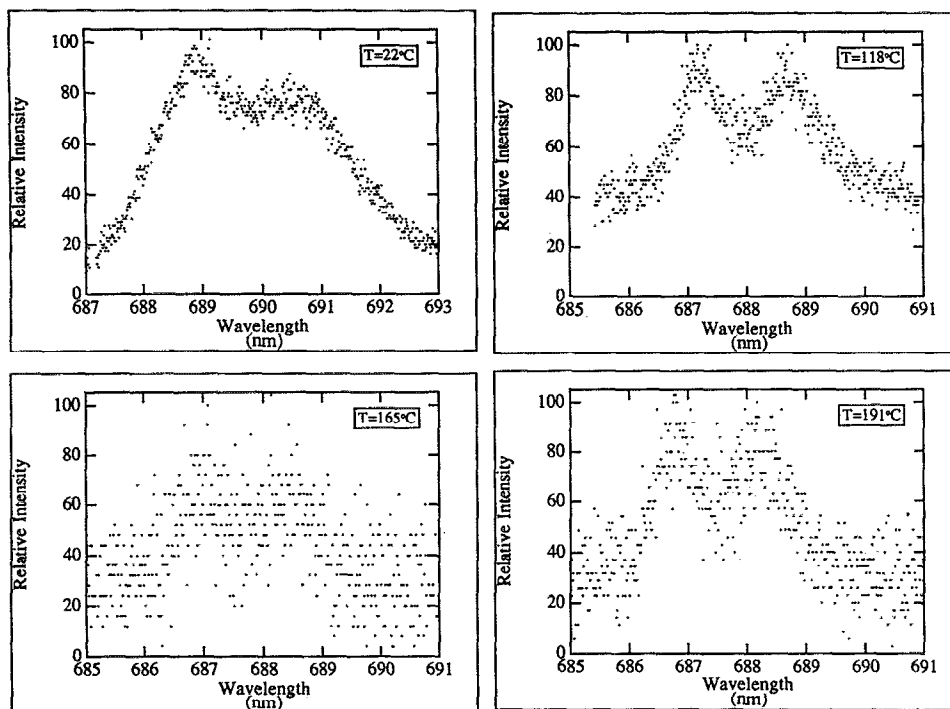
FIG. 1. Spectra of the $R1$ and $R2$ fluorescence lines of alexandrite at $29(\pm2)$ GPa on increasing temperature.

hydrostatic and nonhydrostatic calibrations of the ruby-fluorescence wavelength shifts corresponds to a pressure difference less than 1.2 GPa up to the 35–50 GPa maximum pressures of this study.

All high-temperature measurements were obtained using resistance heaters. At zero pressure, alexandrite was placed on a culet face with a tungsten heater wrapped around the diamond, and with a type S (Pt-10% Rh vs Pt) thermocouple attached to the diamond by means of silver print, in order to insure good thermal contact. The thermocouple was located on a pavilion face and within 0.4 mm of the culet. Data were collected both upon increasing and decreasing the temperature.

For the high-temperature measurements at elevated pressures, a platinum external heater was placed inside a Mao-Bell cell.[22] The thermocouple was attached with silver print to the diamond, either on the pavilion near the culet, as in the zero-pressure measurements, or on the table of the diamond. The thermocouple was connected to a temperature controller [Omega Model #CN2011], which kept the temperatures stable to within 5 °C for the highest temperatures of this study. Separate calibration experiments demonstrate that the thermocouple temperature is within 1 and 8 °C of the sample temperature for thermocouple placements near the culet and on the table of the anvil, respectively. We estimate that our total uncertainties in sample temperature are less than 5 °C for all measurements reported here.

As described below, we use the zero-pressure temperature dependence of the ruby-fluorescence wavelength to estimate the pressure in our samples at elevated temperatures and pressures. Also, we monitor the pressure difference before and after a cycle to high temperatures, and any hysteresis that is observed is well within the uncertainties

that we quote. The hysteresis was found to be less than 2 GPa for all of the measurements reported here.

To illustrate the signal-to-noise ratio in our experiments, an example of the alexandrite fluorescence that we observe as a function of temperature at a pressure of 30 GPa is shown in Fig. 1. In contrast with the ruby fluorescence, the $R2$ peak of the alexandrite fluorescence is more intense than the $R1$ peak at elevated pressures. At zero pressure, the $R1$ peak of alexandrite is always more intense than the $R2$ peak, however we observe, as have others,[5] that with increasing pressure the $R2$ fluorescence becomes more intense relative to the $R1$ peak. We suggest that this may be due to the lifetime of the E state increasing with pressure more rapidly than the lifetime of the $2A$ state, which would result in a relative decrease in the oscillator strength of the E to $^4A_2$ transition as compared to the $2A$ to $^4A_2$ transition.[23] Although the general observation is that the intensity ratio $I(R1)/I(R2)$ of alexandrite decreases with increasing pressure, this ratio is not constant across a sample at a given pressure.

Under nonhydrostatic conditions, we observe that the fluorescence linewidths decrease with increasing temperature when the methanol–ethanol mixture is used as a pressure medium (Fig. 1). These results can be explained by a decrease in the nonhydrostaticity as the temperature is increased.

RESULTS AND DISCUSSION

At zero pressure, the wavelengths of the $R1$ and $R2$ fluorescence lines of alexandrite are found to be linear in temperature over the temperature range of this study (Fig. 2). The temperature shifts are 8.7 $(\pm0.3)\times10^{-3}$ nm/K and 7.8 $(\pm0.3)\times10^{-3}$ nm/K for the $R1$ and $R2$ lines,
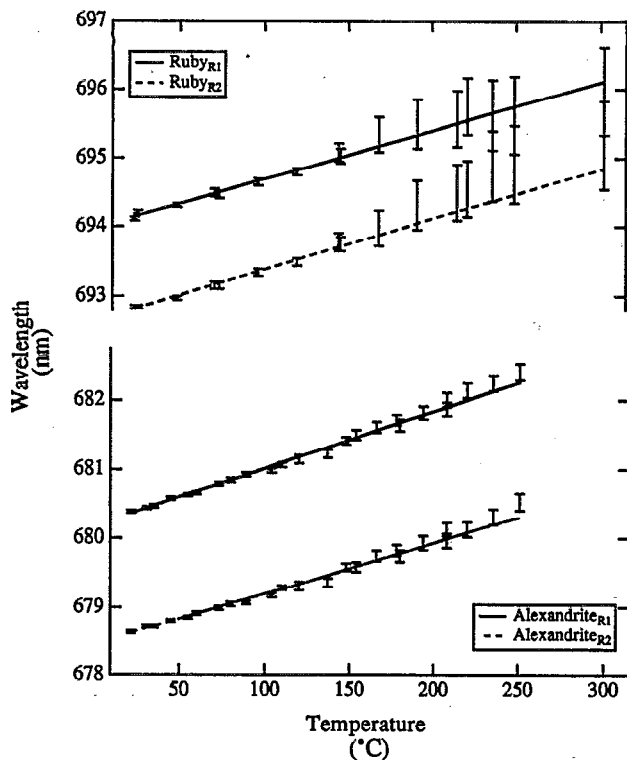
FIG. 2. Temperature dependencies of the $R1$ and $R2$ lines of alexandrite and ruby at zero pressure.
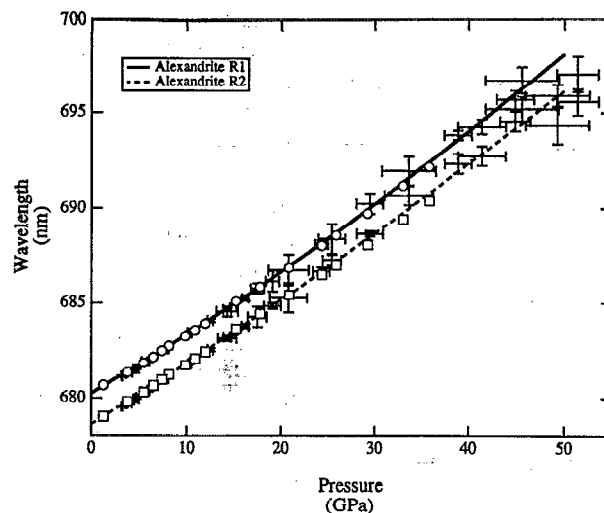

FIG. 3. Pressure dependencies of the $R1$ and $R2$ lines of alexandrite up to 50 GPa, using both argon (open symbols) and 4:1 methanol:ethanol as pressure transmitting medium.

respectively (Table I). For comparison, we find that the $R1$ and $R2$ ruby lines shift by 7.0 (± 0.4)$\times 10^{-3}$ nm/K and 7.3 (± 0.4)$\times 10^{-3}$ nm/K, in good agreement with values reported in the literature (Fig. 2, Table I).[24]

The pressure-dependent wavelengths of the two alexandrite lines are found to fit well to a second-order polynomial, λ(nm) $= a + bP + cP^2$ with P in GPa. As shown in Fig. 3, and indicated in Table I, the pressure dependencies of the alexandrite fluorescence lines differ markedly from those of the ruby $R1$ and $R2$ lines. In particular, for both alexandrite fluorescence lines the constant c is larger than zero, implying a positive curvature of the wavelengths with pressure. This contrasts with the negative curvature ($c < 0$) that is observed for ruby. Also, the positive curvature

would appear to rule out a simple volume dependence for the $R1$ and $R2$ wavelengths of alexandrite, because volume compressibility invariably decreases with increasing pressure.[25]

To analyze the high-temperature measurements at elevated pressures, the pressure was first determined by assuming that the temperature shift of the $R1$ line of ruby is independent of pressure: that is, by ignoring the $\partial^2 \lambda / \partial P \partial T$ cross derivative. We then check this assumption by comparing the implied temperature dependencies of the alexandrite lines at high pressures against the temperature shifts measured at zero pressure (Table I). Our measurements indeed show that the temperature dependencies inferred for the alexandrite lines do not change with pressure, leading us to conclude that the cross derivatives for both ruby and alexandrite are equal and, most likely, negligible.

TABLE I. Pressure and temperature dependence of $R1$ and $R2$ lines of alexandrite and the $R1$ line of ruby.[a]

	a(nm)	b(nm/GPa)	c(pm/GPa^2)	$d\lambda/dT$ (pm/K)
Alexandrite$_{R1}$	680.26(0.01)	0.292(0.003)	1.3(0.1)	8.7(0.3)
Alexandrite$_{R2}$	678.63(0.01)	0.310(0.003)	0.80(0.01)	7.8(0.2)
Ruby$_{R1}$	694.24[b]	0.364[b]	-0.35[b]	7.0(0.4)
	694.24[c]	0.325[c]	-0.34[c]	6.8[d]

[a]The pressure dependence of each fluorescence wavelength is expressed as $\lambda = a + bP + cP^2$. Unless otherwise referenced, all values are from the present study.

[b]Nonhydrostatic calibration, from Ref. 2.

[c]Least squares fit for a second order polynomial to the hydrostatic calibration of Ref. 21.
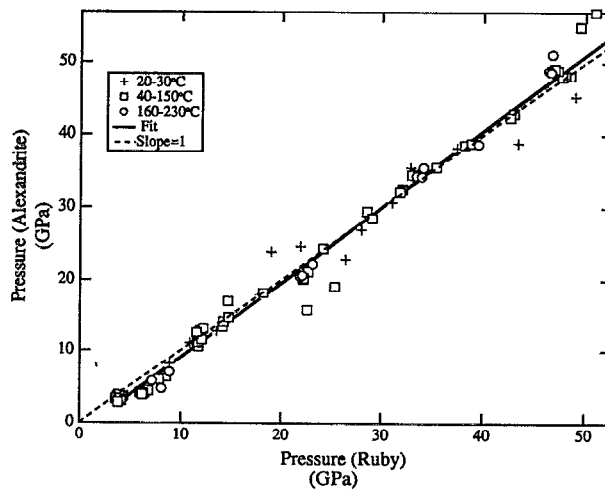
[d]Reference 24.

FIG. 4. Pressure as determined by the alexandrite fluorescence plotted against pressure determined by the ruby fluorescence scale, after the temperature shift has been subtracted. Representative uncertainties are shown in the lower right portion of the graph, (from top to bottom): for the high, medium, and low pressure measurements, respectively. The linear least squares fit to the data, shown by the solid line, has a slope of 1.05, whereas a 1:1 correlation is indicated by the dashed line.

One way to document this conclusion is illustrated in Fig. 4, which compares the pressures determined in our experiments from the alexandrite and ruby fluorescence shifts. For both calibrants, the effect of temperature has been subtracted out, assuming the zero-pressure values for the temperature shifts (Table I). The agreement between the two values of pressure obtained in this manner supports our assumption that the $\partial^2 \lambda / \partial P \partial T$ term is negligible in comparison with the separate temperature coefficients given in Table I. Although these results do not rule out the possibility that the cross derivative is nonzero and equal for the fluorescence lines of both ruby and alexandrite, we view such a coincidence as being unlikely because of the fact that none of the separate pressure and temperature coefficients for alexandrite equal those of ruby.

CONCLUSIONS

The wavelengths of the $R1$ and $R2$ fluorescence lines of alexandrite have been calibrated up to 50 GPa, with no dependence of the results on degree of hydrostaticity being noted within the range of our experimental conditions. In addition, the fluorescence spectra of the $R1$ and $R2$ lines of alexandrite do not reflect a phase transition at approximately 10 GPa, as has been previously thought, and display no measurable hysteresis with either pressure or temperature cycling.[5] Rather, the wavelength shift with pressure is not well fit by a straight line, but by a second-order polynomial as indicated in Fig. 3. Both ruby and alexandrite can be used as secondary-pressure standards at elevated temperatures, (up to 550 K and 50 GPa) and we have found that the pressure–temperature cross derivatives are negligible to within our experimental uncertainties.

ACKNOWLEDGMENTS

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