Dependence of R fluorescence lines of rubies on Cr$^{3+}$ concentration at various temperatures, with implications for pressure calibrations in experimental apparatus

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ABSTRACT

The R fluorescence lines of rubies that contain 0.022, 0.068, 0.211, 0.279, 0.356, 1.221, and 1.676 wt% of Cr$\text{O}_3$ were measured at temperatures of 100–600 K and at atmospheric pressure. The R 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$\text{O}_3$ content in the rubies increased from 0.022 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$\text{O}_3$ 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 cm$^{-1}$/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$\text{O}_3$ in rubies used by previous researchers (0.062, 0.5, ~1, and 2 wt% Cr$\text{O}_3$ 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 wavelength-dispersive spectroscopy (WDS) 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$\text{O}_3$ 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