

Investigations of the Thermal Shifts and Electron–Phonon Coupling Parameters of R_1 and R_2 Lines for Cr^{3+} -doped Forsterite

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The thermal shifts of R_1 and R_2 lines in Cr^{3+} -doped forsterite (Mg_2SiO_4) are studied by considering both the static contribution due to lattice thermal expansion and the vibrational contribution due to electron–phonon interaction. In the studies, the thermal expansion coefficient of the Cr^{3+} center is assumed reasonably as that of the corresponding cluster in the host crystal. The results suggest that for R_1 and R_2 lines the static contributions are opposite in sign and in magnitude about 37% and 45%, respectively, of the corresponding vibrational contributions. The true electron–phonon coupling coefficients α' (obtained by considering both contributions) increase by about 58% and 81%, respectively, for R_1 and R_2 lines in comparison with the corresponding parameters α obtained by considering only the vibrational contribution. It appears that for the reasonable explanation of thermal shift of spectral lines and the exact estimation of electron–phonon coupling coefficient, both the static and vibrational contributions should be taken into account.

Key words: Thermal Shift; Optical Spectrum; Electron–Phonon Coupling; Mg_2SiO_4 ; Cr^{3+} .

1. Introduction

Chromium (Cr)-doped forsterite Mg_2SiO_4 crystals have been paid attention as laser material [1–7]. In the crystals, the impurities Cr^{3+} and Cr^{4+} occupy the Mg^{2+} and Si^{4+} sites, respectively. The tetravalent Cr^{4+} ion with $3d^2$ configuration at the tetrahedral Si^{4+} site of Mg_2SiO_4 is the active center of tunable lasers and of ultrashort-pulse lasers in the near-infrared region of wavelength centered at 1235 nm, whereas the trivalent Cr^{3+} ion with $3d^3$ configuration at the octahedral Mg^{2+} sites is the active center of laser media for the shorter wavelength region [5, 8]. The position and width of a spectral line in laser crystals can change with temperature. Since the thermal shift and thermal broadening of laser lines are closely connected with the output frequency stability, light amplification gain, and thermal tunability of lasers [9–13], the investigations of thermal effects on the position and width of spectral lines are of interest. The thermal shifts (or temperature dependences) of R_1 and R_2 lines in Cr^{3+} -doped Mg_2SiO_4 crystals (Cr^{3+} at Mg(1) site) were measured by Komura et al. [8]. They described the thermal shifts ΔE (or $\Delta\nu$) of both R lines by using the following ex-

pression based on the vibrational contribution due to the dominant Raman two-phonon process in the framework of the Debye model:

$$\Delta E(T) = \Delta E(0) - \alpha \left(\frac{T}{T_D} \right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx, \quad (1)$$

where $\Delta E(0)$, α , and T_D are, respectively, the line shift near $T \approx 0$ K, the electron–phonon coupling parameter, and the effective Debye temperature. From the observed thermal shifts, the authors of [8] deduced following results for the R_1 -line of $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$: $\alpha \approx 345 \text{ cm}^{-1}$, $T_D \approx 490$ K, and for the R_2 line, $\alpha \approx 220 \text{ cm}^{-1}$, $T_D \approx 440$ K (note that for both R lines, $\Delta E(0) \approx 0$). However, it is to be recognized that the thermal shifts $\Delta E(T)$ of a spectral line come from two contributions (or mechanisms). One is the above vibrational or explicit contribution $\Delta E_{\text{vib}}(T)$ due to electron–phonon interaction and the other is the static or implicit contribution $\Delta E_{\text{st}}(T)$ due to lattice thermal expansion [9, 10, 14–17]. Maybe partly for simplicity, partly for the difficulty in the determination of relative importance of both contributions and partly because the above vibrational contribution (i. e., (1)) can

provide the good fits to the observed thermal shifts of many spectral lines in crystals (including R_1 and R_2 lines in $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ considered) [8, 11–13], in many previous papers [8, 11–13, 18–22], the thermal shifts and the electron–phonon coupling parameters of spectral lines have been analyzed considering only the above vibrational contribution. Nevertheless, the neglect of the static contribution can result in an incomplete understanding of thermal shifts and hence in the derivation of apparent rather than true and exact electron–phonon coupling parameters. In this paper, we study the thermal shifts of R_1 and R_2 lines in the $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ crystal by taking both the static and vibrational contributions into account. Based on this, suitable and true electron–phonon coupling parameters are obtained. The results are discussed.

2. Calculation

By considering both the static and vibrational contributions, a new expression of thermal shift similar to that containing only the vibrational contribution (i. e., (1)) was derived by us as [15]

$$\Delta E(T) = \Delta E(0) + (A - \alpha') \left(\frac{T}{T_D} \right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx, \quad (2)$$

where A is a parameter connected with the static contribution and α' is the true electron–phonon coupling parameter if both static and vibrational contributions are taken into consideration. In (2),

$$\frac{A}{-\alpha'} \approx \frac{(dE(R_i)/dT)_{\text{st}}}{(dE(R_i)/dT)_{\text{vib}}} \approx t, \quad (3)$$

in which $(dE)/(dT)_{\text{st}}$ and $(dE)/(dT)_{\text{vib}}$ are the static and vibrational parts of the temperature dependence of the spectral line near room temperature. The ratio t denotes the relative importance of the static contribution. In [15], the ratio t is estimated by means of the pressure dependence $(dE)/(dP)$ of spectral lines. No experimental values of $(dE(R_i))/(dP)$ ($i = 1, 2$) for $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ crystal were reported. We therefore estimate the ratio t by using the following method: The static part of the temperature dependence $(dE)/(dT)_{\text{st}}$ is caused by the structural change of a cluster due to thermal expansion, thus we have

$$\left(\frac{dE}{dT} \right)_{\text{st}} = \left(\frac{dE}{d\ln R} \right) \left(\frac{d\ln R}{dT} \right), \quad (4)$$

where $(dE)/(d\ln R)$ is the bond length dependence of the line position and $(d\ln R)/(dT)$ is the local thermal expansion coefficient of the studied cluster. For the $(\text{CrO}_6)^{9-}$ octahedral clusters in $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ studied, we estimate reasonably the values of $(dE(R_i))/(d\ln R)$ from the values obtained for a similar $(\text{CrO}_6)^{9-}$ cluster in $\text{Y}_3\text{Al}_5\text{O}_{12}(\text{YAG}):\text{Cr}^{3+}$: the parameter $(dE(R_i))/(d\ln R)$ can be defined from the pressure dependence (or pressure coefficient) of the R_i line position, i. e.,

$$\frac{dE(R_i)}{dP} = \left(\frac{dE(R_i)}{d\ln R} \right) \left(\frac{d\ln R}{dP} \right), \quad (5)$$

where $(d\ln R)/(dP)$ is the local compressibility of the studied cluster. For the $(\text{CrO}_6)^{9-}$ clusters in $\text{YAG}:\text{Cr}^{3+}$ crystals, the pressure coefficients $(dE(R_1))/(dP)$ ($\approx -0.78 \text{ cm}^{-1}/\text{kbar}$) and $(dE(R_2))/(dP)$ ($\approx -0.84 \text{ cm}^{-1}/\text{kbar}$) were measured using high pressure spectroscopy [23]. The local compressibility $(d\ln R)/(dP) \approx -1.1 \cdot 10^{-4} \text{ kbar}$ for $(\text{CrO}_6)^{9-}$ clusters in $\text{YAG}:\text{Cr}^{3+}$ was obtained in [24]. Thus, the parameters $(dE(R_i))/(d\ln R)$ can be calculated through (5) and the results are shown in Table 1. These parameters $(dE(R_i))/(d\ln R)$ can be applied approximately to similar $(\text{CrO}_6)^{9-}$ clusters in other crystals.

The local thermal expansion coefficient $(d\ln R)/(dT)$ of $(\text{CrO}_6)^{9-}$ clusters in Mg_2SiO_4 is estimated as follows: for crystals of complex composition and structure, the studies of crystal structure by X-ray diffraction under pressure (or temperature) show that these crystals do not compress (or expand) uniformly. That is to say, different bonds and clusters in the same crystal change by different amounts with the increasing pressure (or temperature) because the interactive forces in different bonds and clusters are not the same [25–28]. So the local compressibilities (or local thermal expansion coefficients) for the distinctive clusters in the same crystal are unlike, while the usual compressibility (or thermal expansion coefficient) of a crystal represents only the mean value for the whole crystal [25–28]. For example, the X-ray data under high pressure for garnets $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ showed that the local compressibilities of oxygen octahedral clusters in both garnets are about 0.61 ± 0.15 of those of the corresponding value in whole crystals [25]. By studying the high pressure spectra of Cr^{3+} ions in garnets YAG , $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ (LLGG), $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG), and $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$

(GSGG), we found that the local compressibilities $(d\ln R)/(dP)$ of the octahedral impurity clusters $(\text{CrO}_6)^{9-}$ are also almost 0.6 of the corresponding values in the whole crystals [24, 29]. This suggests that the local compressibility of impurity cluster is close to that of the corresponding cluster in the host crystals. This point has been further confirmed by the following fact: the pressure-induced shifts of R -lines for Cr^{3+} at both octahedral sites, the mirror site and inverse site, in BeAl_2O_4 crystal can be reasonably explained by using the corresponding local compressibility of both octahedral sites (or clusters) in BeAl_2O_4 [30] obtained from X-ray data under high pressure [31]. For the local thermal expansion coefficient of an impurity cluster in crystals, from the Grüneisen relationship $\alpha_{\text{th}}/\beta = \gamma C_V/V$ [32], one can find that the ratio α_{th}/β (thermal expansion coefficient/compressibility) for a cluster in crystals is very close to that in the whole host crystal [15–17]. As an approximation, we can assume that the local thermal expansion coefficient of an impurity cluster is, similar to the local compressibility, close to the corresponding cluster in the host crystal. From X-ray data as a function of temperature, the local thermal expansion coefficient $(d\ln R)/(dT)$ of the $(\text{Mg}(1)\text{O}_6)^{10-}$ octahedron in Mg_2SiO_4 crystal is about $1.34 \cdot 10^{-5}/\text{K}$ [28]. Thus, from (4), the static contributions $(dE(R_i))/(dT)_{\text{st}}$ ($i = 1, 2$) for $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ can be calculated and the results are given in Table 1. Based on these values, the vibrational contributions $(dE(R_i))/(dT)_{\text{vib}}$ can be obtained from the total or observed temperature dependence of R lines $(dE(R_i))/(dT)_{\text{obs}}$ through the formula [15]

$$\left(\frac{dE(R_i)}{dT}\right)_{\text{obs.}} = \left(\frac{dE(R_i)}{dT}\right)_{\text{st}} + \left(\frac{dE(R_i)}{dT}\right)_{\text{vib}}. \quad (6)$$

The observed $(dE(R_i))/(dT)_{\text{obs}}$ for $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ near room temperature [8] and the calculated $(dE(R_i))/(dT)_{\text{vib}}$ are also listed in Table 1.

From (1)–(3), we have [15]

$$\begin{aligned} A &\approx -\alpha' t, \\ A - \alpha' &\approx -\alpha' t - \alpha' \approx -(t+1)\alpha' = -\alpha. \end{aligned} \quad (7)$$

Thus, from the apparent electron–phonon coupling parameters α for R_1 and R_2 lines obtained in [8] by considering only the vibrational contribution, the true electron–phonon coupling parameters α' and hence the parameters A concerning the static contribution for both R lines in $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ crystal can be acquired. The results are also shown in Table 1.

3. Discussion

In [8], Komura et al. found that the parameters T_D (≈ 490 K) and α (≈ 345 cm^{-1}) obtained for the R_1 line do not give the best fit to the observed thermal shift of the R_2 line in the same $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$ crystal. They therefore assumed another set of parameters, $T_D \approx 440$ K and $\alpha \approx 220$ cm^{-1} , for the R_2 line. These parameters can give a better fit to the observed thermal shifts of the R_2 line. However, it is difficult to understand that for the same $(\text{CrO}_6)^{9-}$ cluster in a crystal, the effective Debye temperature T_D of the R_1 line is unlike that of the R_2 line. In fact, by analyzing the thermal shifts and thermal broadenings of R_1 and R_2 lines for $(\text{CrO}_6)^{9-}$ clusters in YAG, $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG), $\text{Y}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ (YSAG), and $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ (GSAG) garnet crystals, Vink and Meijerink [13] found that for $(\text{CrO}_6)^{9-}$ clusters in each garnet the effective Debye temperature T_D obtained for both R_1 and R_2 lines are the same. Considering the experimental errors, we find that when $T_D \approx 490$ K (the value used for the R_1 line), the parameter $\alpha \approx 260$ cm^{-1} can give the reasonable fit to the observed thermal shift of the R_2 line. Based on the value of α , the parameters α' and A for the R_2 line can be estimated through (7), the results are also given in Table 1. It can be seen that the difference of α (and hence α' and A) between R_1 and R_2 lines in the same $(\text{CrO}_6)^{9-}$ cluster in Mg_2SiO_4 become smaller and so they seem to be more suitable.

From Table 1, one can find that the static contributions to the thermal shifts of R_1 and R_2 lines for Cr^{3+} in Mg_2SiO_4 are contrary in sign and in magnitude about 37% and 45%, respectively, of the corresponding vibrational contribution. So the static contribution cannot be ignored. When both the static and vibrational contributions are taken into account, the true electron–phonon coupling parameters α' increase respectively by about 58% and 81% in comparison with the apparent electron–phonon coupling parameters α obtained by only considering the vibrational contributions for R_1 and R_2 lines in $\text{Mg}_2\text{SiO}_4:\text{Cr}^{3+}$. It should be pointed out that there may be some errors in the relative importance of static contribution and the parameters α' and A because of the experimental errors and the approximation used in the studies. It can be concluded, however, that for a reasonable explanation of thermal shifts and the determination of true rather than apparent electron–phonon coupling parameters of

Table 1. Bond length dependence of line position $(dE(R_i))/(d\ln R)$, observed temperature dependences $(dE(R_i))/(dT)_{\text{obs}}$, and parameters connected with the static and vibrational contributions to the thermal shifts of R_1 and R_2 lines for Mg₂SiO₄:Cr³⁺ crystal, see text.

Line	$\frac{dE(R_i)}{d\ln R}$ (10 ⁴ cm ⁻¹)	$\left(\frac{dE(R_i)}{dT}\right)_{\text{obs}}$ (10 ⁻¹ cm ⁻¹ /K)	$\left(\frac{dE(R_i)}{dT}\right)_{\text{st}}$ (10 ⁻¹ cm ⁻¹ /K)	$\left(\frac{dE(R_i)}{dT}\right)_{\text{vib}}$ (10 ⁻¹ cm ⁻¹ /K)
R_1	0.71	-1.6 [8]	0.95	-2.55
R_2	0.76	-1.2 [8]	1.0	-2.2
Line	t (%)	α (cm ⁻¹)	α' (cm ⁻¹)	A (cm ⁻¹)
R_1	-0.37	345	547	202
R_2	-0.45	220 ^a , 260 ^b	400 ^a , 473 ^b	180 ^a , 213 ^b

^a Obtained with $T_D \approx 440$ K in [8].^b Obtained with $T_D \approx 490$ K, the value of T_D used for the R_1 line, in this paper.

spectral lines in crystals not only the vibrational contribution, but also the static contribution (which is often neglected in the previous papers) should be considered.

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