LETTER TO THE EDITOR

The effect of mass difference between host ions on the thermal shift and broadening of the spectral lines of the active ions in crystals

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Abstract
It is shown in this letter that the mass difference between ions of the host crystals has an effect on the thermal broadening and shift of the spectral lines of active ions in the crystals. The effect is expressed as a multiplication factor D^2 for the thermal broadening and shift caused by the one-phonon absorption and emission mechanism, and a multiplication factor D^4 for the thermal broadening caused by the Raman scattering process. The expressions for the D-factor are given for crystals constituted of two and three kinds of ion respectively.

The broadening and shift of spectral lines of the active ions in crystals relate directly to the pumping and laser output properties and are generally of relevance in studies of laser materials. The subject is also of great current interest in fields such as optical signal processing and storage as well as quantum information technology where line broadening is viewed in the time domain as optical dephasing, which is an important limitation on processing capacity. Nowadays, much attention is being paid to the Yb^{3+} laser tunable in the range of 1030–1080 nm and the Er^{3+} laser amplifier at 1550 nm with a wide gain bandwidth in the solid-state laser field. The performances of these devices are also directly related to the line broadening and shift of luminescence lines. Therefore, the study of this subject has both theoretical and practical importance.

The paper published by McCumber and Sturge [1] is highly regarded as an enormously influential work which has brevity and clarity, and its main conclusions can be applied quite generally [2]. In fact, their model is now very widely used in different publications in the field of luminescence and laser materials [3–6]. In their model, however, they did not take into account the fact that the masses of different ions constituting a practical host crystal are different, but assumed that all of the ions in the host crystal have the same mass. This is a radical approximation and the effect of the mass difference between different ions in hosts on the thermal broadening and shift of the spectral lines of the active ions in crystals cannot be

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estimated from their model. Laser crystals, constituted of oxides or fluorides, are dielectric materials and contain at least two kinds of host ion with different masses in general. Therefore the effect of the mass difference between the host ions has to be considered when the effects of structure and composition of hosts on the broadening and shift of the spectral lines are studied. In this letter, on the basis of the theory of thermal broadening and shift due to the mechanisms of one-phonon absorption, one-phonon emission and Raman scattering, the related formulae are re-derived from the actual mass difference between ions in the hosts. The results show the contributions from mass difference between host ions in crystals to the thermal broadening and shift of the spectral lines.

In the conventional theory, the assumption that host crystals were constituted simply of ions with the same mass m_α was adopted. When distortion of the lattice is caused by thermal vibration, the strain can be expressed by [3]

$$\varepsilon = i \sum_{k,\alpha} \left(\frac{\hbar \omega_k}{2 N m_\alpha v^2} \right) (a(k) - a^+(k)) \tag{1}$$

where $a(k)$ and $a^+(k)$ are annihilation and creation operators. m_α is the mass of the ion, N is the total number of ions in the crystal, k is the wave vector of the phonon and $Q(k)$ the normal coordinate. The dielectric host is generally constituted of more than two kinds of ion with different masses. The assumption of different ions having the same mass is far from reality. In our following analysis, the change of the formulae concerning the thermal broadening and shift caused by the mass difference between host ions is taken into account.

Considering a crystal composed by N_m molecules, each constituted of n_α ions with mass m_α and n_β ions with mass m_β, the number of ions in a molecule is $n = n_\alpha + n_\beta$, the number of the total ions in the crystal is $N = n N_m$ and the mass of the crystal is $M = N_m(n_\alpha m_\alpha + n_\beta m_\beta)$. In general, only one lattice vibration mode plays a major part in the interaction with the active ions, so it is reasonable to analyse the thermal broadening of spectral lines using the single-mode approximation. In this approximation, the average strain of the ions is

$$\bar{\varepsilon} = i \sum_{k,\alpha} \frac{1}{n} \left(n_\alpha \left(\frac{\hbar \omega_k}{2 N_m n m_\alpha v^2} \right) + n_\beta \left(\frac{\hbar \omega_k}{2 N_m n m_\beta v^2} \right) \right) (a(k) - a^+(k)) \tag{2}$$

and then (2) can be written as

$$\bar{\varepsilon} = i D \sum_{k,\alpha} \frac{1}{n} \left(\frac{\hbar \omega_k}{2 M v^2} \right) (a(k) - a^+(k)) \tag{3}$$

where

$$D = \left[\frac{m(n_\alpha \sqrt{m_\beta} + n_\beta \sqrt{m_\alpha})^2}{n^3 m_\alpha m_\beta} \right]^{1/2} \tag{4}$$

and $m = n_\alpha m_\alpha + n_\beta m_\beta$ is the molecular mass. Obviously, when $m_\alpha = m_\beta$, $D = 1$.

If there are three kinds of host ion with different masses in one crystal, the factor D can be derived by the same process, as

$$D = \left\{ \frac{m(n_\alpha \sqrt{m_\beta m_\gamma} + n_\beta \sqrt{m_\alpha m_\gamma} + n_\gamma \sqrt{m_\alpha m_\beta})^2}{n^3 m_\alpha m_\beta m_\gamma} \right\}^{1/2} \tag{5}$$

where $n = n_\alpha + n_\beta + n_\gamma$ and $m = n_\alpha m_\alpha + n_\beta m_\beta + n_\gamma m_\gamma$.

The interaction between electrons and lattice vibrations can be expressed as [6]

$$V_{e-p} = V_1 \bar{\varepsilon} + V_2 \bar{\varepsilon}^2 + \cdots. \tag{6}$$

The first term in this equation is the interaction with one phonon and is given by

$$H_{\mathrm{e-sp}} = iV_1 D \sum_k \left(\frac{\hbar\omega_k}{2Mv^2}\right)^{1/2} [a(k) - a^+(k)]. \tag{7}$$

According to the theory of thermal broadening of the spectral lines of the active ions in crystals [1], which has been generally accepted, the thermal broadening caused by one-phonon absorption and emission can be expressed as

$$\Delta E_{\mathrm{sp}}\ (\mathrm{cm}^{-1}) = \sum_{f>i} \beta_{fi} \frac{1}{\mathrm{e}^{\hbar\omega^{\mathrm{e}}_{fi}/kT} - 1} + \sum_{f<i} \beta_{if} \frac{1}{\mathrm{e}^{\hbar\omega^{\mathrm{e}}_{if}/kT} - 1} + \sum_{f<i} \beta_{if} \tag{8}$$

where

$$\beta_{fi} = \frac{1}{c} \frac{(\omega^{\mathrm{e}}_{fi})^3 D^2}{2\pi\rho\hbar} \left(\frac{1}{v_l^5} + \frac{2}{v_t^5}\right) |\langle f|V_1|i\rangle|^2 \tag{9}$$

or simply

$$\beta_{fi} = \frac{3}{c} \frac{(\omega^{\mathrm{e}}_{fi})^3 D^2}{2\pi\rho\hbar v^5} |\langle f|V_1|i\rangle|^2. \tag{10}$$

Similarly, the second term in equation (6) is given by

$$H_{\mathrm{e-dp}} = -V_2 \frac{\hbar D^2}{2Mv^2} \sum_{kl} \sqrt{\omega_k\omega_l} [a(k) - a^+(k)][a(l) - a^+(l)]. \tag{11}$$

Unlike in the conventional formulae [3], multiplication factors D and D^2 appear in equations (7) and (11) respectively. In the same way, the thermal broadening induced by the Raman scattering mechanism can be obtained:

$$\Delta E(T)\ (\mathrm{cm}^{-1}) = \bar{\alpha} \left(\frac{T}{T_D}\right)^7 \int_0^{T_D/T} \frac{x^6 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\ \mathrm{d}x \tag{12}$$

where

$$\bar{\alpha} = \frac{1}{c} \frac{9D^4}{2\pi^3\rho^2 v^{10}} \left(\frac{kT_D}{\hbar}\right)^7 \left(\sum_{\gamma\neq\alpha} \frac{\langle\beta|V_1|\gamma\rangle\langle\gamma|V_1|\alpha\rangle}{E_\alpha - E_\gamma} + \langle\beta|V_2|\alpha\rangle\right)^2. \tag{13}$$

In the derivation of the formula for thermal shift of spectral lines, the Hamiltonian operators in equations (7) and (11) are adopted. When $|E_i - E_j| \gg \hbar\omega_D$, the shift is expressed in units of the wavenumber as

$$\delta E\ (\mathrm{cm}^{-1}) = \alpha \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3}{\mathrm{e}^x - 1}\ \mathrm{d}x \tag{14}$$

where

$$\alpha = \frac{3V}{4\pi^3 v^3 c} \left(\frac{kT_D}{\hbar}\right)^4 a \tag{15}$$

and

$$a = \frac{\hbar D^2}{Mv^2} \left[\sum_{\beta\neq\alpha} \frac{|\langle\alpha|V_1|\beta\rangle|^2}{E_\alpha - E_\beta} + \langle\alpha|V_2|\alpha\rangle\right]. \tag{16}$$

When $|E_i - E_j| \leqslant \hbar\omega_D$, the second-order term in equation (6) is negligible and the shift is similarly expressed as

$$\delta E_i\ (\mathrm{cm}^{-1}) = \sum_{\beta\neq\alpha} \frac{1}{2\pi^2} \beta_{a\beta} \left(\frac{T}{T_{\alpha\beta}}\right)^2 \left[\mathrm{PV} \int_0^{T_D/T} \frac{x^3}{\mathrm{e}^x - 1} \frac{1}{(T_{\alpha\beta}/T)^2 - x^2}\ \mathrm{d}x\right]. \tag{17}$$

In equation (17), the principal value (PV) of the integral is introduced.

It is easy to show that the factor D equals 1 when all of the ions in a crystal have the same mass, and it increases with the mass difference between different kinds of ion in the crystal. Therefore, when the other conditions are invariable, the thermal broadening and shift of lines increase with the mass difference between ions. The varying range of D^2 is demonstrated by two examples here. Firstly, for the crystals constituted of two kinds of ion Y_2O_3, La_2O_3 and Gd_2O_3, the values of D^2 are 1.68, 2.21 and 2.40 respectively; secondly, for the crystals constituted of three kinds of ion $Y_3Al_5O_{12}$ (YAG), $Y_3Ga_5O_{12}$ (YGG) and $Gd_3Ga_5O_{12}$ (GGG), the values of D^2 are 1.37, 1.55 and 1.86 respectively.

Our analyses show that the mass difference between ions in a crystal has an effect on the thermal broadening and shift of spectral lines of the active ions. The effect is expressed as a multiplication factor D^2 for the thermal broadening and shift caused by the one-phonon absorption and emission mechanism, and a multiplication factor D^4 for the thermal broadening caused by the Raman scattering process. With a larger difference of the masses of different ions in the crystals, the thermal broadening induced by the mechanisms of phonon absorption, emission and Raman scattering will be larger. Of course, other factors such as phonon frequency, crystal density and sound velocity could also influence the thermal broadening and shift of the spectral lines of the active ions in crystals. The density of crystals may increase with the value of D^2. As an example, the values of D^2 for the crystals YAG and $YAlO_3$ (YAP) are 1.36 and 1.44 respectively, and accordingly the densities for the crystals YAG and YAP are 4.55 g cm^{-3} and 5.35 g cm^{-3} respectively. Can the increasing of density countervail the effect of D? The sound velocity in solids is proportional to the quadratic root of the modulus of elasticity and inversely proportional to the quadratic root of the density. As expected, the thermal broadening and shift will increase as the value of D when the modulus of elasticity does not increase as the density. In the examples of YAG and YAP crystals, the density increases with decrease of the modulus of elasticity, so the effect of the factor D is quite obvious.

References

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