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The Polarized Spectra and Thermal Diffusivity of Brown Tourmaline as Studied by Photoacoustic Spectroscopy

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The strong pleochroic band of brown tourmaline at around 24000 cm^{-1} in the E$\perp$c photoacoustic spectra was assigned to d-d($^6A_1 \rightarrow ^4A_1$, ^4E) transition of Fe and to charge transfer of Ti, that in the E//c spectra being entirely assigned to charge transfer of Ti. The analysis of the photoacoustic signal intensity *vs.* chopping frequency gave the thermal diffusivity constant of tourmaline as $\alpha = 0.15$ cm^2/s.

Tourmaline is a complex solid-solution mineral represented by $Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$.[1,2] The color is usually black but varies a great deal with composition, being brown, blue, green, colorless (iron-free varieties) and pink (lithium-bearing varieties). Some varieties with intermediate coloration of brown or bluish green show strong pleochroism. The origin of the colors and the pleochroism of silicate minerals including tourmaline have been extensively studied mainly by means of polarized absorption spectra. Many of the bands or peaks observed are explained in terms of the d-d transitions and/or charge transfer electron hopping within transition metal ions contained.[3] However, the strong pleochroic band of brown tourmaline observed around 22000—24000 cm^{-1}, has not yet been clarified. Two contradicting explanations have been given,[4,5] ascribing the band to (a) the d-d transition of Fe and (b) the electron hopping (charge transfer) of $Ti^{3+} \rightarrow Ti^{4+}$ type.

Polarized photoacoustic spectra of a brown tourmaline we observed in both the in-phase and out-of-phase modes will help clarify the nature of the relaxed thermal energy and make assignment of the band. The dependence of the photoacoustic intensity on the chopping frequency of the irradiating light gives information on the thermal diffusivity of the sample.

Experimental

Sample. A single crystal of brown tourmaline was used (locality unknown). ICP analysis gave the metal contents of Mg:0.64 wt%, Ti:0.32%, Mn:0.28%, Fe:5.74%, and Li:0.54%, showing that the sample has the intermediate composition of typical endmembers of dravite $NaMg_3Al_6B_3Si_6O_{27}(OH,F)_4$, schorl $Na(Fe,Mn)_3Al_6B_3Si_6O_{27}(OH,F)_4$, and elbaite $Na(Li,Al)_3Al_6B_3Si_6O_{27}(OH,F)_4$.[1)]

The structure of dravite has been determined by Donnay and Buerger.[6] Each magnesium ion is surrounded by four oxygen and two OH ions forming a fairly regular octahedron. Three of these octahedra are combined in an arrangement similar to the "trigonal brucite units", where each octahedron shares two of its octahedral edges with its neighbors in the 001 plane. Aluminium ion is centered in distorted (O,OH) octahedra. Each shares two of its edges with another two Al-octahedra diagonally above and below the 001 plane, resulting in spiral chains of Al-octahedra parallel to the c-axis. The ratios Fe^{2+}:Fe^{3+} and Ti^{3+}:Ti^{4+} are not known. However, small amounts of Fe^{3+} and Ti^{4+} are considered to occupy the Al sites.

Apparatus. The apparatus for measuring photoacoustic spectra consists of a 300 W xenon lamp, mechanical light chopper, spectrometer (25 cm, CT-25N, JASCO), photoacoustic cell with a microphone, lock-in amplifier (NF Circuit Design Block, LI-574) and a recorder. The block diagram and a brief account of the setup was reported.[7,8] In order to normalize the power spectrum of the xenon lamp, a part of the incident light was reflected by a mirror and led to another photoacoustic cell with a carbon black reference, the output of which was also lock-in amplified and compared with the signal from the main cell at the dividing unit (Rika-Denki, XB-20).

For the measurement of polarized spectra, the spectra of the tourmaline and the carbon black sample were recorded in separate runs, the comparison (division) of the results being manually conducted. This is because the intensity of the exciting light gets down to 1/4—1/5 of that just before the polarizer, resulting in an unstable work of the dividing unit. Separate measurement is also appropriate for avoiding the polarizing characteristics of the reflecting mirror.

Results and Discussion

Figure 1 shows the photoacoustic spectra of the tourmaline crystal for the case of E$\perp$c, *i.e.*, when the electric vector is vibrating in the plane perpendicular to the c-axis, and for the case of E//c. The solid lines indicate the in-phase spectra and the dashed lines the out-of-phase spectra which show the 90° phase-delayed signal (slow heat) with respect to the in-phase signal. The in-phase spectral patterns are very similar to those of the optical absorption spectra

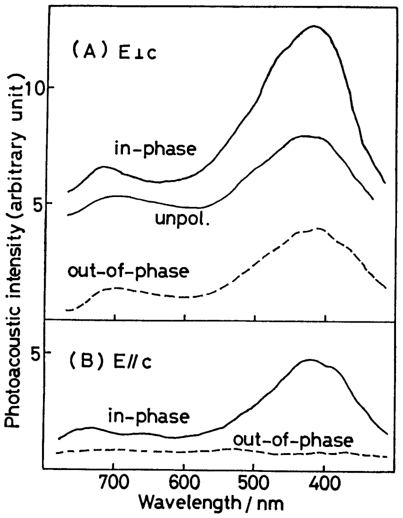

Fig. 1. In-phase and out-of-phase photoacoustic spectra of brown tourmaline at 80 Hz for polarized irradiation of E$\perp$c (A), and E//c (B). Unpolarized spectrum is also shown in (A).

of a Brazilian dravite[4] or a Gouverneur dravite,[5] suggesting that the origin of the color and the strong pleochroism is attributed to a similar mechanism in these tourmalines. The pleochroism is considered to arise from the band at 24000 $\mathrm{cm^{-1}}$, which is larger in the $E \perp c$ spectrum than in the $E // c$ spectrum. The 14500 $\mathrm{cm^{-1}}$ band has little influence on the color of the crystal, since the spectrum is strongly dominated by the pleochroic band at 24000 $\mathrm{cm^{-1}}$.

Wilkins *et al.*[4] assigned the 24000 $\mathrm{cm^{-1}}$ band to the d-d transition of $\mathrm{Fe^{3+}}$ ($^6A_1 \rightarrow {}^4A_1$, ^4E) which might be present in the aluminium position of dravite from Brazil containing 1.38% total Fe. On the other hand, Manning[5] assigned the band to the charge transfer of titanium ions located at Mg and Al site in a dravite sample containing Ti 1.15% and Fe 1.01% (the ratio $\mathrm{Ti^{3+}:Ti^{4+}}$ not known). According to his discussion lobes of t_{2g} orbitals of a cation located in the trigonal units are directed towards neighboring cations in the same trigonal units and in the spiral chains, making t_{2g}-t_{2g} orbital overlap in the 001 plane. Thus the charge transfer is most likely to occur in the trigonal cation plane, as represented by the $E \perp c$ spectra. A small fraction of the $\mathrm{Ti^{3+}}$ is located in the spiral chains which run parallel to the c-axis. Metal-metal orbital overlap also takes place. The transition t_{2g}-e_g would have appreciable intensity in $E // c$ spectra.

The key to the assignment of the 24000 $\mathrm{cm^{-1}}$ band should be found in the out-of-phase spectra, where an appreciable band intensity is observed in the $E \perp c$ spectra and none in the $E // c$ spectra. This shows that the band at 24000 $\mathrm{cm^{-1}}$ in the in-phase $E \perp c$ spectra consists of thermally delayed signal (slow heat) with a certain contribution from fast heat component, while that in the in-phase $E // c$ spectra entirely consists of the fast heat component. Assuming that the transition occurs only between the two energy levels concerned, a rough estimation of the characteristic lifetime of the slow heat is made by means of the relation

$$\tan \theta = 2\pi\nu\tau,$$

where θ is the phase delay angle and ν the chopping frequency. With the data of $\nu = 80$ Hz and $\theta = 10.0°$, lifetime τ is obtained as slow as 3—4×10^{-4} s. This suggests that the transition responsible for the slow heat is due to the forbidden d-d type transition. The fast heat should be attributed to the allowed charge transfer type transition and order of magnitude greater than the d-d transition. Consequently the 24000 $\mathrm{cm^{-1}}$ band in the in-phase $E \perp c$ spectra should be assigned to the d-d ($^6A_1$—$^4A_1$, ^4E) transition of $\mathrm{Fe^{3+}}$ as proposed by Wilkins *et al.*, as well as to the charge transfer of $\mathrm{Ti^{3+} \rightarrow Ti^{4+}}$ as proposed by Manning. The band in the in-phase $E // c$ spectra should be assigned entirely to the charge transfer of Ti located in the spiral chains of Al-centered octahedra as explained by Manning. Although the ratio of the contributions from the d-d transition of Fe and the charge transfer of Ti is not known in the in-phase $E \perp c$ spectra, the latter contribution should not be completely neglected, since the tourmaline sample contains 0.32% Ti which exceeds the detectable amount for the charge transfer band as in the in-phase $E // c$ spectra.

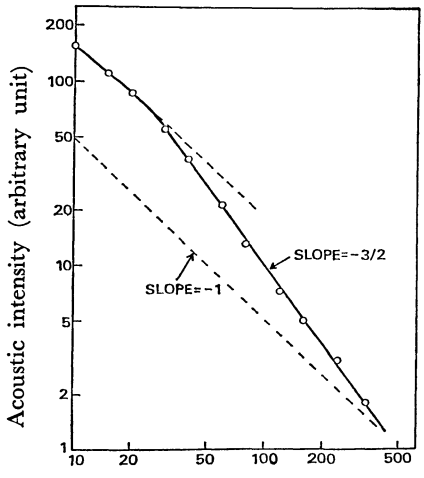

Fig. 2. A log-log plot of the photoacoustic intensity *versus* chopping frequency for brown tourmaline at 588 nm.

Thermal Diffusivity of Tourmaline. By photoacoustic study we can measure the thermal diffusivity of materials, since the intensity of photoacoustic signal depends on the thermal characteristics of the specimen as well as on the extent of the optical absorption. Adams and Kirkbright[9] estimated the thermal diffusivity of macromolecular film by measurement of phase delay as a function of the chopping frequency. An alternative way of measuring the thermal diffusivity of materials is presented here by way of the analysis of the photoacoustic signal intensity as a function of the chopping frequency.

Rosencwaig and Gersho[10] solved a heat flow equation for the treatment of the photoacoustic effect, and showed six cases depending on the relative magnitude of the optical absorption length μ_β and the thermal diffusion length μ_s with respect to the thickness l of the material. The μ_β is defined as an inverse of the optical absorption coefficient β, μ_s being defined by $\mu_s = \sqrt{2\alpha/\omega}$, where α is thermal diffusivity of the material. The photoacoustic signal would show ω^{-1} dependence for the case $\mu_s > l$ corresponding to the cases 1a and 1b, and $\omega^{-3/2}$ dependence for the case $\mu_s < l$ corresponding to the case 1c.[10,11]

The experiment on the tourmaline sample with thickness of $l = 0.044$ cm belongs to the $\mu_\beta > l$ case (case 1), since the μ_β value is obtained as 0.08 cm at the wavelength 588 nm.

Figure 2 shows the plots of the photoacoustic intensity of the toumaline sample as a function of the chopping frequency. With the increase of ω it moves at around $\omega/2\pi = 25$ Hz from a region where the dependence is primarily ω^{-1} to another region where it is $\omega^{-3/2}$. The moving point corresponds to the state of $\mu_s = l$, giving the thermal diffusivity α as

$$\mu_s = l = 0.044 = \sqrt{\frac{\alpha}{\pi \times 25}}$$

$$\alpha \approx 0.15\ \mathrm{cm^2\,s^{-1}}.$$

A similar procedure was applied to a synthetic ruby sample with $l = 0.025$ cm, giving the value of $\alpha = 0.12\ \mathrm{cm^2\,s^{-1}}$, very close to that of tourmaline.

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