Color Centers and Dichroism Investigation in Some Brazilian Species of Tourmaline Using Optoacoustic Tecnique

Rodrigo José da Silva Lima, Reinhard Richard Wegner[a], José Suassuna Filho

Av. Aprígio Veloso, 882 – Campina Grande. Universidade Federal de Campina Grande, Departamento de Física, [a] Departamento de Mineração e Geologia – Centro de Ciências e Tecnologia, Laboratório de Espectroscopia Fotoacústica

rodrigo@df.ufpb.br

Abstract

Photoacoustic Spectroscopy (PAS) experiments in the visible and ultraviolet regions of the electromagnetic spectrum were carried out on a variety of tourmaline species. The results of our investigation show that PAS can be seen as a powerful alternative spectroscopic tool in the identification and characterization of color centers in mineral specimens.

Introduction

Spectroscopic techniques has played an important rule in contemporary mineral studies. It's well known that metal ions (cations) such as Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, V^{3+}, Mn^{2+}, Mn^{3+} either alone or in combination, are responsible for the origin of the colors of many minerals[1],[2],[3]. In some cases, as for instance, green emerald and dark blue beryl was suggested that not only the presence of Fe^{2+}, Fe^{3+} or sometimes Cr^{3+}, but also the Fe^{2+}-Ti^{4+} and Fe^{2+}-Fe^{3+} interactions are necessary for establishing their respective colors[3],[4]. It is a well established fact that under light stimulation, two adjacent metal ions (located at adjacent sites) can originate intervalence charge transfer [IVCT] in which one electron is transferred from one to the other site, giving origin usually to broad and strong optical absorption bands in the visible and, probably, ultraviolet regions of electromagnetic spectra. Also, IVCT mechanism has been pointed out as one of the causes of strong pleochroism in minerals, due to the fact that this kind of interactions is strongly polarized[5]. In the present report we want to describe briefly our photoacoustic spectroscopy (PAS) laboratory as well as to show, to the best of our knowledge, for the fist time, experimental PAS results in minerals. Photoacoustic spectroscopy experiments were carried out in a variety of tourmalines (green, pink and black). The spectral analyses were performed in the visible region of the electromagnetic spectrum in order to try to identify the possible transition metal ions, or their eventual combinations, responsible for the origin of colors of the tourmalines. Our intention is to demonstrate, that photoacoustic spectroscopy can be used as a powerful alternative instrument to characterize color centers in minerals. Some comments on the minerals investigated by us: Following FLEISCHER & MANDARINO[5], the tourmaline group is divided in, at least, 10 independent minerals, all of them are isostructurals, but of different chemical composition. Most colored tourmalines are elbaites, but some may be liddicoatites as well. All Brazilian tourmalines investigated by us are elbaites, except the black one of which is dravite. As we do not have specific information about the colored tourmalines investigated by other authors and cited in this paper, we decided to use the terms green, pink and black tourmaline for all of them.

Experimental Setup

The potential of photoacoustic spectroscopy (PAS) as a powerful method to investigate any material phase (gas, liquid, semisolid and solid) has already been demonstrated[6],[7],[8]. In particular, PAS measurements of solid samples has proved to be useful for determination of some of their optical our thermal properties such as the optical absorption coefficient β, the thermal diffusion length and thermal difusibility. In our effort to investigate a wide variety of materials like polymers, composites, biological and minerals, we have mounted a photoacoustic spectroscopy laboratory, briefly described below. Fig.1 shows the block diagram of our photoacoustic spectrometer.
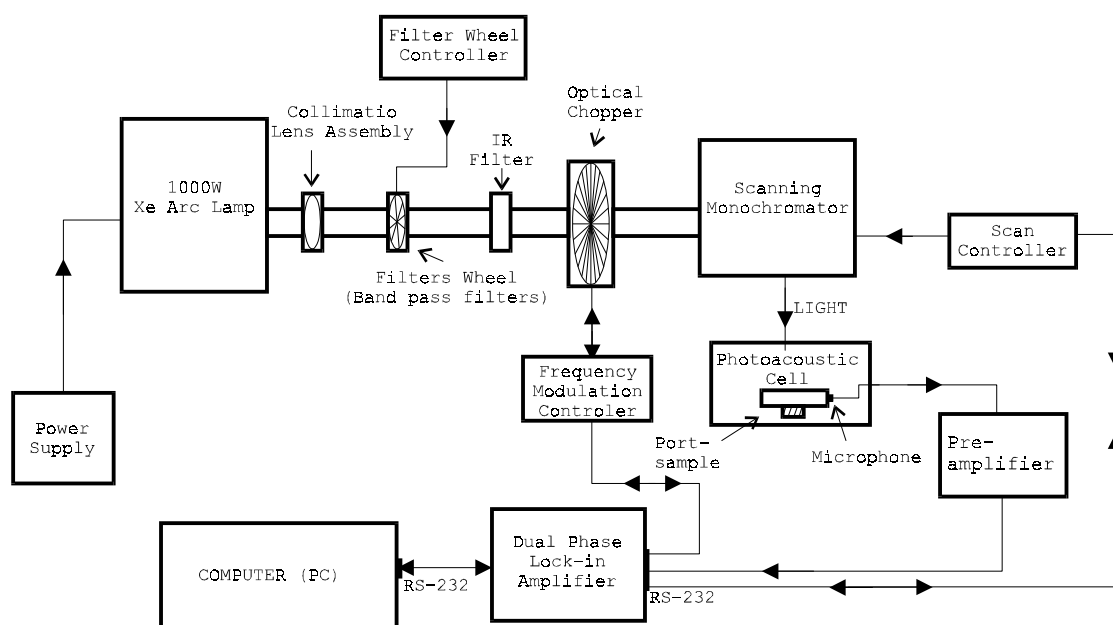
Fig.1 - Block Diagram of the Photoacoustic Spectrometer, Department of Physics, CCT, Federal University of Campina Grande, Pb (Brazil).

In photoacoustic spectroscopy, a process involving absorption of modulated light generates a photoacoustic signal. In the absence of photochemical as well as photophysical reactions an incident light produces heat-generated "thermal waves" which propagate to the sample surface. The intensity of these thermal waves is proportional to the light absorbed by the sample. In other words: "no absorption no signal". The primary detected signal is a sum of the thermal waves component (pure sample spectrum) and the spectrum of the excitation source of light. In order to obtain the pure sample spectrum, normalization is carried out using carbon black spectrum or other black absorber in the spectral range of interest.

Our PAS laboratory is computer controlled and allows to obtain both types of spectra photoacoustic signal intensity (I) and phase (ϕ) as a function of the wavelength of the incident radiation as well as the I and ϕ as a function of the modulation frequency f. As it is well known, the phase of photoacoustic signal lags relative to the phase of the incident light wave and the phase shift can be used to investigate depth profiles of heterogeneous material.

Our PAS system is a high-energy spectrometer. The light source is a 1000W-ozone free xenon arc lamp with a wide spectral range, IR-VIS-Ultraviolet. The radiation, after having passed a water filter to remove excess of heat (IR radiation) and by a five position automatically controlled filter wheel to eliminate the radiation multiple order effects, enter to a chopper modulation system that provide the modulation of the light beam. This chopper is computer controlled and allows continuous frequency scanning from 0 to 2KHz, or discrete frequencies values, allowing the detection of PAS spectra as a function of the wavelength. The modulated beam is then expanded to the entrance slip of the monochromator. A 1710 G/mm holographic diffraction grating (mod. 1710 from the McPherson) provides a high efficient monochromatic light within the Visible-UV region with a high accuracy of $\pm$ .1nm and resolution of $\approx$ 1.0 nm. A computer controlled high-resolution (25000 steps/s) scan controller unit, using a standard RS-232 operates the spectrometer. A focusing exit lens assembly directs the beam 90° downward to hit the sample inside the photoacoustic detector. This system incorporates a two-phase sensitive detector (PSD) lock-in amplifier (mod. SR750 from the Stanford Research), phase electronics and a manipulative software (grams/386). The spectrometer control, acquisition and manipulation of the data are performed by a Macintosh and Windows compatible platform.

Results and Discussions

It seems well established that the colors of tourmalines have their origin in the cations of Fe, Mn, Cr or Cu, usually present in its structure. It is also known that the color spectra are originated from light absorption by individual ions or from light absorbed by interactions between ions (Fe^{2+} - Fe^{3+}, Fe^{2+}- Ti^{4+} or Mn^{2+} - Ti^{4+} intervalence charge transfer IVCT). Many authors have attributed the great adversity of color in tourmalines to

the variability in which these combinations occur[5]. Let us see how this variety of possibilities is manifested in photoacoustic spectroscopy experiments.

TOURMALINE GROUP

a) **Green Elbaite,** from Junco do Seridó, Paraíba State, Brazil: Fig.2 illustrates the PAS spectrum of this green elbaite, which was obtained using polarized light (E∥c and E⊥c) in the UV-Visible regions. The main features of the green elbaite PAS spectra are as follows: a large band (450 - 580nm) centered in a sharp peak at ~ 490 nm; a weak band centered at ~ 430 nm; a moderated intensity band centered at ~ 660 nm; a weak band at ~ 725 nm and a very strong UV-centered band (~300nm) were observed. Our PAS results in this specimen are in line with those published elsewhere, using conventional transmission optical spectroscopy technique for green Fe-containing elbaite. FAYE et al[9] observed an optical absorption peak in green tourmaline at ~ 720 nm and a large weak absorption band (415 - 450 nm) . These authors have attributed the former band to the Fe^{2+} d-d transitions while the latter probably is a response to the Fe^{2+} - Ti^{4+} IVCT interaction. In fact, MATTSON[2] considered the band due to the IVCT interactions plus the Fe^{2+} band to be absolutely necessary to produce green color in tourmaline, mainly in absence of Cr^{3+}. The wide PAS band centered at ~490nm we observed may be due to the Fe^{3+} (d-d) transitions in tetrahedral sites of the tourmaline. WILKINS et al[10] attributed the bands at ~ 500 nm to the presence of Fe^{3+} in green tourmaline sites. PINHEIRO et al[9] have observed additional bands at ~ 430 nm and 660 nm in a Fe - containing green elbaite (from Minas Gerais State, Brazil). Our PAS spectra show peaks at the same positions, indicating that our PAS results are concordant with those of conventional optical absorption measurements. Finally, the strong UV-centered PAS band we observed is also concordant with the UV-centered optical absorption band observed by FAYE et al in a green tourmaline specimen. They associate such a band to the 0^{2-} - Fe^{2+} or 0^{2-} - Fe^{3+} IVCT process that also should influence the pleochroism of some green tourmalines in the visible spectrum.

b) **Pink Elbaite,** from Boulandeira pegmatite near Equador, Rio Grande do Norte State, Brazil: The PAS spectrum obtained from the pink elbaite is essentially dominated by a set of three bands centered at ~ 390nm; (510 - 520 nm) and ~615 nm, nearly the same set of optical absorption bands centered at ~390nm; (520 - 530 nm) and ~630nm observed by PINHEIRO et al[11] in pink tourmaline from Minas Gerais State (Brazil) and attributed to the presence of Mn ions in that specimen. We suggest the presence of Mn^{2+} in our pink elbaite since magnetic susceptibility results, reported by VINOKUROV et al[12] , have lead to the conclusion that Mn^{3+} is not present in pink tourmaline. The low intensity observed for the Mn-bands is probably due to the fact that Mn^{2+} has spin-forbidden bands. An additional low intensity sharp band at ~725 nm and a weak peak at 685 nm were observed and attributed to the Fe^{2+} (d-d) transitions and Cr^{3+} ions, respectively. Probably both ions are present in very low concentration in the pink tourmaline specimen, object of our investigation. Furthermore, a wide PAS UV- band centered at ~ 300 nm and sweeping to visible was observed. This observation seems to be in good agreement with optical absorption results of FAYE and al[9] .They observed strong UV-bands sweeping into the visibleregion which was attributed to 0^{2-} - Fe^{2+} and 0^{2-} - Fe^{3+} IVCT mechanism. These authors believe that ultraviolet charge transfer absorption also have influence in the pink color of tourmaline.

c) **Black Dravite,** from a pegmatite near Juazeirinho, Paraíba State, Brazil**:** A sharp PAS peak at ~ 725 nm; two relatively sharp and strong PAS bands centered at ~ 500nm and a wide and strong PAS UV-centered (~300 nm) band sweeping into the visible region were promptly observed in our black dravite specimen. These results are in qualitative agreement with those of WILKINS et al[10] and confirm the absorption band they observed in a black tourmaline specimen at ~ 725 nm which they attributed to the Fe^{2+}- Fe^{3+} transitions. MANNING[13] made the presence of Fe^{3+} tetrahedral sites of the black tourmaline responsible for the two strong absorption bands centered at ~500 nm. On the other hand, FAYE et[9] al made reference to a strong UV-centered absorption band observed in black tourmaline. They concluded that the color of black tourmaline is strongly influenced by this 0^{2-} - Fe^{2+} IVCT band together with the Fe^{2+}- Fe^{3+} IVCT band. As can be noted, our PAS results for tourmalines we have investigated are, broadly speaking, in good agreement with those reported by other authors. Finally, a weak peak at 685 nm suggests the presence of Cr^{3+} in our dravite sample, even at very low concentration.

Conclusions

To the best of our knowledge, **photoacoustic spectroscopy (PAS),** for the first time, has been used in mineral investigation with appreciable success. As a result of our study, a great diversity of color centers in several tourmalines and were identified using PAS analysis. Ions such as Fe^{2+}, Fe^{3+}, Mn^{2+} and Cr^{3+} had their presence confirmed in these species, as well as the occurrence of Fe^{2+} - Ti^{4+} and possibly Mn^{2+} -Ti^{4+} IVCT interactions that certainly influence the color spectra of minerals. Particularly, the main feature of the PAS results is the sharpness of absorption peaks, indicating that trace elements are really responsible for the variety of colors, as was to be expected. In tourmalines, the photoacoustic spectra are usually constituted of strong and wide bands, characteristic for the presence of metal ions in the mineral structure. Finally, using polarized light, we were able to detect strong anisotropy in the photoacoustic spectra in some tourmaline species with maximum and minimum peak (or band) intensity for E⊥c and E∥c, respectively, for almost all the specimens investigated (c is the optic axis of the tourmaline crystal. This fact constitutes a strong evidence that photoacoustic spectroscopy can also be used as instrument of investigation of the observed pleochroism (dichroism) as well as its origin in certain minerals.

Acknowledgements

References

[1]   U. Henn and H. Bank, Mineral Mag. **54** (1991), 553-557

[2]   S. M. Mattson and C. R. Gosselin, Phys. and Chem. Minerals **14** (1987), 94

[3]   P. G. Manning, Canadian Mineralogist **9**, (1969), 678-690.

[4]   R.V. Dietrich, The tourmaline group , Van Nostrand Reinhold Company, N.York (1985), 300 pg.

[5]   M. Fleischer & J. A. Mandarino, Glossary of Mineral Species, The Mineralogical Record, Inc., Tucson (1991).

[6]   A. Rosencwaig, Anal. Chemistry, 47 (6) (1975), 592A-604A.

[7]   F.A. McDonald, J. Appl. Phys. **49** (1978), 2313-2318.

[8]   A. Rosencwaig and A. Gersho, J. Appl. Phys. **47**(1) (1976), 64-69.

[9]   G.H. Faye, P.G. Manning and J.R. Gosselin, Canadian Mineralogist, **12** (1974), 370-380.

[10] R.,W.,T. Wilkins, E.F.Ferrel and C.J. Naiman, J. Chem. And Phys. of Solids, (1969), 43-56.

[11] M.N.B. Pinheiro, H.S.Junior, A., I.C. Perciano, K., Kranbrock, Depto de Física UFMG (1993).

[12] V.,M. Vinokurov and M.M. Kristalografiya, **4** (1960), 873-877.

[13] P.G. Minning, Canadian Mineralogist, **10** (1970), 57-70.