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Lavender Jade. The Optical Spectrum of Fe^{3+} and $Fe^{2+} \rightarrow Fe^{3+}$ Intervalence Charge Transfer in Jadeite from Burma[1]

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Abstract

The optical spectra of green, white, and lavender jadeite have been studied. Ferric iron is responsible for the color in the green jadeite. It is proposed that ferrous-ferric iron intervalence charge transfer is responsible for the lavender color of jadeite.

Introduction

The growth of interest in the quantitative spectroscopic study of the cause of coloration in minerals has led to an appreciation of the importance of the intervalence charge-transfer process which occurs when nearest metal neighbors in adjacent crystallographic sites are the same element in different oxidation states. The pyroxenes represent an important class of minerals in which adjacent metal sites are favorably disposed structurally for these effects. Wet chemical analyses have indicated that the gem varieties of the pyroxene mineral jadeite, $NaAl(SiO_3)_2$, contain minor amounts of iron in both the divalent and trivalent oxidation states. The color of natural jadeite is strongly influenced by the magnitude of the iron content, its oxidation state, and interactions between ions in different oxidation states.

One particularly interesting variety of jadeite is the lavender variety which can coexist with green jadeite. Since both green and lavender colors are associated with ferric iron in octahedral coordination in minerals, it was of interest to examine the spectrum of jadeite to determine the role of iron, particularly from the point of view of possible interactions among ions.

Experimental

Several specimens of jadeite of Burmese origin were examined in the forms of rough blocks, sawed slabs, and polished cabachons. Their colors ranged from white through lavender to green. All samples were polycrystalline aggregates whose color was nonuniformly distributed throughout the material. Electron microprobe analyses of the green and lavender specimens whose spectra are illustrated appear in Table 1. Optical spectra of self-supporting polished slabs were obtained with a Cary 17I spectrophotometer.

Spectral Results

The optical spectrum of a particularly attractive lavender jadeite cabachon is shown in Figure 1. It consists of absorption bands at 828 nm and 573 nm, a set of narrow bands at 437 and 431 nm, and a broader doublet at 381 and 369 nm. Not readily apparent from the figure is a shoulder at about 536 nm which is obscured by the 573 nm feature. This spectrum is typical of all lavender jadeite samples. The intensities of the 828, 437–431, and 381–369 nm bands are correlated in all samples, implying a common origin, but vary with respect to the intensity of the 573 nm band. In all lavender samples the intensity of the 573 nm band, which is responsible for the lavender color, was equal to or greater in intensity than the 437 nm band.

A block of admixed green and lavender Burmese jadeite was examined spectroscopically. In the spectrum of the lavender portion the 437 nm band was one-third as intense as the 573 nm band, and the resulting region of maximum transmission was at about 465 nm, giving rise to the observed color; whereas in the green portion, the 437 nm band is about 30 percent more intense than the 573 nm band, and the region of maximum transmission moved to the green. In general, in green jadeite the 573 nm adsorption band is less intense than the

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828 nm feature. The spectrum of another block of pale green jadeite is shown in Figure 2. The 573 nm band is essentially absent. Weak features at 875 and ~1160 nm are also evident.

In white jadeite the intensity of all features is low, and the 573 nm band is essentially absent. In the spectra of all samples where the intensity of the 573 nm features is comparable to, or less intense than, the other bands, the 536 nm shoulder can be observed. Its intensity also appears to be correlated with the intensity of the 828, 437, 381 nm set of bands. Additionally, the weak absorption bands at about 875 and ~1160 nm are present in most samples. Their intensities are not correlated with the intensity of the other set of bands.

Interpretation

The correlated set of bands have the characteristic pattern of d^5 trivalent iron in octahedral oxygen coordination. The crystal structure of jadeite (Prewitt and Burnham, 1966) shows that 8-fold sodium sites, 6-fold distorted-octahedral aluminum sites, and 4-fold silicon sites occur in the material. The bulk of the iron is accordingly assigned to the aluminum site. In the nomenclature of an octahedral site, the bands are assigned as follows: $^6A_{1g} \rightarrow {}^4T_{1g}$ – 828 nm; $^6A_{1g} \rightarrow {}^4T_{2g}$ – 536 nm; $^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ – 431, 437 nm; $^6A_{1g} \rightarrow {}^4T_{2g}$ – 369, 381 nm. The observed splittings of the 431–437 and 369–381 nm features are ascribed to the deviation of the iron site from ideal octahedral geometry. It would also be expected that the first $^4T_{2g}$ state would split under these site distortions. The spectrum shown in Figure 2, which in the 600 nm region still has a small contribution from the 573 nm band, does not indicate that such a splitting exists. However, in the spectrum of a colorless Burmese jadeite, which did not have the 573 nm feature but which did have enough iron to produce the characteristic d^5 spectrum, two bands are present at 610 and ~540 nm, which are assigned to components of the

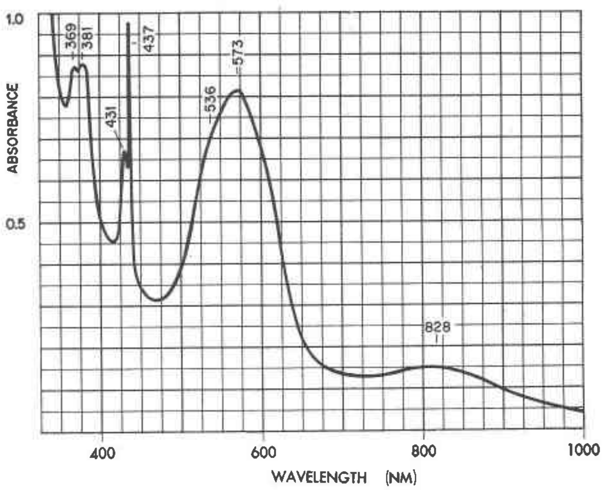

FIG. 1. Optical spectrum of a color-enhanced lavender jadeite cabachon (Burma). This spectrum is representative of both natural and color-enhanced lavender jade. Polished slab 4.6 mm thick, 296 K. Absorbance = $-\log I/I_0$.

TABLE 1. Electron Microprobe Analyses of Burma Jadeite*

	Lavender **		Green ***	
Na_2O	14.11	13.55	14.08	13.94
MgO	0.85	0.47	0.64	0.80
CaO	1.25	0.78	0.87	1.28
MnO	0.00	0.00	0.04	0.00
Al_2O_3	24.20	24.24	24.46	23.67
Fe_2O_3†	0.57	0.37	0.49	0.90
Cr_2O_3	0.00	0.00	0.00	0.02
TiO_2	0.09	0.05	0.00	0.04
SiO_2	60.52	60.27	59.54	59.75
Sum	101.59	99.83	100.12	100.40

* Analyses obtained on two different portion of each sample; spectra of the samples appear in Figures 1 and 2.
** Interior of a "color-enhanced" lavender cabachon.
*** Natural green jadeite block CIT # 7484.
† Total iron reported as Fe_2O_3.

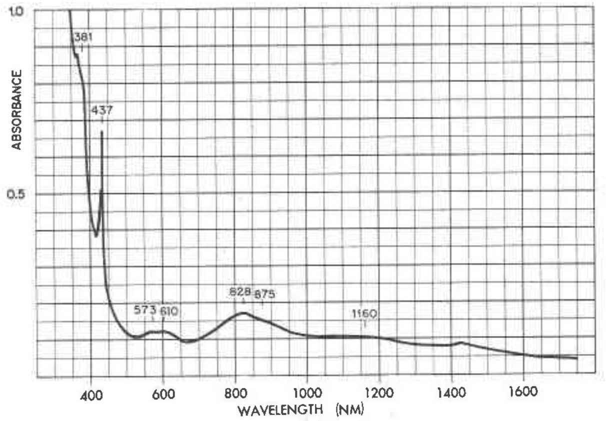

FIG. 2. Optical spectrum of green jade (Burma) showing features of both Fe^{3+} and Fe^{2+}. Mineral slice 2.2 mm thick run against frosted fused silica to compensate for scattering; 296 K.

${}^4T_{2g}$ absorption band. It is interesting to note that ferric iron in jadeite produces a green color, providing another counter-example to the common generalization that green color is associated with ferrous iron.

Analyses of jadeite generally indicate the presence of some divalent iron (Yoder, 1950; Foshag, 1955). Spectra of ortho- and clinopyroxenes have absorption bands in the 900–1000 nm and 1150–1250 nm ranges which are assigned to Fe^{2+} (Burns, 1970). Corresponding weak absorption features are observed in the jadeite spectra at about 875 and 1160 nm (Figure 2). Their low intensity indicates that Fe^{2+} constitutes a minor proportion of the total iron content.

The simultaneous presence of both Fe^{3+} and Fe^{2+} raises the possibility of intervalence charge transfer electronic transitions between Fe^{2+} and Fe^{3+}. It is proposed that the 573 nm band, which is not directly correlated with the iron content, be assigned to an $Fe^{2+} - Fe^{3+}$ intervalence charge-transfer band. Burns (1970) has examined a series of orthopyroxenes and has attributed the $Fe^{2+} - Fe^{3+}$ intervalence charge transfer to an absorption band in the 760–800 nm region. Such a feature similarly occurs in this region for aegirine, the ferric ion endmember $NaFe(SiO_3)_2$. The question arises of why the intervalence charge transfer band of jadeite is at a much higher energy. Burns (1970) concluded that the ~780 nm charge transfer band in high iron orthopyroxenes arises from the interaction of Fe^{2+} in the larger $M2$ position and Fe^{3+} in the distorted octahedral $M1$ position. This conclusion was partially based on polarization information.

Unfortunately, the pleochroic scheme for the lavender jadeite is not known, due to the unavailability of a suitable single crystal. Nevertheless, it is proposed that both the divalent and trivalent iron which give rise to the intervalence charge transfer band are located in the octahedral sites. The spectroscopic evidence supports this interpretation when compared with other minerals wherein intervalence charge transfer is believed to occur between adjacent octahedral sites. Jadeite at 573 nm compares favorably with corundum at ~600 nm (Faye, 1971), kyanite at ~590 nm (Faye and Nickel, 1969), and cordierite at ~571 nm (Faye, Manning, and Nickel, 1968).

Color Enhanced Jade

Samples of authenticated lavender jadeite and material sold as "color-enhanced lavender jade," which has recently become available, have identical color and display the same spectral features, although they may differ from sample to sample in the relative intensities of the intervalence charge transfer band and the Fe^{3+} ligand field bands. It is proposed that the color-enhanced material is formed from natural jadeite by a process such as heat treatment which could affect the clustering and oxidation state of a small proportion of the iron present.

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