

# COMPOSITION, TENEBRESCENCE AND LUMINESCENCE OF SPODUMENE MINERALS

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## ABSTRACT

Transparent spodumenes are shown to be of two types: chromian spodumene (green, the typical North Carolina "hiddenite") and non-chromian spodumene (colorless, yellow, pink and lilac "kunzite," green—whether natural or artificially induced). The pink color of non-chromian spodumene is correlated with the presence of Mn, and more specifically with a low Fe/Mn ratio. Only non-chromian spodumene is luminescent and tenebrescent. Absorption spectra of non-chromian spodumenes of various colors before and after  $x$ -ray irradiation, and after bleaching, show the preferential growth or decay of the 6400 Å band over the 5400 Å band. Both bands are probably due to Mn. The absorption spectrum of chromian spodumene is unchanged by irradiation or bleaching; its 6400 Å band is probably due to Cr, not Mn; its 11,000 Å band may be due to V.

## INTRODUCTION

The striking luminescence and color changes of kunzite, the pink spodumene, have long been the subject of considerable research by mineralogists and physicists alike. Baskerville (1903), when naming kunzite, already noted its phosphorescence after  $x$ -ray irradiation, and Baskerville and Kunz (1904) reported on other sources of exciting radiation for kunzite. It is the general, although vague, impression that these properties are related to the presence of manganese. Furthermore, it is frequently assumed (Pringsheim, 1949; Bayley, 1928) that hiddenite, the green gem spodumene, is nature's equivalent of the green modification produced by high energy irradiation of kunzite.

It is proposed to demonstrate, by a critical review of the literature as well as on the basis of further investigations, that some of these beliefs are erroneous.

The mineral spodumene has the formula  $\text{LiAl}(\text{SiO}_3)_2$ , and is a member of the pyroxene family. Ford (1932) notes two gem varieties—green hiddenite and lilac kunzite. The name "triphane" is retained merely as a synonym. Jahns and Wright (1951), in a comprehensive report on lithium-pegmatites, classify the transparent spodumenes as triphane (colorless to yellow), kunzite (pink, lilac), and hiddenite (green).

The establishment of varietal names for transparent (gem) spodumenes on the basis of color is unfortunate. It will be demonstrated that, on the basis of chemical composition and luminescence and tenebrescence behavior, gem spodumenes are of two types—a chromian spodumene (green, typically from North Carolina) and a non-chromian spodumene (colorless, yellow, pink, lilac or green—whether natural or artificially in-

duced). Use of the varietal names will be avoided hereafter in this paper, except in referring to the literature.

#### LUMINESCENCE OF THE SPODUMENES

There is, apparently, some variation in the luminescence behavior of spodumenes, possibly even among similarly colored specimens from the same localities. This, coupled with occasionally loose application of the terms luminescence, fluorescence, and phosphorescence, has caused some confusion in the reported properties.\*

According to Ford (1932), kunzite phosphoresces a strong orange-pink when excited by any source. Jahns and Wright (1951) report that gem spodumene is thermoluminescent and possibly triboluminescent, and that it is strongly phosphorescent when exposed to  $x$ -ray, ultraviolet, radium, or high tension electric currents. The Ultra-Violet Products Inc. handbook (1948) notes that some Pala kunzites fluoresce yellow and often phosphoresce for long periods, and that spodumene from Portland, Conn., sometimes has a persistent, deep red phosphorescence. Pochettino (1909, 1911) first records cathodoluminescence in various spodumenes when examined through a specially mounted polarizing microscope, and Nichols and Howes (1914) examine the cathodophosphorescence bands. None of our specimens shows strong phosphorescence under ultraviolet or electron excitation.

We have examined a total of 26 specimens of spodumene, including 5 common spodumenes (Andover, Me.; Portland, Conn.; Keystone, S. Dak.; Harding Mine, Taos Co., New Mex.; Argentina), 7 colorless (Maharitra, Madagascar; Minas Geraes, Brazil; Pala, Calif.), 3 lilac (Pala), 3 pink (Pala), 1 yellow (Pala), 1 very light green (Pala), 4 light green and 2 dark green (Stony Pt., Alexander Co., N. C.).† The North Carolina green spodumenes show no luminescence whatsoever under ultraviolet light or spark discharge. Under 2537 Å ultraviolet excitation, fluorescence of the other spodumenes is very weak or missing. Under 3650 Å ultraviolet, all the other spodumenes fluoresce salmon pink—moderate to bright. Under electron excitation of a spark discharge from a Tesla coil, in partial vacuum, most show bright yellow-orange fluorescence but only

\* It should be remembered, of course, particularly when comparing recent data with data obtained in the early days of experimentation, that inherent mechanical differences in the equipment used by various workers, with corresponding significant differences in the intensity and wavelength-distribution of the radiation, may account for many of the apparent discrepancies in luminescence behavior. Pough and Rogers (1947), for example, report on the improved phosphorescence and tenebrescence response to the then newly developed, high intensity, Machlett-type  $x$ -ray tube.

† The North Carolina "hiddenities" were made available through the cooperation of Dr. William Foshag of the U. S. National Museum.

a short weak phosphorescence; two colorless spodumenes (Brazil; Madagascar) fluoresce pink, and one or two of the common variety are non-luminescent.

Another interesting property, which was intensively studied by Przi-  
bram and his colleagues (1922, 1923, 1924, 1932), is the radiophoto-  
luminescence of kunzite. If kunzite is first irradiated with  $\alpha$ -rays or  
radium  $\gamma$ -rays and is then excited by ultraviolet or other source, it  
fluoresces and phosphoresces strongly. The effect is sometimes noticeable  
even years later. All non-chromian spodumenes, regardless of color, be-  
have similarly. It should be noted that Przi-  
bram (1921, 1932) specifically states that North Carolina hiddenite does not show radiophotolumines-  
cence, even after long exposure to radium.

#### TENEbrescence OF SPODUMENES

The property of tenebrescence is the reversible darkening and bleach-  
ing shown by certain crystalline solids. The darkening (or change in  
color) is induced by  $\alpha$ -ray, cathode ray, or other high energy source and  
the bleaching by heat or irradiation with light of the same wavelength  
as the absorption band produced during darkening. Jahns and Wright  
(1951), for instance, note that many gem spodumenes, especially the  
green, lavender, and bluish varieties, fade on prolonged exposure to sun-  
light.

The tenebrescence of kunzite has been studied by Zekert (1927), Bělár  
(1923), Lind and Bardwell (1923), Stuhlman and Daniel (1928), and  
Bayley (1928) among others. X-ray or  $\gamma$ -ray irradiation converts pink  
spodumene to the green; colorless spodumene when  $\alpha$ -rayed passes  
through the pink stage (an intermediate colorless stage has sometimes  
been noted, presumably due to the combined effect of equal amounts of  
pink and green); and finally darkens to green. Exposure to daylight,  
ultraviolet, or moderate heat ( $<250^{\circ}$  C.) bleaches the colors, from green  
 $\rightarrow$ pink $\rightarrow$ colorless. Firing at  $500^{\circ}$  C. converts the green directly to the  
colorless. The cycle can be started at any stage and can be repeated in-  
definitely. In Figure 1, the cyclic color changes in non-chromian gem  
spodumene are summarized.

It is reported by Pringsheim (1949) that the green modification emits  
the same phosphorescence color as the pink, but it is of longer duration.  
The heat-bleaching is accompanied by thermoluminescence (Pochettino,  
1909, 1911; Przi-  
bram and Kara-Michailova, 1923). The colorless  
(bleached) modification no longer phosphoresces (Przi-  
bram, 1921).

We have found that chromian gem spodumene (green) from North  
Carolina cannot be bleached by such heat treatment nor by exposure to  
light. Nor can North Carolina specimens of pale green color be darkened

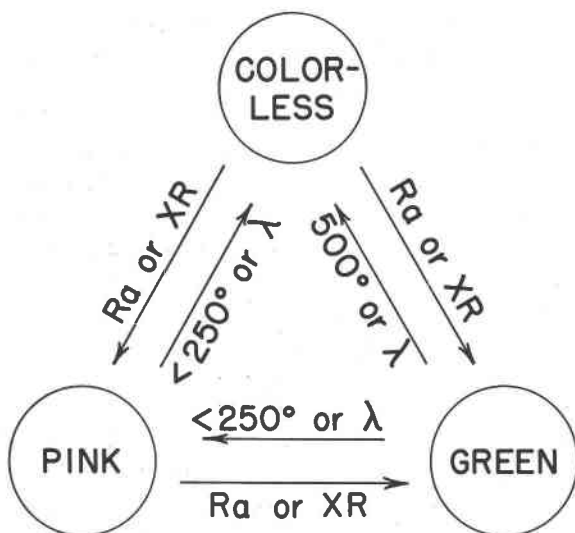


FIG. 1. Tenebrescence of non-chromian gem spodumene.  $\lambda$ =optical bleaching.

by  $x$ -rays or  $\gamma$ -rays. Whereas  $4\frac{1}{2}$  hours' heating at  $250^\circ$  C. produced no visible bleaching of color in a dark green chromian specimen, nor did one additional hour of firing at  $500^\circ$  C., a lilac non-chromian spodumene became completely colorless after one hour at  $500^\circ$  C. The so-called Pala "hiddenite," which fluoresced pale pink, was a deep blue-green after 3 hours' exposure to  $x$ -rays, and fluoresced and phosphoresced brightly. Two crystals of North Carolina chromian spodumene (one dark green, one light green) retained their original color after 3 hours'  $x$ -raying, and were still nonluminescent. Even 96 hours' exposure to a 500 mg. radium source did not darken a specimen of North Carolina chromian spodumene nor induce luminescence. Bayley (1928) also observed that hiddenite from North Carolina showed no marked change after  $x$ -ray irradiation.

The role of Mn in the tenebrescence of kunzite was explained by Stuhlman and Daniel (1928) in terms of a chemical oxidation-reduction process and chemiluminescence. In the light of modern knowledge of solids this explanation seems unlikely. Several workers (Meyer and Przi-  
bram, 1922; Zekert, 1927; Pough and Rogers, 1947) have reported the appearance of an intermediate, unstable brown coloration in kunzite after  $x$ -ray or  $\gamma$ -ray irradiation. According to Pough and Rogers (1947), immediately after irradiation the mineral was brown and showed strong phosphorescence—spontaneous afterglow—and not until this phosphorescence had ended did the usual green color appear. The fact that  $Mn^{+2}$  imparts a brown color to silicate glass and is responsible for its green or

orange fluorescence (Weyl, 1951) is perhaps suggestive of a temporary photochemical reduction of Mn in spodumene by high energy radiation.

#### COMPOSITION AND STRUCTURE OF SPODUMENE

The presence of Mn as a minor constituent in spodumene has long been known, Davis (1904), the first to publish a chemical analysis of kunzite, reporting 0.11% MnO. Wild and Klemm (1925) made the earliest spectrographic analysis and found that all spodumenes, regardless of color, contained Mn, Ga, and Fe—with least Fe in pink kunzite. They were unable, by their technique, to correlate the concentration of Mn with the color of the spodumenes. Apparently equal amounts of Mn, and Ga, were present in all. Fe was believed responsible for the color of the yellow variety. Wild and Klemm did establish, however, that Cr was present in all hiddenites tested and that the deeper the green color, the more Cr was present. They suggested that V, together with Cr, may be responsible for the yellowish green color of some hiddenites.

More recently Gabriel, Slavin, and Carl (1942) analyzed spectrographically a number of transparent spodumenes, one lilac kunzite from Pala and ten colorless or nearly colorless spodumenes, from various localities. There was no attempt to study color as related to composition. We deduce one interesting relationship from their data, nevertheless. Of all eleven samples, the lilac kunzite, as opposed to the ten colorless spodumenes, contained the lowest concentration of Fe (0.020%  $\text{Fe}_2\text{O}_3$ ) combined with high Mn (0.073% MnO). Recalculated in terms of Fe/Mn ratio, the lilac kunzite = 0.25; the colorless spodumenes range from 0.74 (0.44%  $\text{Fe}_2\text{O}_3$ /0.54% MnO) to 24.1 (0.64%  $\text{Fe}_2\text{O}_3$ /0.024% MnO).

The spectrochemical analyses of the minor and trace elements in our spodumenes, as recorded in Table 1, include all specimens for which absorption spectra were measured, as indicated below. The samples were carefully inspected under the binocular microscope for freedom from inclusions and were cleansed of superficial impurities by soaking in hydrochloric acid and rinsing with distilled water. A Baird 3-meter grating spectrograph was used for the analysis. Unfortunately, the press of other spectrographic work did not allow time for precise quantitative determinations.

Of particular interest are the elements Fe, Mn, Cr, V, and Sc. Mn is present in relatively high concentrations in all the spodumenes. These may be arranged in the following sequence of decreasing Mn concentration: #2 pink = #6 lilac = #8 lilac = #10 yellow > #1 colorless = #5 v. lt. green = #7 colorless = #9 colorless > #4 lt. green (N.C.) > #3 dk. green (N.C.). The group of highest Mn content includes the pink and lilac specimens, a yellow, and a colorless. The Fe content of the pink and lilac

TABLE 1. MINOR AND TRACE ELEMENTS IN SPODUMENES†

Element	Colorless #1	Pink 2	Dr. green 3	Lt. green 4	V. lt. green 5	Colorless 6	Colorless 7	Lilac 8	Colorless 9	Yellow 10
Na	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%	.0X-.X%
K	—	—	—	—	—	—	—	—	—	—
Rb	—	—	—	—	—	—	—	—	—	—
Cs	—	—	—	—	—	—	—	—	—	—
Mg	<.0001	.000X	.0X	.0X	.000X	.000X	.000X	.000X	.000X	.000X
Sr	—	—	—	—	—	—	—	—	—	—
Ti	.000X	.000X	.0X	.0X	.00X	.0X	.0X-.X	.00X	.00X	.0X
Ga	.X	.X	.X	.X	.X	.X	.X	.X	.X	.X
Fe	.0X	.00X	.X-X.0	X.0	.0X	.X-X.0	.0X	.0X	.0X	.X-X.0
Mn	.X	.X	.0X-.X	.0X-.X	.X	.X	.X	.X	.X	.X
Cr	<.0001	<.0001	X.0	.X-X.0	<.0001	—	—	—	<.0001	<.0001
V	—	—	.X	.0X-.X	—	.000X	—	—	—	.000X
Co	.0X	.0X	.00X	.00X	.0X	.0X	.00X	.0X	.0X	.0X
Ni	<.0001	<.0001	.0X	.00X	.000X	.00X	.000X	.00X	.00X	.00X
Cu	—	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Sn	.X	.X	.X	.X	.X	.0X-.X	.X	.X	.X	.X
Ge	—	.000X	—	—	<.0001	.000X	.000X	.000X	.000X	.000X
Sc‡	—	—	<.05	—	—	—	—	—	<.05	—

1 —Colorless, Minas Geraes, Brazil.

2 —Pink, Katrina Mine, Pala, Calif.

3 —Dk. green hiddenite, Stony Pt., Alexander Co., N. C.

4\*—Lt. green hiddenite, Stony Pt., Alexander Co., N. C.

5 —V. lt. green, Vanderburg Mine, Pala, Calif.

†—Absorption spectra recorded.

‡—Sc analysis by Martin Cavanagh.

\*—Spectrochemical analysis by Samuel H. Cress.

6\*—Colorless, Pala, Calif.

7\*—Colorless, Maharitra, Madagascar.

8\*—Lilac, Pala, Calif.

9\*—Colorless, Maharitra, Madagascar.

10\*—Yellow, San Pedro Mine, Pala, Calif.

specimens is among the lowest; the yellow and the colorless have considerably more Fe. Wherein the yellow differs from the colorless in this group is not clear from the available data.

The group of intermediate Mn content includes only colorless or very light green spodumenes. The Fe content of the group members is invariably high. The North Carolina green spodumenes contain the least Mn of all, and constitute a separate group; they also contain more Fe than any other spodumene, the yellow excepted. Cr is exceedingly low or absent in all the specimens except those from North Carolina, where the dark green shows more Cr than the light green. As to be expected, V and Ti accompany Fe and Cr. The concentration of V seems to be in direct proportion to the Cr concentration. Whether the presence of V influences the color of the chromian spodumenes is as yet unknown.

Our spectrochemical analyses, therefore, corroborate Wild and Klemm's identification of Cr as the chromophore in hiddenite. Moreover, the data substantiate the supposition that Mn is the probable coloring agent in pink kunzite.

Recently, Heinrich and Levinson (1953) published a detailed report on rose muscovites. The color was found to depend on the absence of  $\text{Fe}^{+2}$  and the predominance of  $\text{Mn}^{+3}$  over  $\text{Fe}^{+3}$ . In lepidolites, also, the color variations were related to fluctuations in the Fe/Mn ratio. The Fe/Mn ratio may play a similar role in the kunzites, as suggested by our chemical data. The valency condition of Mn in spodumene has not been established. Whereas chemical evidence suggests  $\text{Mn}^{+3}$ , the absorption spectra may be indicative of  $\text{Mn}^{+2}$ . It is conceivable that Mn exists in both states.

The fact that chromian spodumene, although colored green by Cr, still contains considerable Mn and yet does not luminesce may possibly be due to the "poisoning" or "killing" effect of Cr. As little as 0.001% Cr in a Mn-activated  $\text{Zn}_2\text{SiO}_4$  (Marden and Meister, 1939), for example, causes detectable reduction in photoluminescence.

The presence of Sc in spodumenes has never before, as far as we have been able to determine, been reported in the literature. Sc is one of the rarer trace elements, although widely distributed in extremely low concentrations. It is more commonly found in granite pegmatite minerals, such as tourmaline, beryl, mica, pyroxene, and hornblende, where it replaces Mg and  $\text{Fe}^{+2}$ , ions of similar size.

Its occurrence in spodumene, however, does not seem unreasonable: (1) spodumene is a Li-pyroxene and a typical pegmatite mineral; and (2)  $\text{Sc}^{+3}$  (ionic radius 0.83) could replace  $\text{Li}^+$  (ionic radius 0.78). The presence of Sc in a spodumene from Madagascar, where the Sc mineral thortveitite occurs, is even less surprising.

*Structure*—Spodumene as it occurs in nature—the  $\alpha$  or low temperature form—has a chain structure of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  tetrahedra. The Li ions act as cross-linkages, and have six-fold coordination, forming  $\text{LiO}_6$  groups.

The  $x$ -ray powder patterns (recorded with a large, 114.5 mm. camera) of spodumenes of varying color and composition are identical. There are no indications of lattice distortion or impurity phases. Whatever minor elements are present must be readily accommodated by the normal crystal lattice.

#### ABSORPTION SPECTRA

It is generally agreed that there are two predominant absorption bands in transparent spodumenes, a red band with a peak at about 5900 Å and a blue band at about 4320 Å. The variations reported in the extent or peak position of the bands are partly due to differences in technique (some early measurements were made with hand spectroscopes or by the use of filter combinations), partly to different crystallographic orientation of the minerals as examined (kunzite is pleochroic, hiddenite highly so), and partly to inherent differences—trace elements—in the mineral specimens.

We have recorded the absorption spectra of several different colored spodumenes, both before and after  $x$ -raying. For this purpose, polished plates approximately 5×8 mm. and 2 mm. thick were prepared from optically flawless portions of the crystals. Measurements were made with a Beckman, Model DU, spectrophotometer, over the range 2200 to 12,000 Å. Either a hydrogen or tungsten lamp, in combination with a blue-sensitive or red-sensitive phototube, was used as needed. The samples were firmly mounted so that the same portion of the plate was measured each time. To avoid inadvertent bleaching, the plates were kept in the dark when not in actual use. After  $x$ -ray irradiation, the plates were stored in the dark at least over-night before measurement, to allow for the decay of the  $x$ -ray induced phosphorescence, which otherwise could have caused anomalously high readings. The  $x$ -ray exposures consisted of approximately 29 hours' irradiation from a tungsten-target tube, with beryllium window, operated at 50 Kv and 15 milliamps., the samples being shielded from visible light during the entire period.

Bayley's (1928) seem to be the only published transmission spectra for any of the spodumenes. He examined one specimen of Pala kunzite and one North Carolina hiddenite, before and after  $x$ -raying, using a photographic technique. Our absorption data correspond well with Bayley's transmission data. However, where Bayley reports that no trace of absorption bands in the ultra-violet or violet could be found for kunzite,



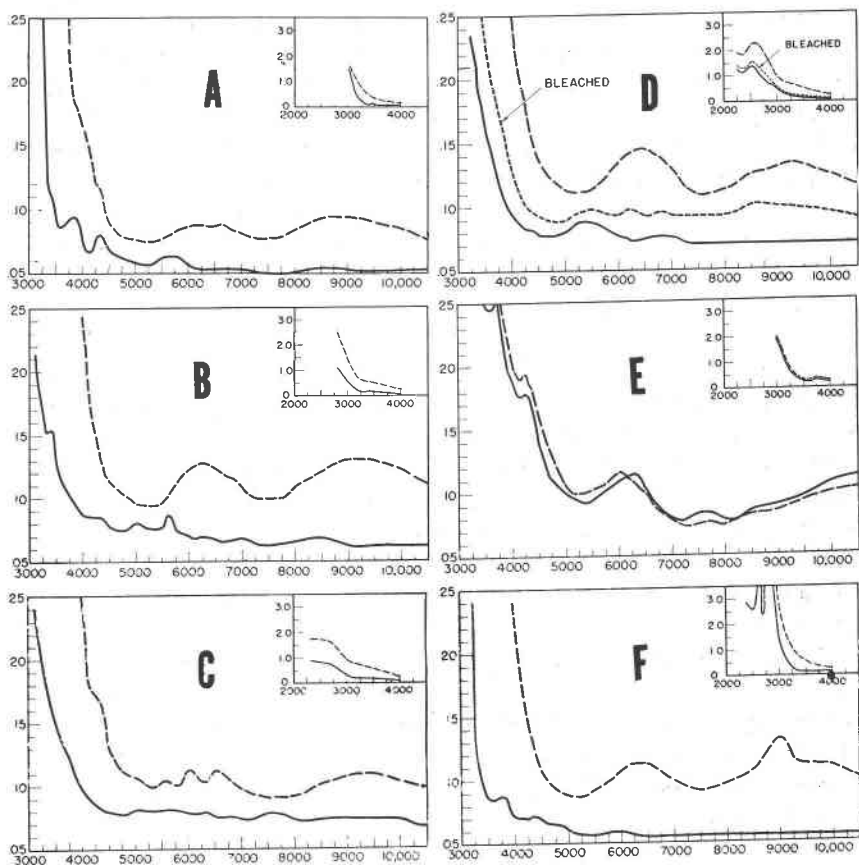


FIG. 2. Absorption spectra of spodumenes, as optical density (ordinate) vs. wavelength in Å (abscissa). Inserts show ultraviolet absorption; solid lines=before  $x$ -ray, broken lines=after  $x$ -ray. A—colorless, Pala; B—colorless, Madagascar; C—colorless Sc-bearing, Madagascar; D—lilac, Pala; E—green, N.C.; F—yellow, Pala.

our spectra definitely show significant ultraviolet absorption at 2500 Å, and at 2600 Å and 2800 Å in yellow spodumene, as well as other bands in the violet for other specimens.

In Figure 2 are reproduced the absorption spectra of the various spodumenes, plotting optical density as a function of wavelength. Absorption bands which appear in most of the spectra and seem characteristic of the natural spodumenes are the 4300 Å and 5400 Å bands. The former may be related to the presence of Mn, as Turner and Weyl (1935) and Weyl (1951) report an absorption band at 4250 Å for  $Mn^{+2}$  in silicate glasses. The 5400 Å band may also be a Mn band. Absorption spectra of  $Mn^{+2}$ -activated silicates and pure  $MnCl_2$  (Klick and Schulman, 1952)

show several characteristic bands including one at about 5200 Å.  $Mn^{+3}$  in silicate glasses, according to Weyl (1951), has a strong absorption band whose maximum lies between 4700 Å and 5200 Å. Grum-Grzimaïlo (1945) shows spectra of ruby, tourmaline, and lepidolite with  $Mn^{+3}$  bands at about 5200 Å. The 5400 Å band is missing in the spectra of the green chromian and the yellow spodumenes. The 6400 Å band appears in all *x*-rayed spodumenes. Traces of an incipient 6400 Å band are seen in two natural colorless samples; it is fully developed in green chromian spodumene. A 9300 Å infrared band also characteristically develops after *x*-ray irradiation. Although apparently missing from *x*-rayed chromian spodumene, it may be masked by the tail of the broad shallow band peaking at approximately 11,000 Å.

By comparing the absorption spectra of a specimen before and after *x*-ray irradiation, the tenebrescence effects can be noted. The behavior of lilac spodumene (Fig. 2D) is typical. After exposure to *x*-rays, the 2500 Å ultraviolet band has increased in density almost two-fold. The very small 4300 Å band, the 5400 Å band, and the small 6800 Å band are masked by the growth of a strong absorption band with a maximum at 6400 Å. The latter is responsible for the green coloration produced by irradiation. In the infrared, a new band with a peak at about 9300 Å, has developed.

The effect of bleaching on the green, irradiated non-chromian spodumene is likewise recorded (Fig. 2D). In this instance, optical bleaching, by exposure to a 100-watt electric light bulb for five hours, was deliberately stopped far short of complete discoloration so that the interim decay—or growth—of the bands could be examined. The 2500 Å band has shrunk and has almost returned to its original density; the 5400 Å band has reappeared; and the 6400 Å band has been replaced by two small bands peaking at 6100 Å and 6800 Å, which were insignificant in the original lilac spodumene; and the 9300 Å infrared band has shrunk and now has apparently shifted to a peak at 8600 Å.

Of the two major bands involved in the color changes of non-chromian spodumene, it is seen that the 5400 Å band in pink spodumene is the more stable. It grows or bleaches more slowly and never becomes as dense as the 6400 Å band in the green. Earlier researchers (Lind and Bardwell, 1923; Stuhlman and Daniel, 1928) had studied these color changes in kunzite qualitatively. Bělár (1923), who first attempted a quantitative spectrophotometric study and made measurements of the effects of increasing radium dosages at several selected wavelength positions, drew similar conclusions.

The absorption spectra of chromian green spodumene (Fig. 2E) before and after *x*-ray exposure are strikingly unlike those of the other spodumenes in that there is essentially no change in the spectra. New bands

do not appear on *x*-raying, nor do the original bands disappear on attempted bleaching. There is only a slight increase in the overall density of some absorption bands with an apparently slight shift in some peak positions. The 6400 Å band is believed to be related to the presence of Cr, on the basis of Grum-Grzimailo's (1945) research on Cr in other minerals. Weyl and Thümen (1933) and Weyl (1951) studied Cr absorption in silicate glasses and also reported a 6500 Å band for Cr<sup>+3</sup>. The 6400 Å band in chromian spodumene may be due in part, however, to the presence of V, for Weyl, Pincus, and Badger (1939) found absorption maxima at 4250 Å and 6250 Å in silicate glasses bearing V<sup>+3</sup>. If so, then the 4250 Å band in chromian spodumene may also be related to V, as well as Mn.

The absorption spectra of green chromian spodumene (Fig. 2E) and green, irradiated non-chromian spodumene (Fig. 2D) should be compared. In the region 4000–7000 Å, the two spectra do seem similar, but the shape of the 6400 Å bands is different, as is their half-width—about 750 Å for chromian spodumene, about 1000 Å for the non-chromian. We believe that these two green bands are due to different types of absorbing centers and are to be correlated with the presence of Cr in the former and Mn in the latter, and that their similar location is coincidental. If these were both Mn bands, then there should also be some similarity in behavior between the two materials.

In the infrared region, the spectra are entirely different: green, irradiated non-chromian spodumene shows a band at 9300 Å; green chromian spodumene lacks this but has a band with a peak at 11,000 Å, which may be due to the presence of V. Fritz-Schmidt, Gehlhoff, and Thomas (1930) reported that V<sup>+5</sup> in silicate glasses is characterized by fairly strong absorption near 11,500 Å. Farther out in the infrared, between 1.5–4.5 μ, the differences are even more extreme, as Bayley's (1928) spectra show.

Because of the presence of a 6300 Å band in both materials, and the presumed identity of a 10,000 Å band in hiddenite with a 9100 Å band in the green irradiated kunzite, Bayley concluded that natural hiddenite and green irradiated kunzite are alike. He further postulated that the presence of monazite sands near the North Carolina hiddenite deposit could account for the radiations that produced the green color in natural hiddenite.

#### CONCLUDING REMARKS

It is particularly fitting perhaps, that a report on spodumene should appear in a publication dedicated to Waldemar T. Schaller. Much of what is known today about pegmatite minerals in general, and Pala spodumenes in particular, is based on the outstanding early researches of Dr. Schaller.

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